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Spectroscopic studies of self-assembled plasmonic nanoparticle arrays



Ruggero Verre

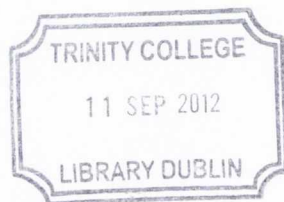
School of Physics

Trinity College Dublin

A thesis submitted to the University of Dublin, Trinity College, in
application for the degree of

Doctor of Philosophy

9th December 2011



Thesis 9509

Declaration

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A Giulio,
cuore gentile ed amico vero.

Summary

In this thesis an alternative self-assembled deposition technique able to produce nanoparticle (NP) arrays ordered on the macroscale is described. Stepped surfaces are produced by high temperatures annealing Al_3O_4 (0001) and metals are evaporated at a glancing angle of incidence towards the surface. In this way NPs are produced on a transparent and insulating substrate. These structures show localised plasmon resonances whose energetic positions depend on the polarization of the exciting light, the template deposition, the NP size as well as the distance between the NPs.

After an introduction, Chapter 1 provides a theoretical background for the understanding of the plasmonic resonances phenomenon. The origin of the absorption plasmonic resonances is described and dipolar models are introduced to explain the behaviour of NP arrays. Chapter 2 describes the experimental tools utilised for the characterisation of the structures and summarizes previous results on glancing angle deposition. Chapter 3 deals with the preparation of the stepped substrates and can be read independently. The faceting phenomenon of Al_2O_3 (0001) via high temperature annealing is investigated as a function off-cut angles and annealing temperature. Chapter 4 studies the in-plane optical properties of Ag NP arrays and their dependency on the parameters governing the growth. The in-plane optical properties are analysed *in situ* with reflectance anisotropy spectroscopy upon changes of the parameters affecting the growth. A theoretical model is utilised to explain the effects of the exposure of the samples to atmosphere, the origin of the Gaussian broadening and to study the dependency of the Ag structures as a function of the initial template periodicity. It is demonstrated that the peak position can be tuned over wide energy ranges.

In chapter 5 the the NP arrays are characterised by spectroscopic ellipsometry in order to obtain information on the out-of-plane resonance. The theoretical concepts necessary for understanding the ellipsometry informations are introduced. Chapter 6 demonstrates that glancing angle deposition is a technique independent on the deposited material and usage of different plasmonic materials allow one to tune the resonant profiles of the structures grown in even greater energy ranges. Finally, we give a short summary of the results included in this thesis and we propose some applications for the structures grown.

Publications:

1. **R. Verre**, B.O'Donowan, S.K Arora, K. Fleischer, H.Gervasi, J.Fontcuberta and I.V. Shvets.
Magneto-Optical properties of anisotropic Co nanostructures grown at glancing angle of incidence.
(*In preparation*).
2. **R. Verre**, R.G.S. Sofin, D. Fox, G. Behan, H.Zhang and I.V. Shvets.
High temperature annealing of Al_2O_3 (0001): sub-100nm engineering and mechanisms of faceting formation.
(*In preparation*).
3. **R. Verre**, K. Fleischer, O.Ualibek and I.V. Shvets.
Self-assembled broadband plasmonic nanoparticle arrays for sensing applications.
Applied Physics Letter, Accepted in December 2011.
4. **R. Verre**, K. Fleischer, J. F. McGilp, D. Fox, G. Behan, H.Zhang and I.V. Shvets.
Controlled *in situ* growth of tunable plasmonic self-assembled nanoparticle arrays.
Nanotechnology, accepted in November 2011.
5. **R. Verre**, K. Fleischer, C.Smith, N. McAlinden, J. F. McGilp and I.V. Shvets.
Probing the out-of-plane optical response of plasmonic nanostructures using spectroscopic ellipsometry.
Phys. Rev. B., **84**, 085440 (2011).

6. R. Verre, K. Fleischer, R.G.S. Sofin, N. McAlinden, J. F. McGilp and I.V. Shvets.

In situ characterisation of one-dimensional plasmonic Ag nanocluster arrays.

Phys. Rev. B., 83, 125432 (2011).

List of Abbreviations:

AFM	Atomic Force Microscopy
ASEF	Anisotropic Surface Excess Function
BSE	BackScattered Electron
CRT	Cathode Ray Tube
EM	ElectroMagnetic
FIB	Focused Ion Beam
FWHM	Full Width Half Maximum
IR	Infrared
IT	Iterband Transition
LPR	Localised Plasmon Resonance
NP	Nanoparticle
PTS	Polarized Transmission Spectroscopy
RAS	Reflectance Anisotropy Spectroscopy
SDA	Surface Dielectric Anisotropy
SE	Spectroscopic Ellipsometry
SEL	Secondary ELection
SEM	Scanning Electron Microscope
SERS	Surface Enhanced Raman Spectroscopy
TEM	Transmission Electron Microscope
UHV	Ultra High Vacuum
UV	Ultra-Violet
vis	visible

List of Figures

1	Example of colloidal plasmonic NPs.	2
2	A schematic view of glancing angle deposition technique.	4
1.1	Polarizability of a sphere embedded in air.	15
1.2	Polarizability of an ellipsoid.	17
1.3	Effects of a dielectric coating shell surrounding the particle.	19
1.4	Schematic of the isolated particle in proximity with a substrate.	20
1.5	Schematics of the long wavelength approximation for NP arrays.	25
1.6	Effects of NP coupling.	27
2.1	Schematics of the RAS setup used during the measurements of plasmonic NP arrays.	32
2.2	Picture of the RAS system utilised.	34
2.3	Picture of the deposition chamber utilised.	36
3.1	Schematic of the Al_2O_3 single crystal unit cell and relative low index stable surfaces.	47
3.2	Al_2O_3 idealised crystal structure.	48
3.3	Faceted $\text{Al}_2\text{O}_3(0001)$ surface after high temperature annealing and its temperature dependency.	52
3.4	Annealing of 2° and 3° off-cut samples.	53
3.5	TEM section of an annealed Al_2O_3 surface.	54
3.6	Defects of a faceted $\text{Al}_2\text{O}_3(0001)$ surface.	55
3.7	Normalised period distribution as a function of the relative period.	56
4.1	RAS spectra of an annealed Al_2O_3 substrate.	61

4.2	Comparison between <i>ex situ</i> RAS and PTS measurements.	63
4.3	SEM and RAS of a sample prepared at glancing angle deposition. . . .	65
4.4	Peak parameters as a function of the deposition parameters.	67
4.5	Simulation of the absorbance of NP arrays utilising the coupled oscillator model.	71
4.6	Fit of experimental spectra using the coupled oscillator model.	73
4.7	Shadowing effect schematic.	75
4.8	Plot of fitted Γ value as a function of the percentage dispersion in the island size.	76
4.9	Plot of the fitted Γ value, as a function of deposition angle, for different coverages.	76
4.10	Simulation of the peak broadening due to morphological distribution. .	77
4.11	Effects of the exposure of the sample to atmosphere.	79
4.12	Measured real (A) and imaginary (B) part of the dielectric function of a native Ag_2S layer.	80
4.13	Simulated RAS spectra for different tarnishing thickness.	81
4.14	RAS and morphology as a function of the initial template periodicity. .	82
4.15	TEM of Ag NP arrays.	84
4.16	RAS as a function of the template periodicty.	85
4.17	Image charge effect.	86
4.18	Simulation of RAS as a function of the terrace dependency.	87
5.1	Morphology of a sample studied.	96
5.2	Sketch of the SE measurement of Ag NP arrays in the parallel configu- ration.	98
5.3	Measurements of SE and RAS.	99
5.4	Extracted and simulated ASEF.	101
6.1	Bulk dielectric function of Au and Cu.	105
6.2	Thin film dielectric function of Au and Cu.	106
6.3	Parametrised dielectric function of thin Au and Cu layer.	108
6.4	Au and Cu NP arrays: SEM and RAS study.	109
6.5	RAS dependence on the the deposited time for Au and Cu.	110
6.6	Simulated Au and Cu NP arrays RAS spectra.	112

- 7.1 RAS spectra of Ag NP arrays after exposure of the sample to atmosphere. 117
- 7.2 Normalised RAS spectra of NP arrays of different plasmonic materials. 117
- 7.3 Normalised RAS spectra of Ag NP arrays immersed in different solvents. 119

List of Tables

3.1	The main surface terminations for Al_2O_3 and their relative free energy from first principle and Wulf construction.	47
3.2	Statistics of the annealed Al_2O_3 substrates.	51
4.1	Morphology and fitted parameters for Ag NP arrays grown at different deposition angles.	73
4.2	Morphology of NP arrays grown on different templates.	83
5.1	Morphology parameters of the sample measured with SEM and AFM. .	97
6.1	Fitted parameters for the thin film dielectric function of Au and Cu. . .	108
6.2	Morphology of Au and Cu NP arrays as measured with SEM and AFM.	111

Contents

Introduction	1
1 Localised Plasmonic Resonances: Theory	7
1.1 Optical properties of metals	9
Drude oscillator model	9
Noble metal dielectric function	11
1.2 Localised plasmon resonances of isolated particles	13
The polarizability of a small metallic sphere: classical model	13
Generalization to general ellipsoid	15
Comparison between dipolar model and Mie theory	18
1.3 Image charge effects	20
1.4 Models of nanoparticle arrays	23
Validity of the quasistatic approximation	23
Classical picture of nanoparticle arrays	24
1.5 Advanced numerical methods	27
2 Experimental Setup	29
2.1 Previous literature on glancing angle deposition	30
2.2 Reflectance anisotropy spectroscopy	31
Applications of RAS	33
Implementation of the RAS setup	33
Three-layers model	34

2.3	The Deposition Chamber	35
2.4	Spectroscopic Ellipsometry	36
2.5	UV-visible spectrometer	38
2.6	Atomic Force Microscopy	39
2.7	Scanning electron microscope (SEM)	40
2.8	Transmission Electron Microscope (TEM)	42
2.9	High temperature furnace	43
3	C-plane Sapphire and the Faceting Mechanism	45
3.1	Al ₂ O ₃ : introduction	46
	Al ₂ O ₃ Crystal structure	46
	Applications	48
	Reports on Al ₂ O ₃ (0001) annealing	49
3.2	C-plane Al ₂ O ₃ : experimental procedure	50
3.3	Results and discussion	50
3.4	Conclusions	57
4	In-plane Optical Properties of Ag Nanoparticle Arrays	59
4.1	Al ₂ O ₃ (0001) RAS signature, role of the miscut	60
4.2	Experimental procedure	61
4.3	Transmission and RAS comparison	62
4.4	Dependency of the optical response on the deposition angle	64
4.5	Coupled oscillator model	68
4.6	The origin of the peak broadening	72
4.7	Exposure of the sample to atmosphere	78
4.8	Dependency of the optical properties on the initial template periodicity	80
	Experiment	80
	Theory	85
4.9	Conclusions	88

5	Ellipsometric Investigation of the Out-of-Plane Optical Response	91
5.1	The Anisotropic Surface Excess Function	92
5.2	Experiment	96
5.3	Discussion	98
5.4	Conclusion	102
6	Deposition of Alternative Plasmonic Materials	103
6.1	Au and Cu dielectric function	104
	Evaluation of Au and Cu thin film dielectric function	105
6.2	Au and Cu NP arrays: results and discussion	109
6.3	Conclusions	113
7	Conclusions and Future Work	115
7.1	Future work, from fundamental studies to applications	118
	Appendix	121
	References	122
	Acknowledgements	139

Introduction

Per me si va ne la citta' dolente,
per me si va ne l'eterno dolore,
per me si va tra la perduta gente.

D. Alighieri, *Inferno*, Canto III

Plasmonics is a dynamic and rapidly evolving field studying the coupling of free electron in metallic low dimensional systems with light [1–3]. Strong absorption peaks [4, 5], extraordinary light transmission [3, 6, 7], Fano resonances [8], wireless waveguiding of energy [3, 9] and enhancement effects [10–12] are some of the discovered plasmonic-related phenomena which might revolutionise different research fields. Computers working in the Terahertz frequency range, single molecule recognition for biophysical applications and solar cells are just a few examples of the broad fields to which plasmonics can contribute and offer promising advantages [2].

Of particular interest are the properties of metallic nanoparticles (NPs). The collective resonant behaviour of the conduction electrons in noble metal NPs has been known for more than a century [4], but recent advances in nanofabrication opened new and exciting opportunities [8, 13]. Devices have already been created and a much deeper understanding of the phenomena related to plasmonic NPs has been achieved. The enormous advances were possible thanks to the versatility in the NP growth, especially through colloidal preparation [14]. In this process NPs are usually produced from an acid solution via the addition of particular reducing agents. As more atoms are formed, the solution becomes supersaturated and the noble metal atoms precipitate in the form of sub-nanometer particles. The rest of the atoms adhere to

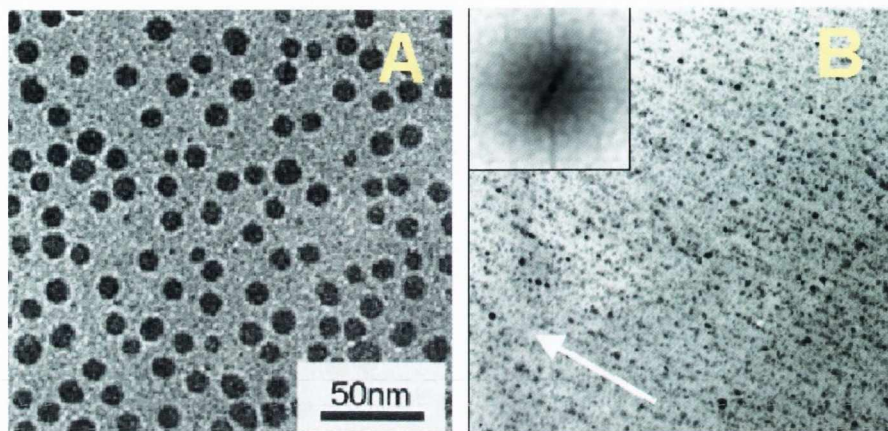


Figure 1: (A) SEM image of colloidal NPs randomly dispersed on a substrate [20]. (B) A possible approach for producing aligned NP structures. The anisotropy was obtained irradiating the NP solution with 30 MeV Si^{+5} ions. The arrow reproduces the flux direction. In the inset a Fourier Transform of the image is shown. Reproduced from [21].

the existing particles and, if the solution is stirred vigorously enough, the particles will be fairly uniform in size. To prevent the particles from aggregating further, some sort of stabilizing agent that sticks to the NP surface can be added. The NPs can be finally functionalized with various organic ligands [15] to create organic-inorganic hybrids with advanced functionality. Modifications in the colloidal synthesis recipes proved to be a convenient scalable technique for tuning the properties and morphology of metallic NPs. Spherical clusters [16], prisms [17], nanorods [18], ellipsoids [18] and nanostars [19] are just a few examples of the NPs grown, obtained often with a minimal dispersion in dimension or shape distributions.

The colloidal bottom-up approaches have a great drawback whenever the particles have to be ordered in a planar geometry [13]. As shown for example in Figure 1 (A), the dispersion of the colloidal solution onto a substrate produces NPs placed randomly on the surface, without any long range order. The scientific community has invested great efforts to overcome this problem, via prefunctionalisation of the surface [13], additional processes on the surface (e.g. see Figure 1 (B)) or through lithographic top-bottom approaches [22, 23]. The first two methods are still lacking proper tunability, while the latter is impractical for its expense and the impossibility of covering large substrate areas.

Obtaining plasmonic NPs ordered on the macroscale is of fundamental interest for multiple reasons. Generally, plasmonic structures can be used as optical sensors as their resonance position depends on the dielectric properties of the surrounding medium. It was shown recently that linear and planar arrays of NPs and planar nanostructures have an added sensitivity upon changes of the dielectric environment [24]. Furthermore, linear chains of metal NPs can channel the flow of electromagnetic energy over hundreds of nanometers due to near-field coupling [9] and hybrid photonic/electronic devices can be produced in this way. Strong amplification of the electric field in the interstitial space between neighbouring particles led to the discovery of enhancement effects. The electric field increase has been utilised for Surface Enhanced Raman Spectroscopy (SERS) [16, 25], second-harmonic generation [11], fluorescence [12] photolithography [26], and optical tweezers [27]. Finally, the NPs can be incorporated in solar cells and, acting as scatterers, increase the optical path of the light inside the absorbing material, thus increasing the overall solar cell efficiency [28].

In this thesis we present a novel and alternative deposition method [29–33] able to combine the large throughput required for any industrial application with a long range order usually attainable with lithography (see Figure 2). A collimated flux of adatoms are sent in an ultra high vacuum (UHV) environment at a glancing angle of incidence towards a stepped surface. The pattern of the template shadows part of the surface and ordered NP arrays can then be reproducibly created on the macroscale. In the course of the thesis it will be shown:

- The glancing angle deposition technique produces NPs below the lithographic limit, highly ordered and strongly coupled.
- Vicinal c-plane Al_2O_3 annealed at high temperature can be used as a stepped substrate for the development of the deposition technique.
- The grown NP arrays possess two in-plane plasmonic resonances dependent on the polarization of the incoming light, resulting in a strong dichroic response.
- Unlike many other self-assembly methods, glancing angle deposition is independent of the deposited materials.

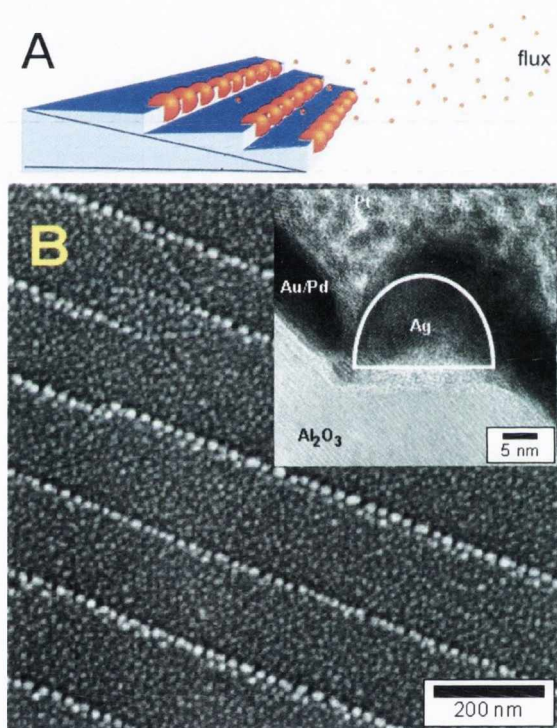


Figure 2: (A) A schematic view of glancing angle deposition technique: flux of collimated Ag adatoms is sent at a tilted angle of incidence towards a stepped surface. The material coalesces on the step forming periodic NPs coupled through electrostatic dipoles. Surface plasmon resonances are then expected with sharp profiles whose position is dependent on the polarization of the exciting light. (B) SEM image of one of the structures grown with the glancing angle deposition approach. In the inset a TEM section of a NP can be observed.

- The NP arrays morphology can be tailored and the corresponding optical properties can be tuned over wide energy ranges, gaining the versatility typical of colloidal preparation methods
- During the deposition an optical technique, Reflectance Anisotropy Spectroscopy (RAS), can monitor the resonant profiles. Resonance energies required for a particular application can be monitored and predicted reliably with RAS.
- Spectroscopic ellipsometry can be used to measure the out-of-plane resonances of ultra-thin plasmonic layers.
- Classical models can be used to describe the feature observed and address the origin of the optical resonance.

Chapter 1

Localised Plasmonic Resonances:

Theory

Physics is mathematical not because
we know so much about the physical
world, but because we know so little;
it is only its mathematical
properties that we can discover.

B. Russell

Localised plasmon polaritons are collective excitations of the conduction electrons in a metal NP interacting with an electromagnetic wave. Light, whose wavelength is much larger than the physical dimensions of the structures, interacts simultaneously with all the free electron, which subsequently begin to oscillate coherently inside the NPs. Usually, for noble metal clusters, the oscillations result in strong reflection or absorption resonances in the visible range. Plasmonics is a subfield of nanophotonics which tries to tailor and understand properties and features related with these charge

oscillations.

From an historical prospective, the discovery of plasmonic properties can be traced to the ancient era as it was discovered that the annealing of metallic salts in otherwise transparent glass could create brightly coloured stain glasses. The only surviving example is the Lycurgus cup, dated 4th century AD. As the cup was illuminated by reflected light the cup resulted in a green colouration while it appeared red when lit in transmission. The unusual property has been explained by the inclusion of both gold and silver particles of sub 100 nm diameter which strongly scatter green light but transmit red.

The first attempts to explain quantitatively the optical behaviour were made at the beginning of the twentieth century. First, Lord Rayleigh studied the light scattering phenomenon of particles below the diffraction limit while, in 1904, Garnett explained the bright colours of metallic particles using a simple Drude oscillator model. The greatest contribution was provided by Gustav Mie and published in 1908 in *Annalen der Physik* [4]. In his formulation, Mie presented a general formulation for the scattering of light from spherical homogeneous particles in a dielectric embedding medium, predicting a dependency of the resonant frequency with particle diameter [1].

Nowadays, a great body of literature is available and plasmonics is emerging as a rapidly evolving field due also to its practical multidisciplinary applications. This chapter will provide a rapid overview on useful theoretical concepts utilised in the rest of the thesis and it is divided into four parts. First, an analytical expression for metal dielectric functions is obtained. Second, the concept of surface plasmon resonance is formally described in both a classical and electrodynamical framework. Third, substrate effects for supported particles are taken into account. Finally, the extension of the optical properties in the case of coupled NP arrays is reported, together with previously published results obtained with advanced numerical methods. Throughout the chapter the simulations presented have been performed using a program developed by the author in order to clarify and demonstrate the concepts described.

1.1 Optical properties of metals

The optical response of any material interacting with light can be described by a complex quantity, called the dielectric function $\varepsilon = \varepsilon' + i\varepsilon''$. If the optical response of a material is linear, the dielectric function is related to its susceptibility χ by

$$\varepsilon = 1 + \chi \quad (1.1)$$

and appears in the Maxwell equations via the polarization $\mathbf{P}$ through the relation

$$\mathbf{P} = \varepsilon_0 \chi \mathbf{E}. \quad (1.2)$$

The band structure of the materials result in different absorption coefficients for different wavelengths and hence a frequency dependant dielectric function. Oxides and transparent materials usually have a positive and almost constant value in the visible spectral range, while, for strongly dispersive materials, the dielectric function assumes very different values even in narrow frequency regions. Metals are among these materials and their properties can be measured by ellipsometry and modelled by a Drude oscillator model.

Drude oscillator model

The simplest model able to describe the metal IR dielectric function is the Drude-Sommerfield model.¹ A system or material is approximated to be a simple harmonic dampened oscillator of mass m and charge e . An external driving force $\mathbf{E}$ displaces the charge from its equilibrium position. Assuming a linear restoring force $\mathbf{F} = k\mathbf{r}$ and a dampening effect $\mathbf{F}_g = g\dot{\mathbf{r}}$ proportional to the velocity, the equation of motion can be written as

$$m\ddot{\mathbf{r}} + g\dot{\mathbf{r}} + K\mathbf{r} = e\mathbf{E}. \quad (1.3)$$

The introduction of the effective damping constant has been considered in Eq. (1.3) in order to take into account the heating losses inside the material and reproduce the

¹The drude oscillator model has been reported by different authors. The formalism here reported is taken from [34].

finite resistance of the material. Equation (1.3) can be rewritten after the renormalisations $\omega_0^2 = K/m$ and $\Gamma = g/m$ as

$$\ddot{\mathbf{r}} + \Gamma \dot{\mathbf{r}} + \omega_0^2 \mathbf{r} = \frac{e}{m} \mathbf{E}. \quad (1.4)$$

For oscillating fields such as electromagnetic (EM) waves the driving force has a sinusoidal behaviour $\mathbf{E} = \mathbf{E}_0 e^{i\omega t}$ and the solution of Eq. (1.4) becomes

$$\mathbf{r} = \frac{(e/m)}{\omega^2 - \omega_0^2 - i\omega\Gamma} \mathbf{E}_0 e^{i\omega t}. \quad (1.5)$$

If we now consider an ensemble of N identical dipoles with a dipole moment $\mathbf{p} = e\mathbf{r}$ in a volume V , the polarization of the system is $\mathbf{P} = (N/V)\mathbf{p}$. According to these relations Eq. (1.5) can be rewritten as

$$\mathbf{P} = \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\Gamma} \varepsilon_0 \mathbf{E}_0 \quad (1.6)$$

where the plasma frequency ω_p was defined as $\omega_p^2 = \frac{(N/V)e^2}{m\varepsilon_0}$. The plasma frequency can be considered as the natural quantised oscillation frequency for the electron sea in bulk materials. This means that bulk electrons oscillate back and forth at this frequency until the energy is lost in some kind of resistance or damping. For low-dimensional structures the system act as a resonator whose resonance frequency ω_0 coincides instead with the minimum of the denominator in Eq. (1.6). Shift in the resonance position are hence found in different positions. Combining finally Eq. (1.1), Eq. (1.2) and Eq. (1.6) the dielectric function of a material can be presented as

$$\varepsilon(\omega) = 1 + \frac{\omega_p^2}{\omega_0^2 - \omega^2 - i\omega\Gamma}. \quad (1.7)$$

Due to superposition principle, the approach can be extended assuming the presence of n oscillators each having a ω_{0j} resonance frequency. The dielectric function can be written as

$$\varepsilon(\omega) = 1 + \sum_j \frac{\omega_{pj}^2}{\omega_{0j}^2 - \omega^2 - i\omega\Gamma}. \quad (1.8)$$

Equation (1.8) is a very general relation which describes the behaviour of any linear oscillator of a point charged system in the presence of an external exciting plane wave. As will be shown in the rest of this chapter, this relation, under opportune modifications, provides both a qualitative description of plasmonic resonances in metal clusters and quantitatively describes the IR dielectric function of metals.

Noble metal dielectric function

The interactions of photon and free electrons in a metal result in the main optical features occurring in the IR region and can be described with the Drude oscillator model described before. The effect is due to the correspondence of fermionic quasi particles next to the Fermi level with free Drude electrons that do not experience any restoring force $F = k\mathbf{r} = 0$. As $\omega_0^2 = k/m$, the free electron system can then be approximated as oscillators with a zero resonance frequency.

The analogy, for metals such as Al and the alkali elements, allow to use Eq. (1.7) directly with $\omega_0 = 0$ to model the dielectric function in the IR range. Other materials, especially those showing a strong plasmonic response such as noble metals, need to take into account the contribution of the bound electrons which will partially polarise the positive ion cores. The effect can be represented by an additional constant contribution ε_∞ and the dielectric function in the IR becomes

$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_0}. \quad (1.9)$$

In the rest of the manuscript, for bulk Ag it will be assumed $\varepsilon_\infty = 5.266$ and $\omega_p = 3.02\text{eV}$. The dampening constant is $\Gamma_0 = v_F/\lambda_b = 7.9 \times 10^{13} \text{ s}^{-1}$, where $v_F = 1.37 \times 10^6 \text{ m/s}$ is the Fermi velocity and $\lambda_b = 57 \text{ nm}$ the bulk mean free path.

When dealing with NPs and low dimensional systems, the presence of interfaces needs to be taken into account as the scattering of electrons at the surface becomes relevant. This is particularly evident as soon as $\lambda_b > R_i$, where R_i is the dimension of the metallic cluster along the i -th direction. Under the assumption that collisions are independent, the different relaxation rates can be simply added together according to the Mathiessens rule and the relaxation rate becomes

$$\Gamma_i = \Gamma_0 + A \frac{v_F}{R_i}. \quad (1.10)$$

In Eq. (1.10) A is a quantity of the order of unity whose exact value depends on the chemical properties of the interface between the NP and the surrounding medium [1, 35]. Unless clearly stated, during the simulations $A = 0.25$ will be assumed. With this modification, the imaginary part of the dielectric function increases in the IR for small R while the real part is almost unchanged.

The choice of these parameters bulk silver for simulating the optical behaviour of Ag NPs is crucial and require further discussion. Generally, two approaches can be used when the metal dielectric function is introduced: either the experimental tabulated data can be directly utilised or the one obtained by fitting the tabulated values using the free electrons model. The first approach has the advantage of taking into consideration also bound electron contributions, while for the second one a direct analytical model is readily available. As for Ag the interband transitions are present at energies higher than 4 eV (hence outside the range where plasmonic resonances are usually found) the second option has been preferred in the present thesis. The non perfect matching between theory and experiment discussed in the rest of the thesis can be explained partly as due to the utilization of non corrected dielectric function for the bulk material. An alternative suggested approach, maybe more general and correct, would require the deposition of a thin layer of material on a flat substrate and the measurement of its dielectric function using spectroscopic ellipsometry. We leave to interested readers the application of this alternative approach for future studies.

In order to completely describe the dielectric function, interband transition components have also to be added. This is particularly important for Au or Cu as interband transition peaks can be measured in the visible range. The resulting contributions can be determined by the band structure $E(\mathbf{k})$ of the element and the matrix transition probability $\langle f|M(\mathbf{k})|i\rangle$ between the initial (i) and final (f) states. An analytical expression for the susceptibility χ^{IB} of the interband transitions under the assumption of an electric-dipole approximation for the electron-photon interaction Hamiltonian can be obtained [36]:

$$\chi^{IB} = \frac{8^3 \pi e^2}{m^*2} \sum_{i,f} \int_{BZ} \frac{2d\mathbf{k}}{(2\pi)^3} |\langle f|\mathbf{e}M(\mathbf{k})|i\rangle|^2 \left(\frac{1}{[E_f(\mathbf{k}) - E_i(\mathbf{k})][(E_f(\mathbf{k}) - E_i(\mathbf{k}))^2 - \omega^2]} \right). \quad (1.11)$$

In equation Eq. (1.11) the integral is over the whole Brillouin zone and $\mathbf{e}$ is the unit vector along the electric field direction. Rather than computing this quantity, in Chapter 6 we will refer to measured values, used as input parameter, during the simulation of Au and Cu NP arrays.

1.2 Localised plasmon resonances of isolated particles

Metal NPs have particular optical properties, different from both molecules and solids due to their reduced dimensionality. In particular, a non null restoring force is present and different finite resonances appear. Their exact position depends on different parameters, such as dimension, shape, dielectric environment surrounding the particles [37] and the possible electrodynamic interaction between different particles. Different approaches can be utilised to describe the plasmonic properties and we report a brief overview of results based both on classical pictures and Mie's theory.

The polarizability of a small metallic sphere: classical model

When discussing the behaviour of particles in a classical context, it is convenient to introduce the quasi-static approximation. If the wavelength of the exciting wave is much larger than the average dimension R of the excited NP ($R \ll \lambda$) retardation effects of the electromagnetic field inside the cluster become negligible and the field can be approximated as a constant inside the material [1].

Consider now a homogeneous isotropic metallic sphere¹ with dielectric function ε_{NP} placed in a homogeneous medium with real dielectric function ε_m . When excited by an external electric field $\mathbf{E}_0$ a charge will be created on the surface of the particle in order to zero the electric field inside the sphere. Introducing the potentials describing the electromagnetic fields and imposing the proper boundary conditions between the different materials, it can be shown that the field outside the sphere is equivalent to the sum of the applied field and that one of an ideal dipole placed at the center of the sphere with a dipole moment

$$\mathbf{p} = 4\pi\varepsilon_m R^3 \frac{\varepsilon_{NP} - \varepsilon_m}{\varepsilon_{NP} + 2\varepsilon_m} \mathbf{E}_0. \quad (1.12)$$

Defining the polarizability α as

$$\alpha = 4\pi R^3 \frac{\varepsilon_{NP} - \varepsilon_m}{\varepsilon_{NP} + 2\varepsilon_m}, \quad (1.13)$$

¹The description here reported follows the derivation present in Chapter 5 of [5].

the proportionality between the applied field and the dipole moment is

$$\mathbf{p} = \varepsilon_m \alpha \mathbf{E}_0. \quad (1.14)$$

A resonance condition for the dipole moment is obtained when the denominator of Eq. (1.13) is minimum, and, if $\Gamma \ll 1$, it corresponds to

$$\text{Re}[\varepsilon_{NP}] = -2\varepsilon_m. \quad (1.15)$$

Several conditions present themselves, which require comment. First we note that, in order to satisfy Eq. (1.15), a negative ε'_{NP} is necessary. This condition in the visible range is satisfied for noble metals NPs and the LPRs effects are then observed mainly for Ag and Au. The resonant behaviour can also be introduced modelling the metal sphere as a free electron gas embedded in a positive jellium. In this case the displacement of the negative charges due to the impinging electric field generates a polarization charge at the surface of the cluster and the linear restoring force due to electrostatic attraction of negative electron gas and positive ion cores generates a resonance frequency at finite values. Within the quasistatic approximation, this coulomb picture is valid but the resonance position does not depend on R . It was effectively shown [1] that for small particles the resonance position is mainly related to the mean free path of bulk electron itself. As this is smaller than the average NP radius, independence of NP resonance position on R is thus motivated. Figure 1.1 shows the resulting real and imaginary part for the polarizability of an isolated silver sphere of different radii assuming air as an embedding medium. A resonance is present in the imaginary part of the NP, correspondent to absorption of the energy of the incoming EM wave [34]. As the position of the peak is determined by Eq. (1.15) and as ε'_{NP} is independent on the NP radius, the position of the resonant peak is unchanged by changes of the NP radius. Conversely, the width of the NP is determined by the imaginary part of ε_{NP} , hence increasing with decreasing NP radius.

In any real experiment, the observable quantities are usually expressed in terms of absorption and scattering cross sections, related to the polarizability of the cluster by the relations

$$\begin{aligned} C_{abs} &= k \Im(\alpha) = k \frac{\varepsilon''_{NP}}{(\varepsilon'_{NP} - \varepsilon_m)^2 + (\varepsilon''_{NP})^2}, \\ C_{sca} &= \frac{k^4}{6\pi} |\alpha|^2 \end{aligned} \quad (1.16)$$

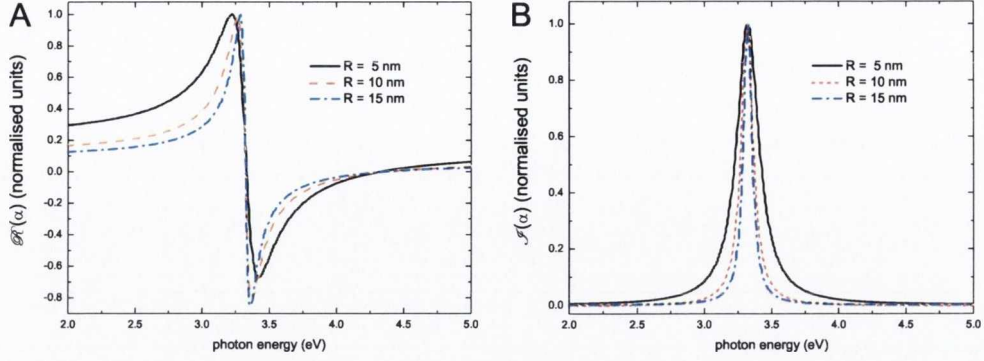


Figure 1.1: Normalised real (A) and imaginary (B) part of the modelled polarizability of Ag spheres embedded in air for $R = 5$ nm, 10 nm and 15 nm radius. A resonance peak is present in the imaginary part, corresponding to absorption of the incoming light. The position of the resonance does not change with changes of the NP radius. However, reduced dimensions of the NP produces broadening of the peak as the scattering rate Γ increase for smaller radius.

with $k = \omega/c$ being the wavevector of the incident electromagnetic wave. Equations (1.16) define the amount of light absorbed and scattered and resonances are expected. As mentioned before, in the case of noble metals, the position of the energy resonances falls in the visible range for most transparent embedding media. Generally speaking, the extinction coefficient is the sum of absorbed, reflected and scattered light. As the absorption coefficient depends linearly on the NP volume while the scattering depends quadratically, for small particles the first contribution will be the dominant one in the visible range. The limit below which the scattering can be disregarded is around 80 nm for Ag and 50 nm for Au NPs. As the glancing angle deposition reported in the next chapters produces routinely NPs with smaller dimensions, absorption (and the correspondent specular reflection) of light will be the observables measured in the rest of thesis and scattering will be disregarded unless clearly stated.

Generalization to general ellipsoid

The polarizability of a sphere was obtained in the precedent section by defining the electric scalar potential and solving the potential equations, in the Gauss gauge, with proper boundary conditions. The same procedure can be developed in the more general

case of an ellipsoid with semiaxes R_i , whose surface is defined by

$$\frac{x^2}{R_x^2} + \frac{y^2}{R_y^2} + \frac{z^2}{R_z^2} = 1. \quad (1.17)$$

In this case, the correct potential can be calculated using ellipsoidal coordinates and the polarizability can be written as [5]

$$\alpha = \frac{4\pi R_x R_y R_z}{3} \frac{\varepsilon_{NP} - \varepsilon_m}{\varepsilon_m + L_i(\varepsilon_{NP} + \varepsilon_m)} \quad (1.18)$$

where the shape depolarization factors L_i are

$$L_i = \frac{R_x R_y R_z}{2} \int_0^\infty \frac{dq}{(R_i^2 + q)f(q)} \quad (1.19)$$

with $f(q) = [(q + R_x^2)(q + R_y^2)(q + R_z^2)]^{1/2}$. Furthermore, the shape depolarization factors L_i satisfy the relation

$$\sum_i L_i = 1. \quad (1.20)$$

The departure of the particle shape from spherical to ellipsoidal has important modification on the resonant profile of the charge oscillations. The peaks, that in the spherical case were degenerated due to symmetry considerations, are now split into 3 different resonant modes corresponding to resonances along the three main axis of the ellipsoid. The resonant positions become function of the shape of the particle and inserting Eq. (1.9) into Eq. (1.18) the resonance frequency $\omega_{res,i}$ becomes

$$\omega_{res,i} = \sqrt{\frac{\omega_p^2}{\varepsilon_\infty + (\frac{1-L_i}{L_i})\varepsilon_m} - \Gamma^2}. \quad (1.21)$$

The polarizability of an anisotropic ellipsoid can be found in Figure 1.2, where three distinct peaks can be seen. The NP radii were fixed to be $R_x = 16$ nm $R_y = 8$ nm and $R_z = 5$ nm. The elongation along a particular direction produces a red shift of the corresponding resonance and, at the same time, blue shift the other two resonances as the shape depolarization factors are related by Eq. (1.20). In order to clearly illustrate the concept, the inset in Figure 1.2 shows the resonance position of the three peaks as a function of R_x while keeping constant $R_y = 8$ nm and $R_z = 5$ nm. It can be noticed that the resonant peak energy along the elongated x direction is effectively decreased, while the resonant energy of the other two peaks increase. This behaviour can be

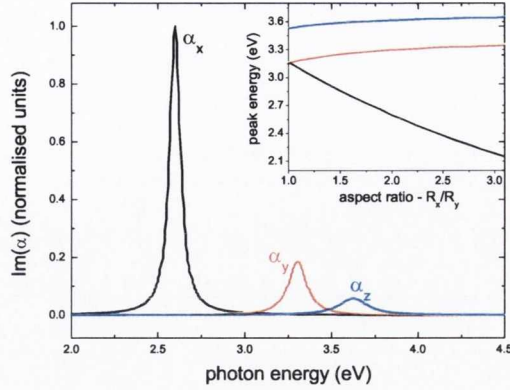


Figure 1.2: Calculated imaginary part of the polarizability of an ellipsoid with radii $R_x = 16$ nm, $R_y = 8$ nm and $R_z = 5$ nm. Elongation along the x direction produces a shift of the resonance at lower energy. Inset: resonance position as a function of the aspect ratio R_x/R_y obtained changing of R_x while keeping fixed R_y (8 nm) and R_z (5 nm). It can be notice that the resonance along the x direction red shift with increases of R_x , while the other resonances blue shift.

understood qualitatively using the classical coulomb picture. The Coulombic restoring force between free electron and positive ion cores scales in fact as R_i^{-3} and red shift of the resonance for elongated structures is thus expected. Furthermore, from Eq.(1.20), it appears also clear that changes along one of the directions modifies the whole spectral response of an anisotropic NP.

A further refinement in the ellipsoidal model can be done taking into account the effects of a coating dielectric shell surrounding the particle. In this case, three mediums are present in the system with permittivity of ϵ_{NP} (metal), ϵ_s (coating dielectric shell) and ϵ_m (embedding medium) respectively. It is assumed here that shell and core have the same aspect ratio, s_x is the shell thickness along the x direction, $f_v = R_x^3/(R_x - s_x)^3$ is the volumetric fraction occupied by the core and V_p is the volume of the overall cluster. The net polarizability of the isolated particle can hence be written as[5]

$$\alpha_\vartheta = V_p \cdot \frac{(\epsilon_s - \epsilon_m)[\epsilon_s + (\epsilon_{NP} - \epsilon_s)(1 - f_v)L_\vartheta] + f_v \epsilon_s (\epsilon_{NP} - \epsilon_s)}{[\epsilon_s + (\epsilon_{NP} - \epsilon_s)(1 - f_v)L_\vartheta][\epsilon_m + (\epsilon_s - \epsilon_m)L_\vartheta] + f_v L_\vartheta \epsilon_s (\epsilon_{NP} - \epsilon_s)}. \quad (1.22)$$

The effects of the dielectric layer depends on the dielectric function of the coating shell and its thickness. Generally speaking, if the coating shell has a dielectric function with $\epsilon'_s > \epsilon_m$, a red shift in the peak position is expected. This is confirmed in Figure 1.3 (A), where the polarizability of an ellipsoid with with the same radii as before (16 nm,

8 nm and 5 nm along the x , y and z direction respectively) is shown for different thickness s_x for a dielectric shell having $\varepsilon_s = 6$. In particular, it can be noticed that increases in the dielectric shell thickness red shift all the resonance peaks, regardless of the dielectric function of the dielectric shell (Figure 1.3 (B)). The peaks also red shift once the dielectric function of the coating shell increase, as shown in Figure 1.3 (C). Finally, if the dielectric shell assumes complex values, part of the energy is absorbed, resulting in a decrease of the peak intensities and in a broadening the resonances. This is shown in Figure 1.3 (D), where a coating shell of thickness $s_x = 1$ nm and $\varepsilon_s = 9$ is compared with one of the same thickness but having $\varepsilon_s = 9 + 2i$.

Comparison between dipolar model and Mie theory

In his original paper, G. Mie solved the Maxwell equations for an incoming plane wave interacting with a isolated spherical particle. The solution was obtained by introducing the electromagnetic potentials and expanding them in a spherical orthonormal system. A solution for each component was obtained and the extinction and scattering coefficients calculated. The initial hypothesis of homogeneous isotropic spheres surrounding a dielectric medium were valid only in very specific cases. Nevertheless, they provided a full analytical description of the optical properties based only on the validity of Maxwell equations.

In the particular case of long wavelength approximation, only the dipolar term in the Mie theory is non negligible and the extinction cross section becomes

$$\sigma_{abs} = 9 \frac{\omega}{c} (\varepsilon_m)^{3/2} V \frac{\varepsilon_{NP}''}{(\varepsilon_{NP}' - 2\varepsilon_m)^2 + (\varepsilon_{NP}'')^2}. \quad (1.23)$$

A striking correspondence between the simple dipolar result of Eq. (1.16) and Eq. (1.23) can be noticed. In both cases, under the hypothesis of small damping ($\varepsilon_{NP}'' \ll 1$), the resonance condition is given by Eq. (1.15) and a similar resonant behaviour is expected. The similarity is inherited in the calculations process: in Mie theory a full analytical calculation of the potential has been obtained and the dipolar term alone considered subsequently as $R \ll \lambda$. Similarly, in the classical picture, each particle was modelled as a simple dipole and the potential solving Maxwell equations obtained in the second step. Within the long wavelength approximation the classical approach is validated at least for a qualitative understanding of the results obtained.

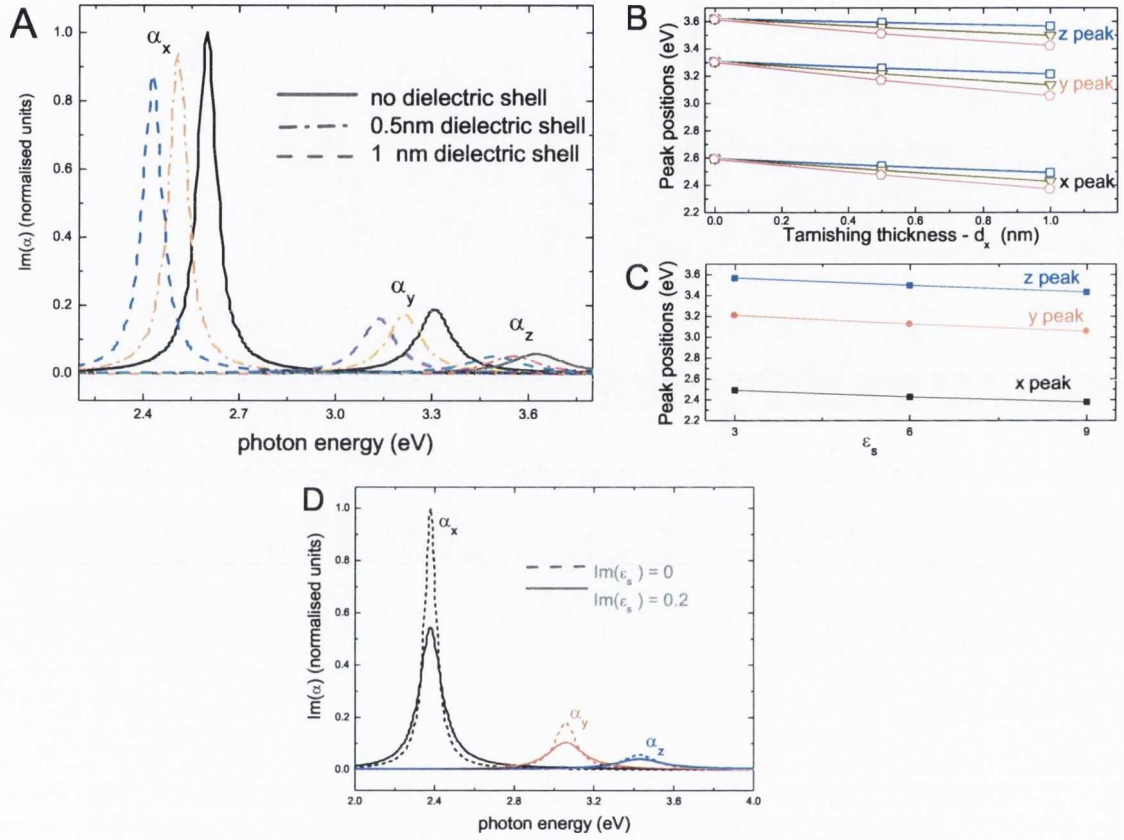


Figure 1.3: Effect of a coating shell dielectric shell surrounding a Ag particle. (A) Three distinct resonance peaks in the polarizability can be observed for an ellipsoid with radii $R_x = 16$ nm $R_y = 8$ nm and $R_z = 5$ nm. Once a dielectric shell with $\epsilon_s = 6$ replace the outer shell of the Ag NP, all the peaks red shift and decrease in intensity. The shift is proportional to the thickness s_x (B), regardless of the value of ϵ_s . The different colours refer to $\epsilon_s = 3$ (blue), 6 (yellow) and 9 (pink) respectively. Red shift in the resonance peak can then be obtained by increasing in the value of ϵ_s (C) (s_x was fixed to be 1 nm). (D) Once the dielectric shell becomes dispersive the peak intensities decrease and broaden. In the simulation $s_x = 1$ and the imaginary part was changed from $\epsilon_s = 9$ to $\epsilon_s = 9 + 2i$.

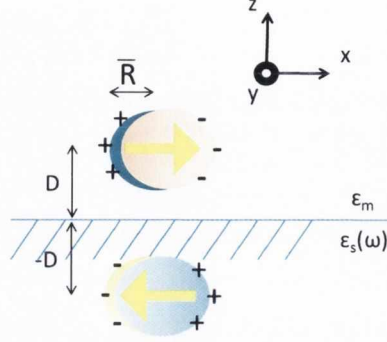


Figure 1.4: Schematic of the isolated particle in proximity with a substrate.

1.3 Image charge effects

In the previous section the resonant behaviour of an isolated ellipsoidal particle embedded in a dielectric homogeneous medium was described. Once the particle is supported on top of a substrate, the presence of a discontinuity in the dielectric function of the surrounding medium modifies the behaviour of the system.

The theoretical approach necessary to solve the problem is based on the well known image charge problem [34]. When a point charge q is located near the plane interface between two media with different dielectric permittivities ε_m (medium) and ε_b (substrate), the potential at a point P at the upper half space is given by a sum of the potentials ϕ of the charge q and its image charge q' . In particular the image charge is placed symmetrically underneath the NP and is given by [34]

$$q' = Fq \quad (1.24)$$

where

$$F = \frac{\varepsilon_b - \varepsilon_m}{\varepsilon_b + \varepsilon_m}. \quad (1.25)$$

Consider now a NP located in the proximity of the substrate at a distance D . The substrate is supposed flat in the x - y plane (see Figure 1.4). Within the quasistatic approximation the NP can be modelled as a point dipole p placed in its center. Similarly to the case of the isolated charge previously mentioned, the effects of the substrate can be represented by an imaginary dipole moment p' with intensity

$$\mathbf{p}' = F\mathbf{p}. \quad (1.26)$$

The imaginary dipole produces an electric field which will interact with the free electron in the real NP, modifying the resonance of the system. A few remarks are necessary: i) whenever the isotropic case is recovered ($\varepsilon_b = \varepsilon_m$), $F = 0$ and, from Eq. (1.26), the image dipole disappears. ii) The image dipole produces an electric field which decays with the typical $(2D)^{-3}$ dependency, where D is the distance of the NP center from the substrate. The determination of the exact position of the image charge becomes then fundamental. iii) The direction of the electric field generated by the image charge depends on the relative values of the embedding medium and substrate. As in our experiment $\varepsilon_b > \varepsilon_m$ the image dipole produces an electric field which has the same orientation as the dipole moment p , red shifting the resonance frequency of the particle. Even though a quantitative analysis of the substrate effects for an arbitrary shaped particle requires great computational efforts [37], an analytical formulation can readily provide insights on the substrate effects and can be easily incorporated in the theory developed in the last section.

In the first analytical approaches reported, the point dipole representing each NP was placed at the center of the NP, corresponding to a distance D above the substrate interface, and its image charge was placed symmetrically underneath the NP at a distance $-D$ inside the substrate [38]. We will call this model the symmetric approach. Even though this approach has been used, and is still used by many authors [39, 40], it has been shown both theoretically [41, 42] and experimentally [43, 44] that it does not lead to accurate results, especially for flat particles. It was shown that for flat particles the calculated red shift was much larger than the experimental one, and it was not possible to reproduce any multipolar resonance [45]. The overestimation of the red shift due to substrate effects is due to the fact that, once the particle is flattened, the self-imaginary dipole is placed at a very short distance from the real charge. As the electric field of $\mathbf{p}'$ decays as $(2D)^{-3}$, such a close proximity produces strong particle/image-particle interactions leading to large modelled red shifts of the resonance peaks due to the substrate effects.

An exact analytical treatment of the image charge effect can be performed in order to correct the limitations of the spherical approach. The solution can be obtained considering an infinite series of multipolar modes, i.e., of multipolar distributions of charges at the surface of the particle, which fully describes the interaction with the substrate [46]. These multipoles are located at the center of the particles and their

image counterparts at the image of this center with respect to the surface of the substrate. The truncation of this infinite series defines the accuracy of the calculation but, for flat spheroidal particles, the convergence of the calculation requires very large truncation numbers, which lead to quite heavy calculations. A similar approach can be developed using a spheroidal multipole distribution, which leads to a much faster convergence. This approach will be defined as the ellipsoidal approach and will be compared with the symmetric approach in the following. The main limitation of the ellipsoidal approach is that the theory has been developed only for in-plane rotational symmetric ellipsoidal NPs and cannot be applied to the general anisotropic ellipsoid case. We will limit the discussion to oblate spheroid with $R_x = R_y = \bar{R}$.

The differences in modelling the optical response of supported NP using the symmetric or the ellipsoidal approach has been clearly explained in literature [47] and we will report here the main results. In simple terms, the utilisation of the ellipsoidal approach corresponds to placing the image charges deeper in the substrate, correcting the symmetric approach where the close proximity of the image charges was overestimating the image charge effects. In [47] it was also reported how the presence of the substrate effectively modifies the optical response of the system and the modifications were expressed as changes in the analytical expression of the shape depolarization factor L_i . Within the symmetric approach the effective shape depolarization factor $\bar{L}$ are

$$\begin{aligned}\bar{L}_{x,y} &= L_{x,y} - \frac{\bar{R}^2 R_z}{24D^3} F \\ \bar{L}_z &= L_z - \frac{\bar{R}^2 R_z}{12D^3} F.\end{aligned}\tag{1.27}$$

In the ellipsoidal approach, if $r = \bar{R}/R_z$ is the ellipsoid aspect ratio and $\xi = 1/\sqrt{r^2 - 1}$, the effective depolarization factor becomes

$$\begin{aligned}\bar{L}_i^* &= L_i + \frac{1}{2} F \chi \\ \bar{L}_z^* &= L_z + F \chi\end{aligned}\tag{1.28}$$

$$(1.29)$$

In Eq. (1.29) the quantity χ is defined by

$$\chi = (1 + \xi^2) \left\{ \left(\frac{3}{2} + \xi^2 \right) \xi^2 \ln \left(1 + \frac{1}{\xi} \right) - \xi \operatorname{atan} \left(\frac{1}{\xi} \right) - \xi^2 \right\}.\tag{1.30}$$

Finally, equating the two expressions Eq. (1.27) and Eq. (1.29), an effective distance D^* of the image dipole from the real dipole can be introduced:

$$D^* = \left(-\frac{\overline{R}^2 R_z}{12\chi}\right)^{\frac{1}{3}}. \quad (1.31)$$

In Eq. (1.31) D^* is positive as $\chi < 0$. Furthermore, $D^* > D$ and the image dipole is effectively placed further away from the real charge, hence decreasing the red shift of the the optical resonance.

1.4 Models of nanoparticle arrays

The presence of an electric field causes the confined electrons of the single NPs to be displaced from their equilibrium position and with respect to the positive ion core. The surface charge distribution generated produces attractive forces due to the localization of the charge resulting in LPRs. In the case of closely interacting NPs additional forces come into play. When the driving field is parallel to the NPs array the energy required to the system to be in resonance is a reduced as the positive charges of neighbouring NPs tend to displace the negative charges. This interparticle attractive Coulomb force will lead to a lower resonant frequency resulting in a redshift of the resonance peak. When the driving field is perpendicular to the NPs arrays the charge distribution is such that neighboring NPs will produce an electric field which produces additional interparticle repulsive interaction which enhances the resonant frequency and blueshifts the resonance peak to lower wavelengths. The plasmon resonance in nanoparticle arrays is thus related to the interaction between the NPs and depends in turn on the distribution of the islands on the substrate.

Validity of the quasistatic approximation

When particles are placed in close proximity with each other, neighbouring NP interact with each other. If the interactions are strong enough, the response can depart from that of a isolated cluster case. In the quasistatic approximation the forces that come into play are dipolar in nature and thus possess the typical r^{-3} dependency with r

being the distance between dipoles. A nanocomposite layer composed by NPs below the 50 nm range will interact noticeably only for distances below the visible wavelengths due to short range dipolar interactions and each NP will oscillate then in phase with its neighbours. The structure can hence be regarded as a continuous layer with an effective homogeneous dielectric function ε_L which can in turn be anisotropic. The quasistatic approximation is then assumed to hold also in the case of NP arrays below diffraction limit and a schematic of the approach used is shown in Figure 1.5. Rather than computing the total dielectric function at the interface with solutions of complex integral equations, the NP array layer is modelled as an effective homogeneous layer anisotropic along and perpendicular to the array axis. The overall optical response of the system considered as a whole homogeneous single layered system can be finally considered introducing a pseudo dielectric function $\langle \varepsilon \rangle$ describing the substrate and effective layer together.

In the approach developed in this thesis, all the multipolar effects will be hence disregarded. However, it was recently shown [48, 49] that possible inhomogeneities in the field generated by neighbouring particles becomes significant whenever the particles are placed in close proximity, even when the NP spacing is much smaller than the wavelength of the exciting light. However, these contributions can still be disregarded in the first order and the quasistatic picture developed in the next section will be still regarded as a valid approximation.

Classical picture of nanoparticle arrays

In the course of this thesis arrays of ellipsoidal NPs will be grown. We will define x as the direction along the array row, y as the in-plane orthogonal one and z as the out-of plane direction. The grown NPs will also be elongated along the same x direction. An analytical expression for the effective anisotropic layer dielectric function will be obtained in this section. The solution is based on point dipolar interactions combined with the theory of the ellipsoid covered in Section 1.2. Such a derivation will be utilised, under opportune modifications, in Chapters 4-6. According to literature, the model used considers infinite arrays of *identical* spheroidal NPs supported on a substrate of

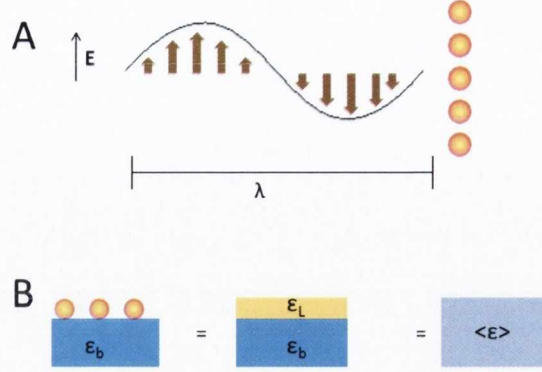


Figure 1.5: (A) As the wavelength of the exciting light is much larger than the average NP dimensions and distances, the NPs oscillate in phase and the quasistatic approximation also holds for NP arrays well below the diffraction limit. The nanocomposite layer can then be considered as an effective homogeneous layer of dielectric function ϵ_L (B). In addition, a pseudo dielectric function $\langle \epsilon \rangle$ describing the overall optical response of the sample, considered as a whole, can be introduced.

dielectric function ϵ_b . The metal clusters are placed in a rectangular lattice with center to center distance l_x and l_y .

Due to the identity of the metallic cluster, the effective dielectric function ϵ_L of the anisotropic layer satisfy the relation

$$(\epsilon_L - \epsilon_m)\mathbf{E} = N\epsilon_m\alpha\mathbf{E}_{loc} \quad (1.32)$$

where $\mathbf{E}$ is the electromagnetic field inside the anisotropic layer and $\mathbf{E}_{loc}$ the local field felt by each particle. The local field is the sum of the applied electric field $\mathbf{E}_{ext}$, of the image charges generated by the substrate $\mathbf{E}_{im}$ and of the electric field generated by the neighbouring particles $\mathbf{E}_{int}$

$$\mathbf{E}_{loc} = \mathbf{E}_{ext} + \mathbf{E}_{im} + \mathbf{E}_{int}. \quad (1.33)$$

The electric field generated in the center of the i -th NP by an electric dipole $\mathbf{p}_j$ in the space is

$$\mathbf{E}_{int} = \frac{1}{4\pi\epsilon_0\epsilon_m} \cdot \frac{3(\mathbf{p}_{ij} \cdot \mathbf{u}_{r_j})\mathbf{u}_{r_j} - \mathbf{p}_{ij}}{r_{ij}^3}. \quad (1.34)$$

In Eq. (1.34), u_{r_j} is the unit vector that connect the i -th NP p_i with the dipole p_j and r_{ij} is the distance between the i -th and j -th point in the in-plane direction. A

similar relation can be obtained for the image charges generated by the presence of the substrate. If the point dipole representing a NP is placed at the distance D^* from the substrate, the electric field generated by its image charge is

$$\mathbf{E}_{im,i} = \frac{1}{4\pi\epsilon_0\epsilon_m} \times F \frac{3(\mathbf{p}_{ij} \cdot \mathbf{u}_{r_j})\mathbf{u}_{r_j} - \mathbf{p}_{ij}}{((2D^*)^2 + r_{ij}^2)^{3/2}}. \quad (1.35)$$

The electric fields generated by the particle ensemble and their image charges can be written as

$$\begin{aligned} E_{int,i} &= \frac{p_i}{4\pi\epsilon_0\epsilon_m} \sum_j \frac{3\cos^2\theta_{ij} - 1}{r_j^3} = \frac{p}{4\pi\epsilon_0\epsilon_m} C_{int,i} \\ &= \frac{1}{4\pi} \alpha_i E_{loc,i} C_i. \end{aligned} \quad (1.36)$$

$$E_{im,i} = \frac{1}{4\pi} \alpha_i E_{loc,i} F C_{im,i}. \quad (1.37)$$

The external field is then related to the local one using Eq. (1.33) by

$$E_{ext,i} = E_{loc,i} \left(1 - \frac{1}{4\pi} \alpha_i C_{int,i} - \frac{1}{4\pi} \alpha_i F C_{Im,i}\right) = E_{loc,i} (1 + \alpha_i \beta_i) \quad (1.38)$$

where β_i was defined as

$$\beta_i = \frac{1}{4\pi} (-C_{int,i} - F C_{Im,i}). \quad (1.39)$$

From Eq. (1.32) and Eq. (1.38), it results that

$$\epsilon_0(\epsilon_L - \epsilon_m) \mathbf{E} = N \epsilon_0 \epsilon_m \alpha \frac{\mathbf{E}_{ext}}{1 + \alpha \beta}. \quad (1.40)$$

where the electric fields are related by the boundary conditions of the Maxwell equations

$$E_j = E_{ext,j} \quad E_z = \frac{\epsilon_m}{\bar{\epsilon}_z} E_{ext,z}. \quad (1.41)$$

with $j = (x, y)$. Using Eq. (1.40) and Eq. (1.41) we finally arrive at the important results:

$$\begin{aligned} \epsilon_{L,j} &= \epsilon_m \left(1 + \frac{N \alpha_j}{1 + \alpha_j \beta_j}\right) \\ \frac{1}{\epsilon_{L,z}} &= \frac{1}{\epsilon_m} \left(1 - \frac{N \alpha_z}{1 + \alpha_z \beta_z}\right). \end{aligned} \quad (1.42)$$

Equation (1.42), under opportune modifications, will be utilised in the modelling of the experimental results of Chapters 4-6. As an example, Figure 1.6 shows the effective

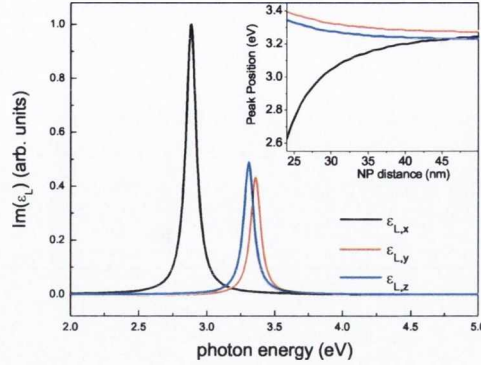


Figure 1.6: Imaginary part of the layer dielectric function ε_L of interacting spheres of average radius $R = 12$ nm, placed on a rectangular lattice of $L_x = 26$ nm and $L_y = 80$ nm and supported on a substrate having $\varepsilon_b = 3$. (Inset) Resonance position as a function of the NP distance L_x .

dielectric function of a layer of uncoated interacting Ag spherical NP arrays of radius $R = 12$ nm. The distance L_y between the NPs arrays was fixed at 80 nm while the distance between NPs along the arrays was $L_x = 26$ nm. The particles were supported on a substrate with $\varepsilon_b = 3.0$. The proximity of the particles along the x direction red shifts the peak along the closed packed direction and blue shifts the other two resonances. As expected, the shifts are more pronounced whenever the particles are placed in closer.

1.5 Advanced numerical methods

So far analytical methods have been used to describe the NP arrays. Different numerical models can also be utilised to simulate the optical spectra of noble metal NPs and NP arrays. Different CPU intensive methods are available, such as Finite Time Domain Transform (FDTD) [50, 51], T-Matrix methods [52] and Discrete dipole approximations (DDA) [53, 54]. All simulations show a qualitative agreement with the models previously developed, in particular:

- Increases in the aspect ratio of a isolated ellipsoid result in splitting of the peaks due to reduced symmetry of the system. In particular, the elongated direction

appears to red shift while the others blue shift.

- The presence of the substrate red shift the resonance positions.
- When particles are placed in proximity, a splitting in the peak position is also produced with a red shift of the resonance along the chain axis and a blue shift in the perpendicular directions.
- CPU intensive simulations confirm the presence of enhanced electric field in the interstitial space between the nanoparticles.

The latter phenomenon has attracted recently enormous attention due to the Plasmon related enhanced phenomena. For example, when a molecule is placed in the interstitial place of interacting metallic clusters an enhancement factor up to 10^{14} [55] in the molecule Raman scattering cross section has been predicted, enabling ease in the molecule detection. Furthermore, enhancement effects have been successfully demonstrated in recent years in fluorescence, second harmonic generations, lithography and optical tweezers.

Chapter 2

Experimental Setup

No amount of experimentation can
ever prove me right; a single
experiment can prove me wrong.

A. Einstein

The project developed in this thesis began few years ago, when limitations of lithographic and bottom-up techniques emerged. Glancing angle deposition appeared to offer an alternative way to produce planar nanowires on stepped templates capable of overcoming the physical limitation of the standard lithographic procedures.

The project can now be divided into three main strands: Si nanowire growth, magnetic nanowires and plasmonic NPs. For any strand, the measurements of the nanostructures can be performed following a three step procedure. The first step consists in the creation of stepped substrates, the second aims to grow structures aligned along the step edges and finally the characterisation can be pursued with optical, magnetic or electrical means. This thesis focuses on the plasmonic research strand and demonstrates how glancing angle deposition can produce ordered structures on a stepped c-plane Al_2O_3 . The properties of the NP arrays have been characterised with spectroscopic techniques, in particular reflectance anisotropy spectroscopy (RAS).

In this chapter previous results on glancing angle deposition are summarised, followed by the description of RAS and of the other experimental tools used throughout the rest of the thesis.

2.1 Previous literature on glancing angle deposition

As already anticipated in the introduction, deposition at a glancing angle onto a patterned surface can produce highly ordered NP arrays on the macroscale. This approach was first proposed and demonstrated in 1979, when two groups independently showed the possibility of producing structures below the optical lithographic limit of the time [56, 57].

The idea remained dormant for almost 20 years and new interest arose recently as an alternative nanofabrication tool. Typically, a material is either deposited through a shadow mask or onto a textured surface, which serves as its own shadow mask for certain deposition directions. Common textured surfaces used for shadow deposition include self-organized crystalline facets of NaCl [29, 58, 59], sapphire [30, 60, 61], semiconductors [32, 62] and substrates with microfabricated features [63]. Stepped surface could also be prepared by accelerated Ar^+ or Xe^+ ions sent at a tilted angle onto a surface [64]. Si [65], amorphous glasses [33] and amorphous Al_2O_3 [66] have been utilised as templates for glancing angle depositions. Different materials such as Fe [29], Ag [30], Ge [67] and Au [59] have been deposited on the various patterned templates and different morphologies obtained, ranging from NPs to nanowires. Recently, NPs [68, 69], nanowires [70, 71], DNA [72] and carbon nanotubes [73] have also been utilized as shadow masks for glancing deposition to enhance nanofabrication resolution and patterns with 50 nm dimensions or smaller have been routinely prepared.

Our research group produced important contributions in this direction and 3 years ago the possibility of growing both NP arrays [31] and nanowires [32] of dimensions smaller than 30 nm was shown. The structures were deposited both on off-cut c-plane Al_2O_3 or step-bunched Si (111), whose bunches were prepared by electromigration.

Devices based on glancing angle deposition have been also proposed in order to produce magnetoresistive memory cells.

Other groups proposed modified approaches to the one reported in this thesis, being able to produce anisotropic structures with comparable order. The Buatier de Mongeot group produced gold nanowires in a two step procedure [74]. They first deposited a Au film at normal incidence and the successive patterning of the surface was obtained with accelerated Ar^+ directed at glancing angle towards the surface. Other approaches produced anisotropic structure using a normal incidence deposition on stepped templates, while the surface was kept at very high temperature. The increase in the adatom mobility thus produced structures with similar order and morphology [75, 76].

The properties of the systems grown were investigated with normal incidence polarised transmission spectroscopy (PTS) [31, 65], magneto-optic kerr effect setup [29], grazing angle X-Ray scattering [66] and the morphology analysed with scanning electron microscope (SEM) [76], transmission electron microscope (TEM) [58, 67] and atomic force microscopy (AFM) [30]. These techniques allowed the study of the surface properties of the materials in a non destructive way (except TEM) and were particularly suitable for the study of the planar structures grown.

2.2 Reflectance anisotropy spectroscopy

The reduced symmetry of an area probed by optical means can produce anisotropic signals and this phenomenon explained the changes in reflectivity observed in early experiments during sample rotations [77, 78]. Much later Aspens and Studna [79] and independently Berkovits [80] developed a technique able to measure these anisotropies: reflectance anisotropy spectroscopy (RAS)¹. RAS probes the difference, at normal incidence, of the in-plane complex reflection coefficient r_i measured along two orthogonal directions normalised to the overall reflection:

$$\frac{\Delta r}{r} = 2 \frac{r_x - r_y}{r_x + r_y}. \quad (2.1)$$

A detailed review of both experiment and theory of RAS has been published recently [81]. The advantages of RAS are that it provides surface sensitivity, where the substrate

¹The technique is also known as reflectance difference spectroscopy.

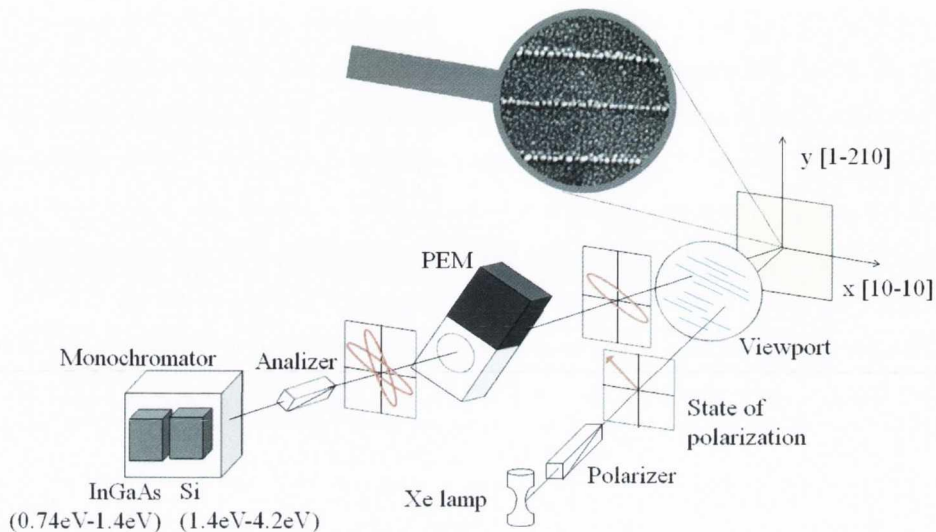


Figure 2.1: Schematics of the RAS setup used during the measurements of plasmonic NP arrays.

is optically isotropic and the surface is anisotropic, and it is possible to use it for monitoring directly in UHV and other environments [82].

The experimental setup used in this manuscript follows the Aspnes photoelastic modulator, two polarisers setup (see Figure 2.1). Light from a Xe lamp passes through a polariser and a low-strain window and is reflected from the sample through a photoelastic modulator, an analyser polariser and a monochromator before finally reaching a double diode detector system. The great advantages of this configuration are the *in situ* possibility as no sample rotation is required and the possibility of recording both the imaginary and the real part of $\frac{\Delta r}{r}$, being related respectively to the signal at $2\omega_0$ and at ω_0 , the frequency of polarisation modulation of the PEM [83, 84]. As the imaginary signal of RAS is more sensitive to strains in the viewport and is related by the Kramers-Kronig relations to the real signal component, in this work we will report only the $Re(\Delta r/r)$.

Applications of RAS

Since its beginning, RAS has proven to be a useful tool for the characterisation of semiconductor [79, 85] and metallic surfaces [86, 87]. In addition, RAS has become important in characterising the growth in gaseous environment, such as metal organic vapour phase epitaxy, as any electron based analysis cannot work. Finally it has been used to monitor surface reconstructions and interfaces during growth. Monolayer oscillations have been observed and even determination of doping levels in semiconductors is possible. More recently, due to developments of IR measurement setup, free electron optical response of anisotropic metallic structures have been measured [88].

Very little work has been devoted in the studies of plasmonic structures with RAS [39] due to the limitations of the colloidal preparation techniques. For RAS the particles have to be dispersed on the surface and they need to rearrange anisotropically on the macroscale with a defined anisotropic direction. Where glancing angle deposition is used to create anisotropic plasmonic structures, RAS can then be used, in principle, to determine their plasmonic properties, *in situ*, during growth.

Implementation of the RAS setup

In the course of the experiment, two systems were utilised, one portable for *in situ* measurements and one for *ex situ* measurements, more precise. Measurements were performed over a broad spectral range, from 0.76 eV up to 5 eV. In order to measure over such broad spectral range, conventional Si detectors were not sufficient, being limited to an energy range higher than 1.2 eV. The extension of the measurement range was hence realised with the development of a double detector measurement system with both an InGaAs detector for the 0.75-1.4 eV measurement range and a standard Si detector for higher energy ranges. A photograph of the the small RAS, more extensively used during the project, is shown in Figure 2.2. The setup used two α -BBO Rochon polariser (extinction ratio $\sim 10^{-5}$) which operated between 0.6-5.0 eV. A fused silica PEM modulated the polarization between 0.6/6.6 eV and a double grating monochromator, one for the IR and one for the vis-UV were utilised. In order to provide a broad and homogeneous optical spectrum in the measured optical range, a Xe high pressure lamp light source was utilised. The setup was fully CPU automated.

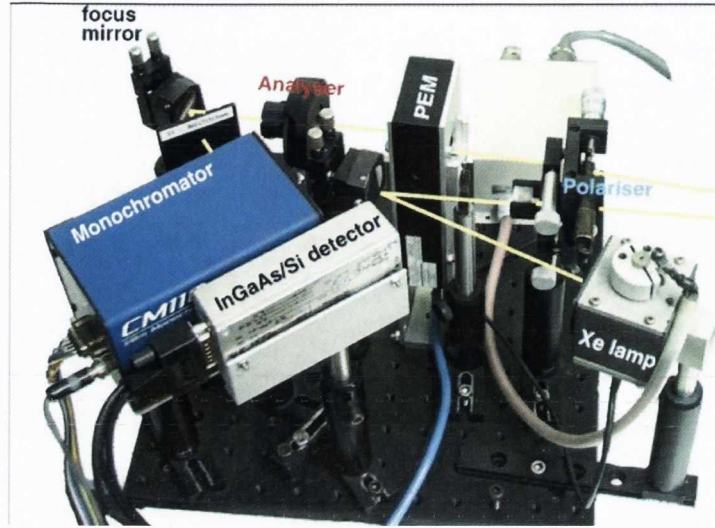


Figure 2.2: Picture of the RAS utilised. The components are labeled and described in detail in the text.

Three-layers model

Any RAS signature observed is a consequence of the inherited anisotropy of the system measured. In the approximation of a linear optical response of non-magnetic media, the investigated materials can be described with a dielectric tensor with only three non zero diagonal elements $\varepsilon_{x,y,z}$. As RAS works at normal incidence it can measure only changes in the in-plane dielectric functions $\varepsilon_x \neq \varepsilon_y$.

In the particular case of homogeneous bulk anisotropic samples, RAS can probe the difference in reflectance between R_x and R_y and the in-plane dielectric tensor components can be directly calculated using Eq. (2.1) and

$$R = \left| \frac{n - 1}{n + 1} \right|^2 \quad (2.2)$$

with $n^2 = \varepsilon$.

In order to address the optical properties of more complicated systems such as anisotropic structures on top of an isotropic material, the measured response is modified as a result of the substrate reflectivity influence. A more general description utilises a three layer model, where a thin anisotropic layer of thickness d is comprised between a semi-infinite isotropic bulk dielectric function ε_b and a semi-infinite ambient layer of

dielectric function ε_m . The anisotropy is then expressed by the two different diagonal tensor components $\varepsilon_{L,i}$ of the anisotropic layer and the RAS signal is described as [79]

$$\frac{\Delta r}{r} = \frac{4\pi i d \sqrt{\varepsilon_m} \varepsilon_{L,x} - \varepsilon_{L,y}}{\lambda (\varepsilon_b - \varepsilon_m)}. \quad (2.3)$$

Since both ε_b and ε_m are usually known, the RAS signal can be related to the degree of anisotropy of the interface layer only. The term $d(\varepsilon_{L,x} - \varepsilon_{L,y})$ is called the surface dielectric anisotropy (SDA) and its value can be directly related to the RAS signal. This approach is particularly useful since the influence of the substrate is removed in SDA and similar surface structures on different substrates can be directly compared. Models mimicking the anisotropic layer dielectric function can be finally compared with the experiments. A drawback of this approach is the difficulty in determining the effective thickness and, as a consequence, only relative results can be compared. Nevertheless, a semi-quantitative understanding of the results can be obtained as a result of a fitting procedure, a process similar to the analysis usually performed on ellipsometric measurements.

2.3 The Deposition Chamber

The system consists of a 6'' diameter stainless steel spherical deposition chamber connected to a turbomolecular pump (Osaka TG550, with pumping speed of 550 l/s) via a CF elbow, which maintains the chamber at pressures in the high 10^{-8} Torr. Baking the system helps to reduce residual gases and provides near UHV conditions (low 10^{-8} Torr range). A rotary vane pump is used as a backing pump for the turbomolecular pump.

The sample is mounted in the centre of the deposition chamber on a sample manipulator. The sample is loaded on a manipulator which ensures an accuracy of 0.1° in the choice of the deposition angle. The deflection of a reflected laser spot pointing towards the sample surface ensures the exact alignment of the surface with respect to the adatom flux. A strain free window is mounted exactly in front of the sample stage in order to perform *in situ* optical measurements with RAS. There is no loadlock, so the chamber must be vented each time a sample is loaded or removed.

The top flange of the chamber is equipped with a quartz crystal monitor in order to control the deposition flux during the experiment. The pressure is monitored using

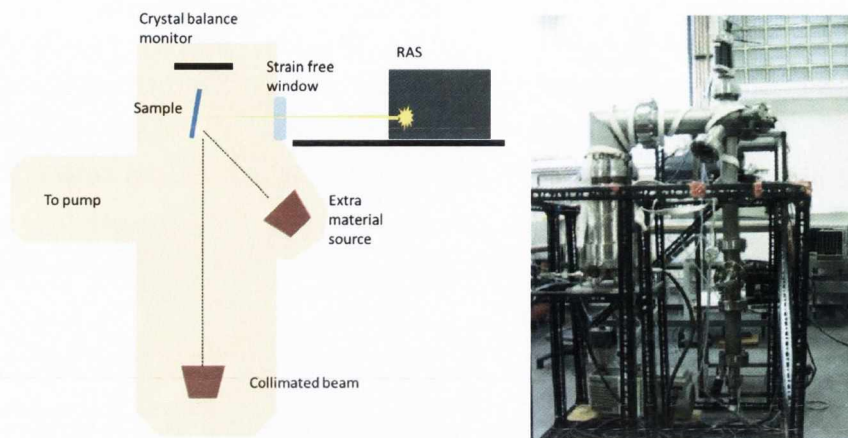


Figure 2.3: (left) A schematics of the deposition chamber setup utilised and (right) a picture of the system for glancing angle depositions.

a wide-range Bayard-Alpert ion gauge mounted on a side port. On the bottom of the growth chamber a DN64 flange is connected through extension tubes to a 10cc capacity high-temperature Knudsen cell. The distance between the source and the centre of the chamber, where the sample is placed, is approximately 70 cm so that the beam reaching the substrate surface is highly collimated. A shutter is mounted between the source and the growth chamber. When mounted, the sample sits vertically in the center of the growth chamber, directly above the effusion cell. A schematics of the deposition chamber is sketched in Figure 2.3.

2.4 Spectroscopic Ellipsometry

Spectroscopic ellipsometry (SE) is a RAS setup which does not work at normal incidence.

Generally speaking, a linearly polarized light beam reflected by a media at a oblique angle of incidence becomes elliptically polarised. The reflection amplitude parallel (r_p) and perpendicular (r_s) to the plane of incidence undergo to both phase and amplitude changes. If the reflected signal is modulated it is possible to extract the changes in phase and intensity, hence determining r_p and r_s . Based on this principle, SE measures

their complex amplitude ratio [89]

$$\rho = \frac{r_p}{r_s} = \tan(\psi)e^{i\Delta}. \quad (2.4)$$

The quantities in Eq. (2.4) are defined by

$$\begin{aligned} \tan\Psi &= \left| \frac{r_p}{r_s} \right| \\ \cos\Delta &= \delta_p - \delta_s \end{aligned} \quad (2.5)$$

and are related to the intensity ratio and the phase difference δ in the outgoing reflected beams. Due to measurements of only relative changes between r_p and r_s , the measurements are independent on the absolute intensity and hence highly accurate.

The main drawback of SE is that the extraction of physical information from ρ cannot be directly obtained and modelling is required. Furthermore, multi layered structures, roughness and inhomogeneities do not allow for easy modelling of the system. An analytical solution exists for an ideal semi-infinite, homogeneous and isotropic material with dielectric function ε which is related to ρ and to the angle of incidence Φ by

$$\varepsilon = \sin^2 \Phi_0 + \sin^2 \Phi_0 \tan^2 \Phi_0 \left(\frac{1 - \rho}{1 + \rho} \right)^2. \quad (2.6)$$

In case of additional layers and complexities, Eq. (2.6) can still be used, but ε is then describing the overall response of the interacting region sampled and it is named for this reason pseudo dielectric function or effective dielectric function $\langle \varepsilon \rangle$:

$$\langle \varepsilon \rangle = \sin^2 \Phi_0 + \sin^2 \Phi_0 \tan^2 \Phi_0 \left(\frac{1 - \rho}{1 + \rho} \right)^2. \quad (2.7)$$

The SE used is a commercial GESP5 model which follows the rotating polariser ellipsometer configuration. It consists of a light source and a rotating polariser which produces the modulated signal. After sample reflection the signal is measured by an adjustable analyser, a monochromator and the detector. The advantage of this configuration is its relative simplicity and its ability in performing measurements in ambient light. The main drawback is its inaccuracy when Δ is close to 0° or 180° . The latter does not represents a real limitation as measurements will be performed around the Brewster angle of the system, hence Δ being different from the values which result in inaccurate measurements.

The Xe lamp is contained within its housing and has a xyz positional adjustment to ensure good alignment. It has a low residual polarisation and the intensity can be varied by two attenuators mounted in the polariser arm. The light is guided to the polariser by two adjustable mirrors. The polariser and the analyser both consist of quartz Rochon polarisers attached to stepper motors, which enable rotation with an accuracy $< 0.02^\circ$. The polariser is rotated at 9 Hz. The beam diameter is 6 mm, but in our measurements a microspot has been put in place in order to reduce the scanned area to $350\mu\text{m}^2$. During the measurement the analyser is adjusted to an angle of $\pm 45^\circ$ alternatively thus correcting any possible errors due to any angle offset between the analyser and polariser. The double monochromator spectrometer is connected to the analyser stage via an optical fibre. The spectrometer is fully automated allowing selection of any wavelength with a 0.2 nm resolution. The detector is a Si photomultiplier tube with a spectral range of 1.38 eV to 6.7 eV.

2.5 UV-visible spectrometer

A UV-vis spectrophotometer measures the intensity ratio between the light passing through a sample (I), and before passing through it (I_0). This ratio I/I_0 is called transmittance, and is usually expressed as a percentage.

The basic parts of a spectrophotometer are a Xe light source (often an incandescent bulb for the visible wavelengths is also used), a holder for the sample, a monochromator to measure single wavelengths of light, and a detector. A spectrophotometer can be either single beam or double beam. In single beam setup all the light passes through the sample cell and I_0 must be measured by removing the sample. In a double beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference; the other beam passes through the sample. Samples for UV/Vis spectrophotometry are most often liquids and their absorbance can be easily measured. In the present case solids are measured and rather than absorbance, we will referred to extinction coefficient E , sum of absorbed (A), scattered (S) and specular reflected intensities (R). If T is the transmitted intensity, the following relation ensures then the conservation of energy

$$E + T = A + S + R + T = 1. \quad (2.8)$$

For reliable transmission measurements, double side polished substrates can be utilised, as they minimise the scattered losses due to rough sample back sides. In this case $S \sim 0$ and, as the heat losses are negligible, transmission and reflection on the samples can be compared.

As the sample measured present a strong optical anisotropy, the possibility of measuring a polarization dependent response of the NP arrays can be obtained inserting a polariser into the system before the light interact with the system. The polarized transmission spectroscopy (PTS) allow to measure T_x and T_y independently and a comparison with the RAS can be obtained.

Measurements will be performed with a Cary 50 UV-vis-NIR spectrophotometer equipped with a Xe lamp between 1.2 eV and 5 eV. A Glan Taylor polariser working from 0.6 eV till 5 eV is utilised for PTS.

2.6 Atomic Force Microscopy

Under the interaction of a sample surface, a macroscopic cantilever provided with a sharp tips can be bended by atomic forces by a sufficiently large amount to be measured by laser deflection. An atomic force microscopy (AFM) based on this principle was invented by Binnig, Quate, and Gerber [90]. Their original AFM consisted of a diamond shard attached to a strip of gold foil. Detection of the cantilevers vertical movement was done with a second STM tip placed above the cantilever. Today, most AFMs use a laser beam deflection system, where a laser is reflected from the back of the reflective AFM lever onto a position-sensitive detector [91]. The output of the detector is provided to a computer for processing of the data and providing a topographical image of the surface. AFM tips and cantilevers are usually microfabricated from Si or Si_3N_4 . The sharp tip (~ 10 nm radius) is scanned over a surface with feedback mechanisms that enable the piezo-electric scanners to maintain the tip at a constant force (to obtain height information) above the sample surface. As the tip scans the surface of the sample, moving up and down with the contour of the surface, the laser

beam is deflected into a dual element photodiode. The photodetector measures the difference in intensities of the light between the different photodetectors, and converts them to a voltage. Feedback loop, through software control from the computer, enables the tip to maintain a constant force on the sample surface.

Depending on the interaction of the tip with the sample surface, the AFM can be classified as contact mode, noncontact or tapping mode. The latter is the only scanning mode utilised in this thesis and will be described in the following. Tapping mode is done by alternately placing the tip in contact with the surface and lifting it off. The contact provides the high resolution required while the lifting off avoids dragging the tip across the surface. Tapping mode imaging can be implemented both in ambient air or in liquid and the oscillations are obtained using a piezoelectric crystal oscillating near the cantilever resonance frequency. After a voltage input, the piezo vibrates and the mechanical oscillations generated result in a oscillatory behaviour of the cantilever with a height amplitude greater than 20 nm. Generally, the cantilever is excited just below its fundamental resonance frequency and, in this frequency range, the behaviour of the cantilever can be represented by a simple harmonic oscillator with a good approximation. The oscillating tip is then moved toward the surface until it taps the surface. The intermittent contact with the surface reduces the cantilever oscillation due to energy loss caused by the tip touching the surface and the reduction in oscillation amplitudes is used to measure surface features. The digital feedback loop adjusts the tip-sample separation to maintain a constant amplitude and force on the sample.

All the AFM images presented in this work were obtained with a Asylum Research Force Microscope obtained in tapping mode. Tips utilised were generally Budgetsensor cantilevers with a 250 kHz resonance frequency and a nominal tip apex radius smaller than 10 nm.

2.7 Scanning electron microscope (SEM)

Scanning electron microscopy (SEM) uses a focused and accelerated beam of electrons for imaging and analysing samples at a resolution far beyond that possible with light microscopy [92]. A monochromatic electron beam is produced by a field emission gun

and accelerated by the chosen acceleration voltage, typically from 0.5 to 30kV. The electron beam subsequently enters an electromagnetic lens system which focuses the beam on the specimen in a circular spot. As a result of the impact of the incident beam, a variety of electrons and photons are produced. The chosen signal is then collected, amplified and sent to a cathode ray tube (CRT) that produces bright spots on the screen. The beam is successively rastered on the selected area of the specimen, producing the frame viewed by the operator. If the CRT area has dimensions $A \times A$ and the scanned one $B \times B$ the magnification is then B/A . The advantages of an SEM are:

- The magnification is achieved in a purely geometrical manner by changing the dimension of the scanned area.
- The resolution of a SEM is much better than an optical microscope due to the lower electron diffraction limit. Its maximum resolution is determined by the signal intensity, the current generated by the gun and by the real dimensions of the spot, which is increased by the presence of aberrations in the optical path.
- It is possible to simultaneously record different signals produced by the interaction of the sample with the incident beam.

When the beam of electrons interacts with a sample it can undergo different scattering events forming secondary particles. These scattering events occur in an interaction volume which has a pear like shape due to broadening. The exact size and shape of this depends on the accelerating voltage of the electron beam and the constituent materials in the probed sample. The main types of electrons involved in SEM imaging are secondary electrons (SEL) and backscattered electrons (BSE). Collectors are positioned in different parts of the system to selectively collect these different electrons.

SEL are produced by inelastic scattering between the incident electrons and the material being imaged. These are low energy electrons (<50 eV) with a small mean free path and so stem from regions near the surface probed (a few nm deep). SEL images give then good topographical information. Higher energy electrons are classed as backscattered electrons (BSE) and are produced by elastic collisions deeper in the interaction volume of the sample. BSE carry information on chemical composition as materials with higher atomic numbers are better scatterers and appear brighter. The

incident electron beam can also cause the probed material to emit characteristic X-rays. This occurs when an incident electron knocks an electron from the K-shell of the specimen material creating a hole which is subsequently filled by an electron from a higher shell. The difference in energy between the higher and lower energy levels can be emitted in the form of an X-ray which carries information on chemical composition. The probing of these X-rays is known as energy dispersive X-ray spectroscopy and requires a specialised detector inside the SEM apparatus.

The SEM analysis in this work was carried out on a Zeiss ULTRA Plus field emission SEM. This is fitted with in-lens and Everhardt Thornley detectors for SEL imaging and an energy and angle selective detector for BSE imaging. Samples were mounted on carbon tabs and typically imaged with an accelerating voltage of 1-5 kV.

2.8 Transmission Electron Microscope (TEM)

The working principle of a TEM is similar to that of a SEM, but the analysed electrons are transmitted through the sample. A TEM consists in a vacuum system, a high voltage source, a sample holder and an aperture and lens system. The electrons are emitted from a tungsten Zr-coated Field Emission Gun and accelerated by high voltage up to ~ 300 KeV. They are then focused onto the sample by the lens system which controls the imaged area. The focused electrons pass through the sample and enter the objective lens. As the transmitted electrons can either pass straight through the sample or be diffracted, two modes of imaging are possible, selecting which electrons are used to produce the image on the CRT. In diffraction mode the diffracted electrons pass through the objective lens and produce the diffraction pattern in the back focal plane of the objective lens.

The principal mode of operation utilised in this thesis is the bright field imaging mode. Using a classical picture, in this mode the contrast formation results by absorption of electrons in the sample. The regions where the electrons get absorbed will appear dark whilst the areas in the sample where the electrons can pass freely will appear as bright spots. The obtained image thus becomes a projection of the sample down the optic axis. In this image mode electrons enter an objective aperture and the

image formed at the image plane becomes the object for intermediate lens in order to achieve higher magnifications.

The main limitation of TEM is it requires extremely thin samples due to the small mean free path of the electrons in the media. In order to image the samples, a lamella of the sample has to be obtained. TEM is a destructive characterisation tool. TEM sections were prepared for both annealed surfaces and surface with Ag NP deposited at glancing angle. A 10 nm Au/Pd layer was deposited by sputtering in order to protect the interface. Subsequently, the sample was prepared in a Carl Zeiss Auriga CrossBeam focused ion beam FIB-SEM. The *in situ* lift out technique was used to remove a section of the sample and affix it to a TEM grid. The sample was then polished to ~ 100 nm thickness with 30 keV gallium ions. In order to reduce surface damage and amorphisation, the sample was finally polished with 5 keV gallium ions. Once prepared, the samples were imaged by a FEI Titan TEM, operating at 300 kV.

2.9 High temperature furnace

The sample preparation required the annealing of sapphire substrates at high temperature in order to obtain stepped surfaces. All the experiments were performed using a MTI GSL1600 XL tube furnace which has a maximum nominal working temperature of 1550° C. The furnace can be equipped with a high purity alumina tube surrounded by Kantal defect free SiC rods heating elements. High current passes through the rods and the heat is generated by the Joule effect. Both S-type and B-type thermocouples have been utilised for measuring and calibrating the furnace temperature. The input current was regulated by a PID controller.

Chapter 3

C-plane Sapphire and the Faceting Mechanism

Science never solves a problem
without creating ten more.

G. Bernard Shaw

The preparation of ordered stepped surfaces is the key feature for successful glancing angle depositions. Different routes can be followed to produce the textured templates but we will concentrate in this chapter onto the effects of high temperature annealing of c-plane α -Al₂O₃ (sapphire).

The crystal structure and the technological importance of this material are described at the beginning of the chapter and reports on previous annealing studies of α -Al₂O₃ (0001) will be discussed substantially. In addition to the studies performed in previous reports, a complete annealing study of the c-plane sapphire surface which is off-cut few degrees along the $[1\bar{2}10]$ direction will also be presented. It will be shown here how to produce a periodic terrace and step structure by annealing and the possibility of tailoring both surface periodicity and step height will also be discussed.

The origin of the resulting surface morphology is attributed to faceting formation, i.e. the rearrangement of the crystal surface into alternating flat faces following low-index directions.

Such ordered templates will be utilised in the rest of the thesis for the growth of NP arrays. Being the argument here treated independent from the rest of the document, we try to provide self-consistency to this chapter.

3.1 Al_2O_3 : introduction

Al_2O_3 Crystal structure

$\alpha\text{-Al}_2\text{O}_3$ crystallizes in a hexagonal structure. In the hexagonal unit cell the lattice vectors of the basal plane (sides a_1 , a_2 and a_3) are equivalent to 0.4758 nm, with a relative angle of 120° between them. The lattice vector c is equal to 1.2992 nm and it is normal to the basal plane. Figure 3.1 shows a schematic of the unit cell of Al_2O_3 and the low-index surfaces plane usually encountered. These surface terminations have been reported to be stable at room temperature and the respective surface free energies are listed in Table 3.1 in J m^{-2} and in relative values compared to the (0001) surface. Even if some discrepancies are present in literature, most of the previous reports confirm the (0001) surface to be the most stable one, having the lowest free energy configuration.

The position of the atoms within the unit cell is shown in Figure 3.2. The ideal unit cell can be represented placing atoms in two types of sites: hexagonal and octahedral. The hexagonal corner sites are occupied by oxygen atoms while the octahedral sites are present between a face which adjoins two layers of vertical stacking. Aluminium cations are in $2/3$ of the octahedral sites, and oxygen anions are in the remaining $1/3$. Each oxygen is shared between four octahedra. The oxygen presence in octahedral sites permits strong bonding and gives rise to the characteristic properties of hardness and electrical insulation of sapphire. Along the [0001] direction a succession of six oxygen layers separated by a double Al layer can be observed. The distance between each oxygen layer is then $c/6 = 0.22\text{nm}$.

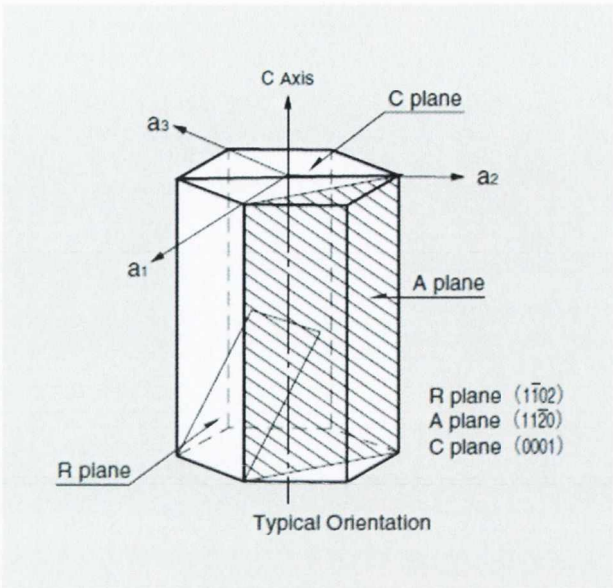


Figure 3.1: Schematic of the Al₂O₃ single crystal unit cell and relative low index stable surfaces.

Plane	Index	Energy (theory)[93]		Energy (experiment)	
		J m ⁻²	relative	relative[94]	relative[95]
c-plane	(0001)	1.92	1.00	1.00	1.00
a-plane	(112̄0)	2.34	1.18	1.12	0.97
m-plane	(1100)	2.25	1.13	1.06	0.96
n-plane	(112̄3)	2.25	1.13	1.06	0.96
s-plane	(1101)	2.57	1.30	1.07	0.95

Table 3.1: The main surface terminations for Al₂O₃ and their relative free energy from first principle and Wulf construction.

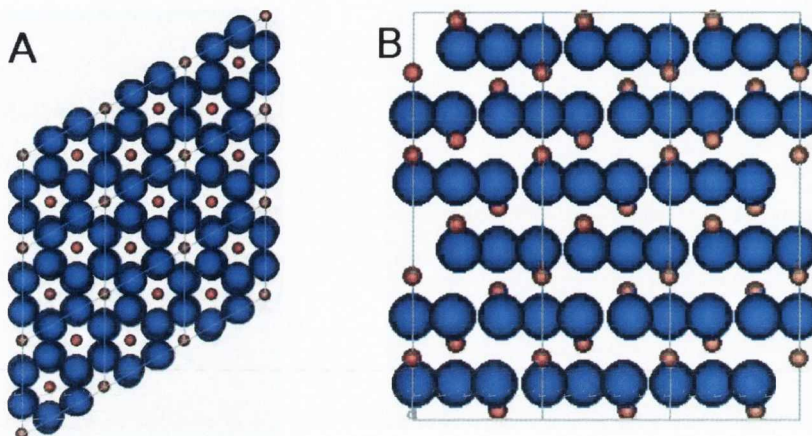


Figure 3.2: (A) The surface of c-plane α - Al_2O_3 . (B) Side view of the idealised crystal structure unit cell.

Different idealised surfaces, without taking into consideration any reconstruction or relaxation, have been proposed in recent years for Al_2O_3 (0001). Experiments [96] show that the most favourable one is a single Al layer terminated surface which matches the configuration predicted by first principle calculations. A priori, we expect that neighbouring steps with same direction can exhibit different step energy densities.

Applications

The preparation of metal oxide surfaces with high quality is of fundamental interests for optical and electronic devices. Sapphire, among the others, possess properties which make it a very promising material [97]. The high mechanical strength, its transparency, the chemical stability, the high thermal conductivity and its insulating properties renders α - Al_2O_3 surfaces particularly important for many applications. For example, epitaxial crystal growth on sapphire has been confirmed for GaN [98], ZnO [99], Pt [100], diamond [101] and TiO_2 [102]. Low-dimensional carbon structures have been also produced on Al_2O_3 : graphene has been shown to strongly adhere on the $(10\bar{1}0)$ surface [103] and aligned carbon nanotubes were grown on patterned substrates [104]. It has been recently proposed that heparin coated sapphire implants are biocompatible, rendering them useful for bio-applications [105]. Among the stable surfaces orientations,

Al₂O₃ (0001) surface is so far the most interesting and most deeply studied. Epitaxial Co monolayers [106] ZnO nanorods [107] GaN quantum wells [108] and fluorinated organic layers [109] have been recently grown using Al₂O₃ (0001) as a substrate for different applications, like spintronics, light emitting diodes, UV sources and "green" applications respectively. Also from a fundamental point of view, Al₂O₃ (0001) templates have been recently exploited to answer very important questions, such as the role of linear defects in a single crystal surface [110] or for understanding the growth mechanism of overlying low-dimensional structures [111, 112].

Reports on Al₂O₃ (0001) annealing

One of the reasons that makes the study of the single crystal Al₂O₃ relevant is the possibility of reconstructing the surface in a hill and valley structure after high temperature annealing [113]. The departure from a perfectly flat surface obtained by annealing can produce advanced functionalities which can be incorporated in the Al₂O₃ based devices. If the surface is off-cut along the $[1\bar{2}10]$ direction, the resulting vicinal surface appears covered by steps running along $[10\bar{1}0]$ which present a monoatomic height of $c/6 = 0.22$ nm. A successive annealing at high temperature of the vicinal surface produces periodic step-and-terrace arrangements with a height $h \sim 1.3$ nm [114].

The results of the step rearrangements have been already investigated as a function of annealing temperature [114–117], time [113, 115, 117, 118], atmosphere [116], pressure [119], off-cut angle [117, 120] and orientation [117]. Never the less, the reports present contradictory results and require clarifications. It is now generally believed that the upon annealing at temperatures of $\sim 1100^\circ\text{C}$ in atmosphere, the monoatomic steps gather forming double height steps [114] and, if the temperature increases, the double steps step increase further in height. On the other hand, contrary to the early reports where the surface rearrangements was related to a faceting formation [113], latest reports define the surface instability to be a step bunching phenomenon. The first corresponds to a thermodynamic equilibrium surface state where flat low-energy facets alternate, while the second is the consequence of an kinetic instability where neighbouring steps gather together producing a step train. No clear picture of the rearrangement mechanisms has been proposed for the (0001) surface so far.

The strong anisotropy in the adatom diffusion and the relatively slow diffusion rate (the reconstructions happens to take place in times of the order of hours), makes finally the system a perfect candidate to clarify doubts and open questions for instabilities of metal oxides in general, such as SrTiO_3 [121] and MgO [122].

3.2 C-plane Al_2O_3 : experimental procedure

Single crystal single-side polished c-plane Al_2O_3 substrates (MTI, USA) were prepared with three different nominal off-cut along the $[10\bar{1}0]$: 2° , 3° and 6° . The quality of the substrate was checked by high resolution X-ray diffraction. The study confirmed the (0001) surface orientation and the absence of defects. For each sample an accuracy within 0.1° of the nominal off-cut was measured. If required, several pieces were cut from each substrate, cleaned in HCl and washed in DI water. In order to remove any contamination, a solvent treatment with Methanol, Acetone and high grade propanol-2-ol was finally performed in a ultrasonic bath. After the cleaning procedure the surfaces were checked with Atomic Force Microscopy (AFM) to confirm the absence of impurities and the surfaces appeared remarkably flat. The samples were then placed in a high purity alumina crucible and put in a alumina tube furnace. To avoid the presence of any contaminant and a homogeneous heating the tube was then closed by alumina bricks. Each piece was loaded into the furnace already at a temperature of 1000° and annealed for 24 hours at temperatures T between 1300°C and 1450°C . A heating and a cooling rate of $10^\circ/\text{min}$ was used to reach the required annealing temperature. As the diffusion rate of the surface adatoms increases exponentially on the temperature, such a quick cooling rate ensures that the observed morphology corresponds to the state of the surface at the annealing temperature.

3.3 Results and discussion

During the experiment, the temperature dependency was studied for the same 6° sample at temperatures of 1300°C , 1350°C , 1400°C and 1450°C and the role of the off-cut was analysed at the temperature of 1400°C . The results are presented in Table

	2°	3°	6°			
T (°C)	1400	1400	1300	1350	1400	1450
L (nm)	132 ± 25	129 ± 28	77 ± 21	79 ± 22	132 ± 15	197 ± 58
H (nm)	4.8 ± 1.7	5.7 ± 1.6	7.6 ± 1.7	7.7 ± 2.0	11.5 ± 3.1	20.8 ± 4.6

Table 3.2: Average terrace width and step height with the relative standard deviation as a function of annealing temperature and off-cut angle . The terrace and the standard deviation increase by increasing the annealing temperature. If the same periodicity is obtained, changes in the off-cut angle produces different step heights.

3.2. For each sample annealed the statistics were obtained analysing at least 4 different areas and the results averaged over more than 100 points. Figure 3.3 shows a typical resulting morphology. The surface appears remarkably uniform after annealing. Parallel steps run along the $[10\bar{1}0]$ direction and cover the whole surface in a almost periodical fashion. The rearrangement of the surface preserve the overall surface orientation, as confirmed with both XRD and AFM. The average period $\langle l \rangle$ increases exponentially with the temperature. The behaviour can be explained considering the faceting formation as a thermally activated diffusion process, assuming an equivalence between surface periodicity and adatoms average displacement. In this case, through the Einstein equation $l^2 \propto D$, an effective diffusion constant $D = D_0 \exp(-E_{ac}/k_B T)$ can be obtained, with E_{ac} being the activation energy and k_B the Boltzman constant. As the annealing time is the same for each sample, the exponential increase in the periodicity is then expected with rises in the annealing temperature. In order to confirm this relation, the inverse of the temperature is plotted vs the logarithm of the average periodicity in the inset. This plot, known as Arrhenius plot, allows one to extract, from the slope of the linear fit, the activation energy activation energy of the process, being in our case $E_{ac} = 2.8 \pm 0.8 \text{ eV}$. Such an energy is bigger than the 2.0 eV reported for the nominally flat sapphire. However, the differences between different the two off-cut are not very pronounced and the large errors in the data do not allow to produce a conclusive understanding in the origin of the measured changes.

Different substrate off-cut angles produce similar results (see Figure 3.4 (A) and (B)). However, for a given periodicity, changes in the initial off-cut angle results in

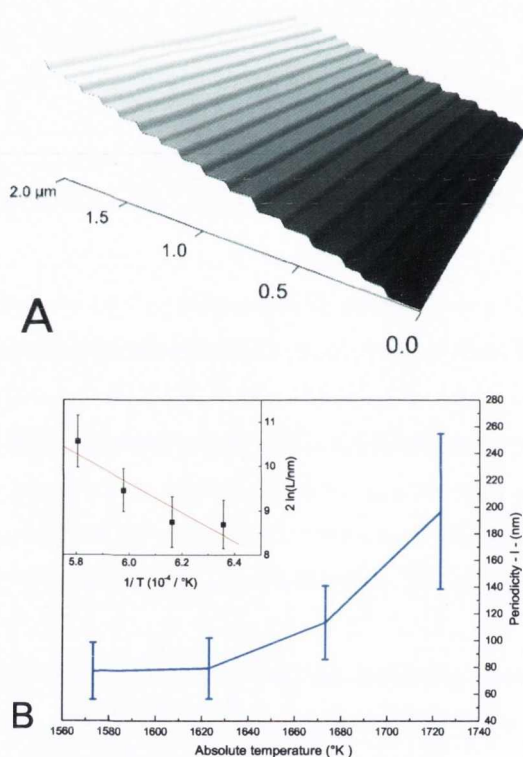


Figure 3.3: Faceting formation after annealing of $\text{Al}_2\text{O}_3(0001)$ at high temperature. (A) $2 \times 2 \mu\text{m}^2$ AFM image after first-order subtraction. The surface is off-cut 6° along the $[\bar{1}210]$ direction. After annealing in atmosphere at 1350°C for 24 h, the surface appears remarkably uniform and nearly periodic facets can be observed. (B) Temperature dependence of the period as a function of the annealing temperature. Rises in the annealing temperature increase the period exponentially. The linearity in the Arrhenius plot (inset) confirms the dominantly diffusion activated process with an activation energy of $2.8 \pm 0.8 \text{ eV}$.

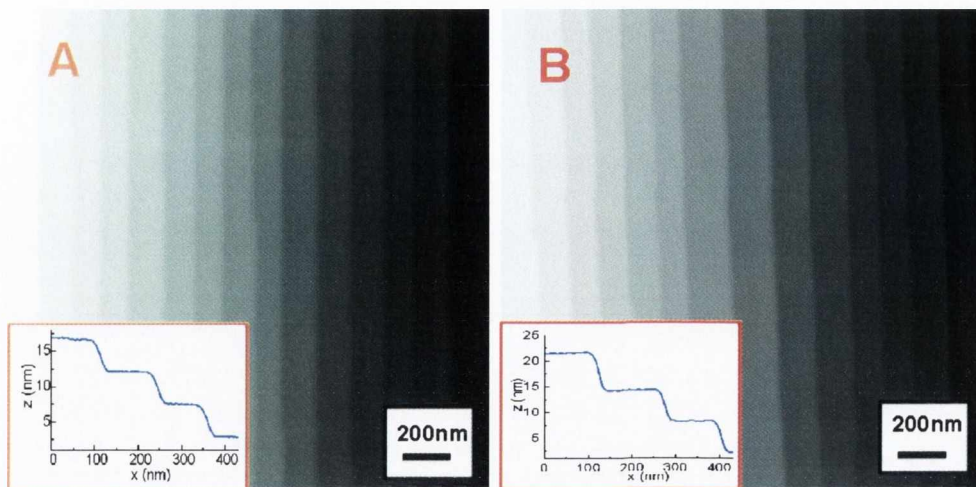


Figure 3.4: $2 \times 2 \mu\text{m}^2$ AFM images of $\text{Al}_2\text{O}_3(0001)$ off-cut 2° (A) and 3° (B) along the $[1\bar{2}10]$ direction. The surfaces were annealed at 1400°C for 24 hours. A typical AFM section can be observed in the inset.

steps with different step heights. Surfaces with comparable periodicity were analysed, and the step height appears smaller for smaller off-cut in order to preserve the overall surface orientation. The periodicity can be varied, for a given miscut angle, by changes in the annealing temperature and a step height tuned by changing the initial sample off-cut. A full modulation of the parameters describing the morphology of the surface can hence be obtained.

In order to clarify doubts about the mechanism behind the rearrangement of the surface, whether it is bunching or faceting of the surface, AFM cannot be used as the AFM tip radius ($\sim 10 \text{ nm}$) is comparable with the surface features. A high resolution TEM analysis has been performed for different periodicities for the 6° samples. All steps appear inclined of the same 42° angle with respect to the $[1\bar{2}10]$ direction shown in Figure 3.5 (B). Such an inclination corresponds to the $(1\bar{2}16)$ orientation. This angle appears independent on the step height and it is also in accordance with previous TEM results obtained for different off-cut samples [120]. Being such orientation also independent on the step height, the mechanism can be effectively addressed as a faceting mechanism, the two facets being the (0001) plane of the terrace and the $(1\bar{2}16)$ plane of the steps.

The faceting formation is also confirmed by the presence of bowtie merging defects

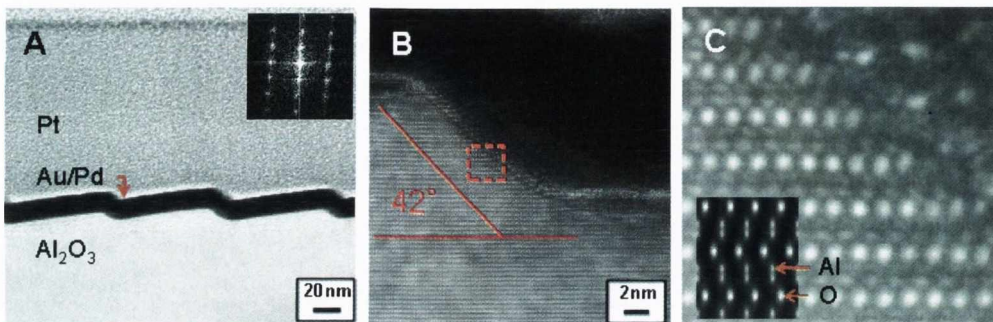


Figure 3.5: TEM section of a sample off-cut 6° and annealed at 1350° for 24 hours. A Pt protecting coating layer has been sputtered on the surface before the section preparation in order to protect the surface. (A) Low magnification of the surface, obtained after alignment of the crystal axis with the TEM optical axes (see diffraction pattern in the inset). (B) High magnification image, the crystal structure can be clearly observed. The step inclination of 42° with respect to the $[1\bar{2}10]$ is shown, corresponding to a surface orientation of $(1\bar{2}16)$. (C) Magnified view of the outlined area in (B). In the inset a java electron microscope simulation shows the expected Al and O position using the tabulated crystal structure of Al₂O₃.

on the surface as shown in Figure 3.6 (A). Different defects are outlined and the merging points never appear isolated (see Figure 3.6 (B)). This is a consequence of coarsening of the facet domains: when different faceted areas grow and overlap, they produce the observed junctions [123].

The mechanism underlying the facets formation is common for all samples. This is suggested by Figure 3.7, where the probability $P(l)$ of observing two steps separated by a distance l is plotted with respect to the relative period $l / \langle l \rangle$. It appears evident the distribution does not remarkably depends neither on the annealing temperature nor the off-cut angle.

Thermodynamic arguments can then be used as a basis for understanding the faceting phenomenon as we noted that the surface morphology has reached thermodynamic equilibrium after one day annealing. The calculated diffusion constant [117] of adatoms on the surface of Al₂O₃ is $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ at 1500°C . This means that the surface reaches equilibrium over a distance of $10 \mu\text{m}$ in annealing durations of the order of 1 hour, which is much smaller than the 24 hours spent in this study. Two samples were annealed for 24 hours and 72 hours to confirm this, as no change in the periodicity of the two substrates were observed, in line with previous reports [118, 120].

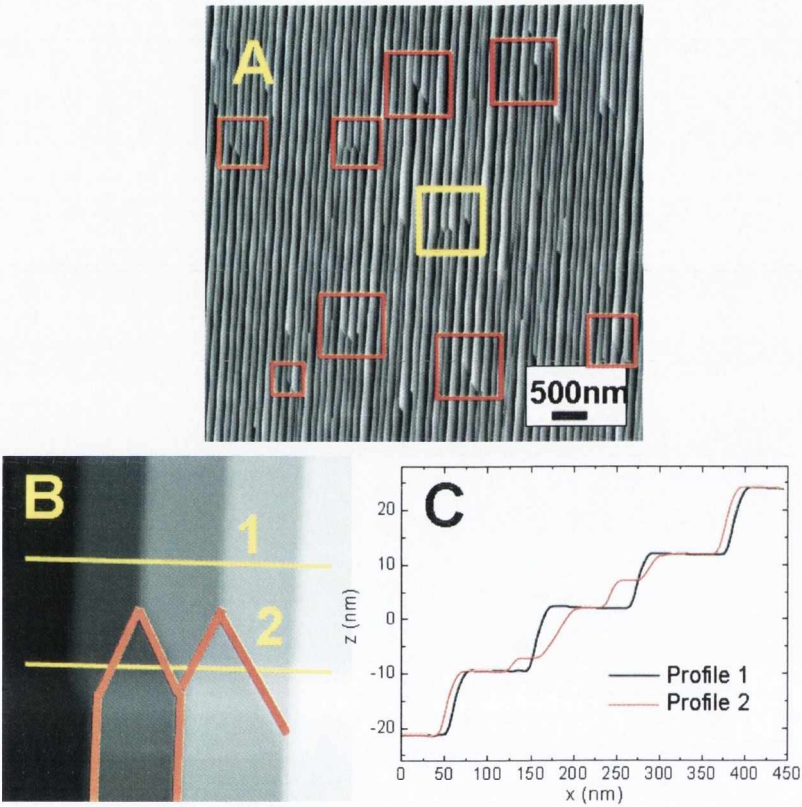


Figure 3.6: (A) Small magnification of the 6° off-cut sample after annealing at 1400 °C. Defects can be identified and were attributed to coarsening of faceted domains [113]. (B) A magnification of the yellow area can be observed. (C) Profile and the along the first and second line.

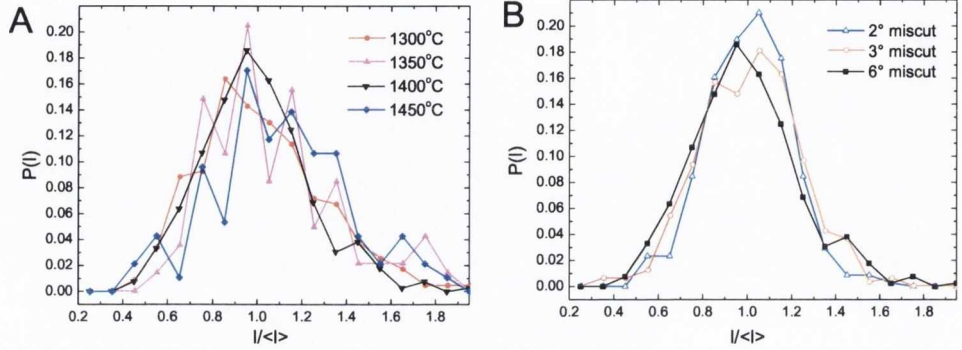


Figure 3.7: Normalised distribution of the period as a function of L/L_{opt} for different annealing temperatures (A) and initial substrate off-cut (B). The curves follow the same Gaussian distribution.

The resulting equilibrium conditions observed during the annealing temperature corresponds to minima of the surface free energy of the system. Generally speaking, the surface free energy is the integral of the surface free energy per unit surface $\gamma(\mathbf{m}, T)$ over the overall surface σ

$$F_{surf}(T, \sigma) = \oint_{\partial\sigma} \gamma(\mathbf{m}, T) dA. \quad (3.1)$$

In Eq. (3.1) T is the temperature of the heat reservoir (the annealing temperature in our case) and $\mathbf{m}$ is the orientation of the surface element dA . The equilibrium morphology is obtained by minimisation of the quantity F_{surf} under the constraint of a fixed volume included inside the surface. The stable surfaces can be obtained using the Wulff construction [124]. In this case the stable facets result at the high symmetry directions of the crystal, where cusps in $\gamma(\mathbf{m}, T)$ can be found. At high temperature these cusps blunt and additional orientations not present for $T = 0$ can be found. It was shown by Herring [124] that, if only the top crystal surface is allowed to be modified, the surface can rearrange in a hill and valley structure in order to minimise its overall free energy.

Different models can explain the faceting of the vicinal surface. The first possibility to produce the periodic step arrangement is due to an attractive step-step interaction. A model for faceting involving attractive elastic forces and was proposed by Marchenko around 30 years ago [125]. In his approach, the constraint of conservation of the average surface orientation of a vicinal surface implies the coexistence of alternating directions.

At the intersections between different facets, the strains are unbalanced and will generate elastic forces which will propagate into the bulk. These forces can be represented by long-range elastic attractive monopoles having a logarithmic dependency and it was found that these structures exhibit an optimum period, correspondent to the minimum of the surface free energy of the system. However, the explanation provided by Marchenko is not the only plausible one. An other possibility is that faceting is due by simple entropic contribution of step wandering and repulsive stress-mediated interactions. As a result, most faceting transitions could be because of competing free energy curves induced by changes in surface composition due to adsorption or reconstructions [126]. As the measured $(1\bar{2}16)$ step orientation was never reported to be stable, this explanation appears also to be possible.

Finally, the annealing of the templates also lacks precise control over the resulting morphology. Differences in the resulting morphology for samples prepared by identical procedure were observed. These differences are attributed to the substrate quality and possible contaminants and the impurities can then interfere with the kinetic processes involved creating more complex instabilities. It was reported that common segregation of contaminants such as Ca, Mg, Ba, Si can affect the step and surface structure evolution of sapphire samples, generating mesoscopic steps [127]. For this reason the annealing study of the 6° off-cut sample at different temperatures was performed cutting different pieces from the same substrate.

The faceting formation of the Al_2O_3 (0001) surfaces remains then rather unclear and a complex interplay among the discussed possible causes is likely to be responsible for it. Deeper investigations of the phenomenon is required to describe the evolution of the surfaces and new measurements will be performed in the future to provide a definitive answer.

3.4 Conclusions

The morphology of off-cut c-plane $\alpha\text{-Al}_2\text{O}_3$ was investigated by annealing at high temperatures. The procedure followed to produce stepped templates was described and the formation of a step and terrace structure is attributed to faceting formation. The possibility of changing both periodicity and step height was demonstrated by modifying

annealing temperature and substrate off-cut respectively. The statistical properties and the presence of surface defects have been described. Various mechanisms which may be responsible for the regular faceting arrangement have been proposed. These substrates will be utilised in the rest of the thesis as templates for glancing angle depositions.

Chapter 4

In-plane Optical Properties of Ag Nanoparticle Arrays

If I have seen further than others, it
is by standing upon the shoulders of
giants.

I. Newton

In this chapter the possibility of growing Ag NP arrays on a stepped Al_2O_3 (0001) templates via glancing angle deposition is demonstrated and the features of their in-plane optical signature investigated. This chapter outlines the main results of the entire thesis. The Ag NP results ordered on the macroscale and their dichroic response is investigated. In particular, RAS was utilised to measure their plasmonic features and its equivalence with normal incidence polarised transmission spectroscopy (PTS) is shown.

First, the RAS signature of Al_2O_3 off-cut substrate was discussed. Afterwards, the morphology and LPRs were investigated as a function of deposition time, deposition angle and initial template periodicity. When the angle of deposition is greater than

the initial template off-cut, part of the material was observed on the terraces resulting in a diminished measured RAS intensity. Conversely, at extremely shallow deposition angles it is demonstrated that the shadowing of the bigger particles increases the NP morphological dispersion in the latest stages of deposition. This increase causes a broadening of the resonance peaks. An optimum deposition angle was hence found as a trade off of the two effect in order to minimise the morphological dispersion of the metal clusters without observing deposition on the terraces.

A simple phenomenological model based on dipolar interaction was developed to reproduce the features seen in the spectra. With this model it was possible to use the inhomogeneous broadening as a guide to the NP dispersion.

The effect of the exposure of the sample to atmosphere are also discussed. It is found that the resonance peaks red shift due to the formation of a thin silver sulphide layer surrounding the particle, in accordance with the results simulated with the classical model of Chapter 1.

Finally, the dependency of Ag NP arrays as a function of the initial template periodicity was investigated. The different templates have been produced changing the annealing temperature of the Al_2O_3 templates as shown in Chapter 3. Different initial template periodicities result in different NP dimensions and shifts of the resonance energetic positions have been obtained. In order to extract detailed information on the origin of the dichroic response the semi-quantitative model based on dipolar interactions developed in Chapter 1 has been utilised and compared directly with the experimental results and a qualitative agreement obtained.

4.1 Al_2O_3 (0001) RAS signature, role of the miscut

Prior discussing the LPRs of NP arrays, the optical properties of c-plane α -alumina need to be introduced. The choice of c-plane α -alumina as a template for the growth of NP has been motivated not only by the possibility of faceting the vicinal surface, but also by symmetry considerations. RAS measurements of Ag dipolar excitations were recently reported by the Zeppenfeld group on a birefringent substrate [128]. In their report it was shown that such an anisotropic substrate can create anisotropic image charges that can produce a RAS signal in the spectrum measured. Flat c-plane Al_2O_3

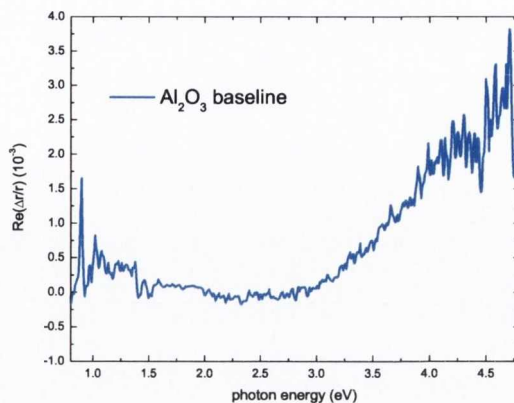


Figure 4.1: RAS spectra of a Al_2O_3 substrate, 6° off-cut along the $[\bar{1}210]$ direction, after annealing at 1450°C .

possesses a three-fold symmetry that should not give rise to any distinct signature in the RAS spectrum [81]. Despite that, the presence of the miscut could in theory introduce anisotropic contributions that can modify the optical properties of the Ag assembly. In order to disregard this possibility we measured the RA spectra on the bare substrates obtaining a small signal in the UV of 2×10^{-3} (see Figure 4.1). The RAS signal of the substrate can then be considered negligible if compared with the ~ 200 RAS units of the samples after the deposition of plasmonic materials.

4.2 Experimental procedure

In this section the full experimental procedure used to obtain NP arrays is described in detail. A consistent growth method is utilised in Chapter 5 and 6.

Single crystal c-plane sapphire samples ($\alpha\text{-Al}_2\text{O}_3$ (0001)), miscut along the $[\bar{1}210]$ direction, were used to obtain stepped templates. The substrates were prepared with either 3° or 6° nominal miscuts and polished on one side. The stepped surfaces were produced as already described in chapter 3.

The annealed templates were subsequently loaded into the growth chamber and the average sample surface aligned at a required grazing angle with respect to the

Ag atom flux. The proximity of each loaded sample and the large distance (70 cm) between the crucible and the samples ensure the same coverage for each of the deposited sample. Unless clearly specified, the NPs were prepared by depositing Ag onto the substrates at room temperature with at a calibrated rate at normal incidence equivalent to 0.23 nm/min.

When we refer to nominal NP height we will use the relation

$$h = F \times t \times \sin \Theta / f, \quad (4.1)$$

where F is the adatom rate flux at normal incidence, t is the deposition time, Θ is the grazing deposition angle and f is the nanocluster filling factor, typically approximated to be $f \simeq 0.12$.

4.3 Transmission and RAS comparison

To understand the origin of the RAS signature we will first demonstrate the equivalence between RAS and PTS for the system investigated. For this, a test sample with a 3° off-cut angle was annealed at 1400°C. AFM confirmed the periodic surface morphology. Subsequently, the substrate was loaded into the chamber and aligned at 6° with respect to the collimated beam of evaporant metal. Ag was deposited for 20 minutes for an estimated NP height $h = 4$ nm. After exposure of the sample to atmosphere both RAS and PTS were measured and the results were compared qualitatively in Figure 4.2 (A). PTS shows a distinct peak and its resonant position depends on the polarization angle of the incident light. When the beam is polarized along the miscut direction the absorption spectrum contains a main peak in the UV, while if the beam is polarized along the step edge the main peak resonance is present at lower energy and has a higher intensity. This is in accordance with previous literature reports [30, 31, 33, 65]. Similarly, the RAS spectrum presents a double resonance whose positions match the absorption profiles. To compare the relative peak intensities, the difference between the two absorption spectra $E_{(x)}$ and $E_{(y)}$ is compared with the RAS spectra and the qualitative agreement is evident (Figure 4.2 (A) brown and red lines).

As the UV-VIS spectrophotometer used in this study only records the specular transmission, the measured losses are not directly equivalent to an absorption, but

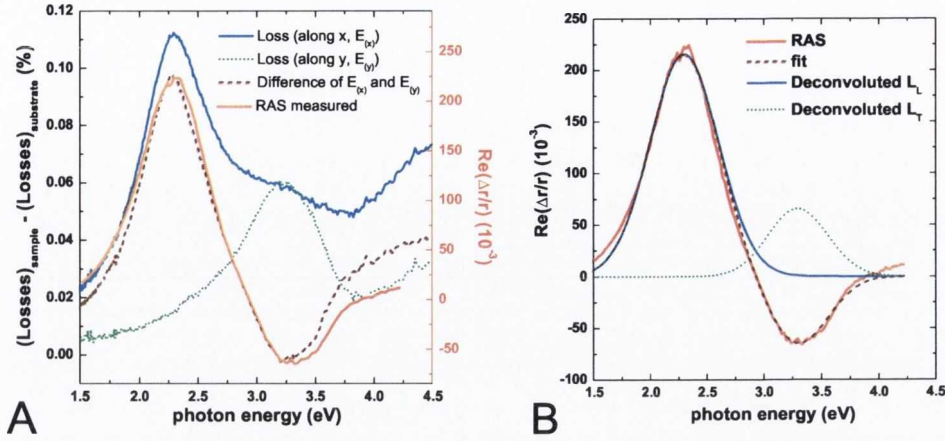


Figure 4.2: (A) Comparison between *ex situ* RAS and PTS measurements. The absorbance and scattered loss along the step direction ($E_{(x)}$) is shifted with respect to the perpendicular direction ($E_{(y)}$). The spectral shape of the difference between the light losses matches well with the RAS spectra. (B) Fitting of a double Gaussian to the RAS spectrum in order to extract the exact minor peak position.

include reflective and scattered losses. On single-sided polished samples, as used here, this leads to significant light losses caused by Rayleigh scattering at the rough backside of the sample. The data in Figure 4.2 have been recorded with respect to a reference sample without Ag islands. At this stage we can not distinguish between absorption or scattering, as an integrating sphere would be required. However, for comparison of the absorbance and RAS data, this is not a significant problem as both effects can be treated separately. The substrate is fully transparent from 0.45-6.5 eV. The apparent UV absorbance in the PTS measurements is simply a Rayleigh scattering contribution and has its characteristic ω^4 dependence[34]. We stress the point that this is not caused by substrate absorbance, which would complicate the comparison with RAS. The scattering can be caused by possible different losses at the back side of the sample or by enhanced scattering by the Ag islands themselves. This loss is purely added in our simple transmission measurements. The RAS measurements themselves only account for the specular reflected light and hence do not show differences in scattered losses as the signal is solely generated at the polished front surface.

Even though it is possible to reproduce the RAS features from PTS, the inverse operation is not trivial. RAS measures the difference between the real part of the complex

reflection coefficients for light polarised in two orthogonal directions *averaged* on the overall reflection. In order to extract the exact peak position and relative intensities it is necessary to deconvolute each RAS spectrum. This was done by modelling the signal with a double Gaussian, with each peak having a position, amplitude and width. The deconvolution performed was possible because of substrate transparency. With six free parameters, different choices of the peak positions can reproduce the RAS features. However, by fixing the positive peak position using the absorption PT spectra along the array, a reliable fit was then possible (see Figure 4.2 (B)) and the negative peak position, relative peak intensities and an estimate of the full widths at half maximum could be extracted from the RAS signal.

RAS and the polarisation dependent transmission have been shown to provide similar information, but RAS has the advantage of a greater sensitivity and also allows *in situ* measurements to be performed. Because of these advantages RAS was the main technique used in the following discussions.

4.4 Dependency of the optical response on the deposition angle

The RAS signal is expected to depend critically on the growth conditions of the Ag NP arrays. In order to examine this, a systematic study was undertaken to establish how the RAS changes with deposition angle at different deposited thickness. For this purpose two samples with off-cut angles of 3° and 6° respectively were annealed at 1350°C for 24 hrs. AFM inspection confirmed the faceting of the surface. The step-step distance was measured as 137 ± 46 nm for the 3° off-cut sample and 79 ± 22 nm for the 6° off-cut sample. The prepared stepped templates were subsequently cut into 4 smaller pieces. A piece from each off-cut was then loaded into the vacuum chamber and aligned at the required angle. A correction to the deposition time depending on deposition angle was included to ensure that Ag coverage was consistent.

A typical result is shown in Figure 4.3. All the RAS spectra show a double peak feature (Figure 4.3 (B)). Figure 4.3 (A) shows an example of the morphology of a

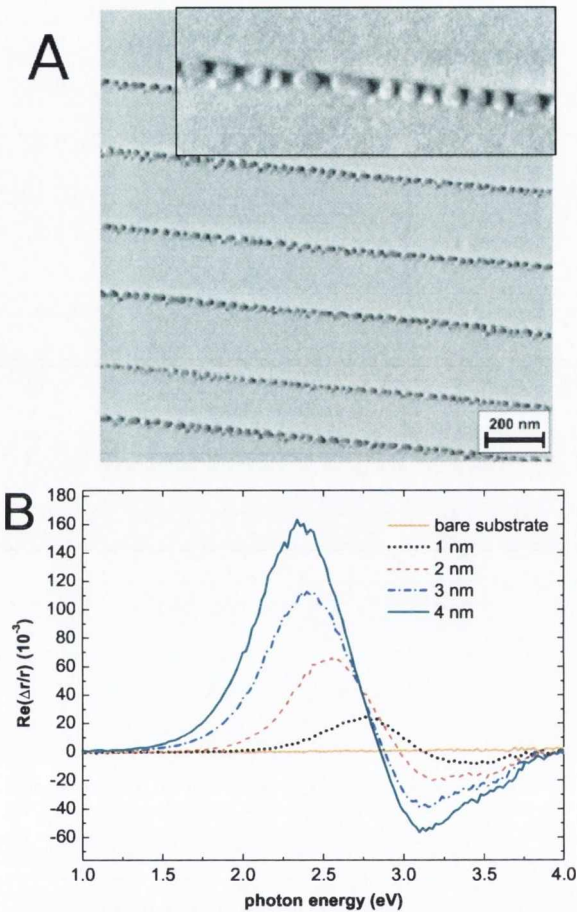


Figure 4.3: (A) $1.5 \times 1.5 \mu\text{m}^2$ SEM image and magnified (inset) $300 \times 100 \text{ nm}^2$ image of the substrate after 4nm Ag deposition. The substrate was a 6° miscut sample previously annealed at 1350°C for 24h. The sample was loaded in the chamber and inclined at 6° to the Ag atom flux. (B) RAS spectra of the same sample monitored *in situ* for different thickness. With increasing deposited thickness the peak amplitudes increase and the peak positions appear to red shift.

cluster layer determined by SEM. The surface morphologies are remarkably uniform: the entire $5 \times 5 \text{ mm}^2$ sample surface is covered by NPs having an average radius of $7.9 \pm 1.9 \text{ nm}$. NPs are positioned along the outer edge of the steps. This confirms the intuitive view of the growth mechanism that the adatom flux is directed towards the steps, which act as preferential growth sites. Once the Ag ad-atoms stick to the surface, they start to diffuse following a characteristic three dimensional growth mode [129]. As the (0001) terraces have the lowest surface free energy configuration [130], the adatoms cannot overcome the diffusion barrier between step and terraces and all the material distributes on the facets as islands. Using this model a linear increase with coverage in the RAS for both the positive and negative peaks is expected, if the peak profiles do not change significantly.

To obtain quantitative information the curves have been fitted using the two gaussian model after fixing the positive peak position and the extracted peak information has been plotted as a function of the nominal NP height for different deposition angles and substrates (see Figure 4.4). Both the positive and the negative peak amplitudes increase with the Ag coverage. In particular, all samples that do not show significant increase in the peak width with increasing thickness present a linear increase in the peak amplitudes (Figure 4.4 (A)). While the negative peak position appears to be almost constant, the positive peak shifts are dependent on the deposition parameters (Figure 4.4 (B), 4.4 (C)). The largest separation occurs at high coverage and high deposition angles.

Figure 4.4 (D) shows that the amplitude generally reduces as the deposition angle increases. This can be understood by reference to the SEM image shown in Figure 4.4 (E) where, for 12° angle of deposition, significant isotropic island formation on the terrace can be seen, which reduces the RAS amplitude. In contrast to the 6° miscut, the 3° miscut shows little change between 6° and 12° angle of deposition. This is consistent with shadowing effects which are reduced for deposition angles greater than the miscut angle.

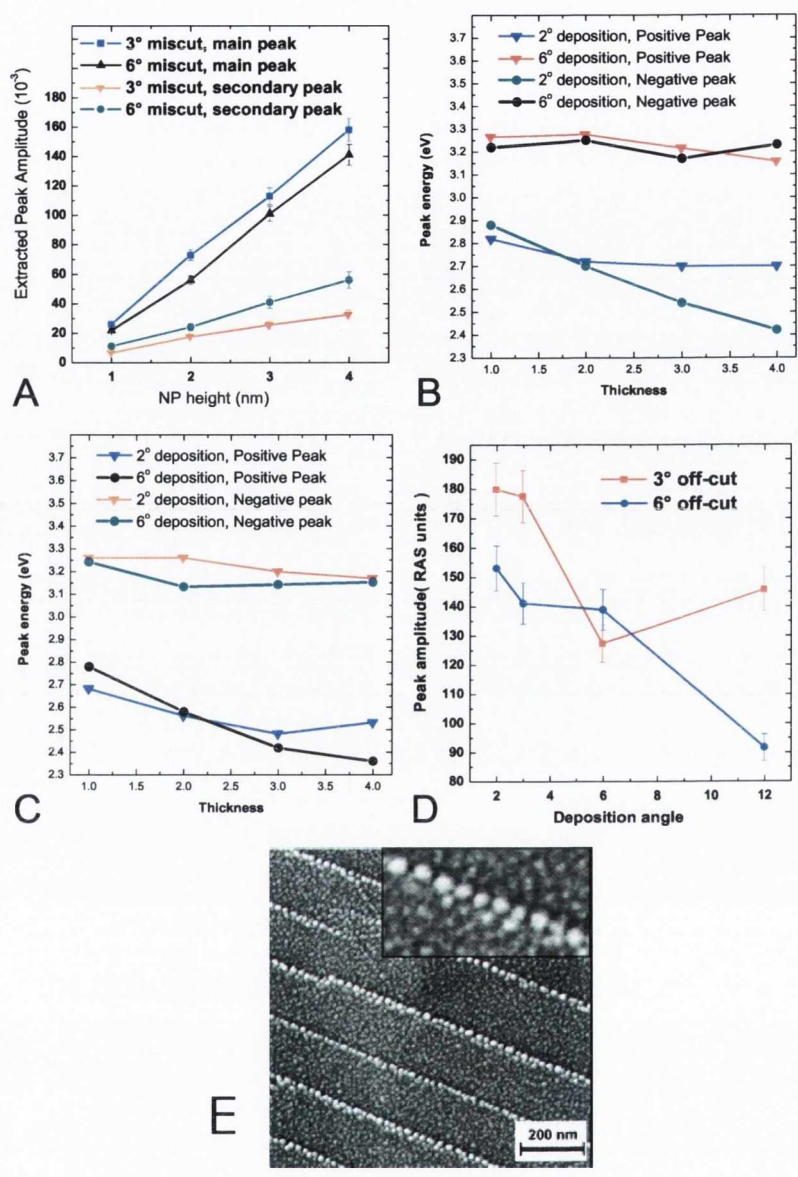


Figure 4.4: (A) Peak amplitude as a function of the deposited thickness for 6° deposition angle and different off-cut angles. Extracted peak position as a function of the deposited thickness for the 3° (B) and 6° (C) substrate off-cut. (D) Average positive peak height, normalized to 4 nm average height, as a function of deposition angle. (E) SEM image of the 6° miscut, for 4 nm average NP height, at 12° angle of deposition. Significant isotropic deposition on the terrace can be seen, leading to a reduced RAS peak amplitude.

4.5 Coupled oscillator model

In the previous section we have shown the dependency of the plasmonic peaks with coverage and deposition angle. In order to address the changes in a more quantitative way utilising a model we need to discuss the measurements within a theoretical framework. There have been numerous discussions on the optical response of LPR [1] and reports of RAS measurements on anisotropic arrangements of metal island [39, 128, 131, 132]. However, none of the theoretical models described there can be directly applied to our structures.

From the perspective of the large optical anisotropies (> 50 RAS units) similar RAS amplitudes have been reported for large indium islands on GaAs(001) with a tunable peak position [131]. The response was explained in terms of multipole Mie resonances as the islands had shape anisotropies and were comparable in size to the wavelength of light. This mechanism cannot be the origin in our case as the Ag islands are significantly smaller than the wavelength used.

Another system, where an anisotropic response of Ag islands on m-plane sapphire was reported [128], was explained by the introduction of image charges within the anisotropic substrate. The resulting RAS structures, though similar in shape, are significantly smaller (< 10 RAS units) and appear even with isotropic island distributions. This contrasts to the findings of this work, where a significant morphological anisotropy leads to signals > 100 RAS units on a negligibly anisotropic substrate plane.

There are other reports of smaller, or partly aligned metallic clusters, which give rise to optical anisotropies measured by RAS [132, 133]. In contrast, the separation between individual nanocluster rows is much greater here and the measured anisotropy is one or two orders of magnitude larger. Despite similarly low coverages, the islands are large enough to show metallic behaviour, which is not the case for smaller islands of Ag on Si(111) [132], and the substrate is not metallic as for Co islands on Au(111). This is a strong indication that the plasmonic effects of metallic NPs in an insulating environment is the physical origin of the measured anisotropy.

In order to give a qualitative understanding of the results obtained we developed a phenomenological approach, similar to the framework of oscillators excited by an external electric field presented in Section 1.3. The Ag NP arrays were modelled as an infinite 1D array of equally spaced metallic NPs of radius R , interacting via coupled

dipolar plasmon modes. In the quasi-static limit ($R \ll \lambda$) this is the positive excitation mode and each nanodot acts as a point antenna. In particular, if the particles are closely spaced, the electric field generated by the m -th antenna in the direction i produces an electric field in its neighbours vicinity which is given by [134]

$$E_{m,i}(t) = \frac{\gamma_i p_{i,m}(t)}{4\pi\epsilon_0 n^2 d^3}, \quad (4.2)$$

where ϵ_0 is the free permittivity, n is the effective refractive index of the medium surrounding the particles and d is the distance between each dipole. γ_i is a polarisation dependent constant, where $\gamma_y = 1$ and $\gamma_x = -2$ for polarisation perpendicular and parallel to the dot arrays, corresponding to transverse and longitudinal plasmon modes. If each nanodot is represented as an electric point dipole $p_{i,m} = n_e e x_{i,m}$, where n_e is the number of free electrons displaced by $x_{i,m}$ from the equilibrium position, the equation of motion for the m -th oscillator becomes

$$\ddot{p}_{i,m} + \omega_{0,i}^2 p_{i,m} + \Gamma \dot{p}_{i,m} + \sum_{k \neq 0} \gamma_i \omega_{cp,k}^2 (p_{i,m+k} + p_{i,m-k}) = \frac{n_e e^2}{m^*} E_0 e^{i\omega t}. \quad (4.3)$$

Equation (4.3) has the same form as Eq. (1.4). In particular, the last term represents the incident oscillating electric field, m^* is the optical effective mass, Γ is the electronic relaxation frequency of each NP due to resistive losses in the nanodot and $\omega_{0,i}$ is the eigenfrequency of the isolated particle. As described in Section 1.2, $\omega_{0,i}$ can be calculated taking into account shape anisotropy which could lead to splitting of the resonant peak. In the derivation below an in-plane isotropic NP is assumed and the i index suppressed. The additional fourth term in Eq. (4.3) represents the electrodynamic interaction between the dipoles and it determines the polarisation dependence of the optical spectra via a coupling frequency

$$\omega_{cp,k}^2 = \frac{n_e e^2}{4\pi m^* \epsilon_0 n^2 (kd)^3}. \quad (4.4)$$

Assuming periodic boundary conditions and the in-phase oscillations of the long wavelength approximation, it is easily shown that, under the assumption of small damping ($\Gamma \ll 1$) and nearest neighbour interaction, the system behaves like a series of damped harmonic oscillators with an overall effective resonance frequency $\omega_{i,e}^2 = \omega_0^2 + \gamma_i \omega_{cp}^2$,

which is polarisation dependent. Calculating the difference between the overall effective frequencies for the polarisation along ($\omega_{x,e}$) and perpendicular ($\omega_{y,e}$) to the chain and using a Taylor expansion, the following simple formula for the peak separation is derived:

$$\Delta\omega \approx 3 \frac{\omega_{cp}^2}{\omega_0}. \quad (4.5)$$

For higher neighbour interactions Eq. (4.3) can be solved exactly with coherent oscillations obtaining a complex polarisation-dependent electric dipole

$$p_{i,m}(\omega) = \frac{n_e e^2}{m^*} (\omega_{i,e}^2 - \omega^2 + i\Gamma\omega)^{-1} E_0 e^{i\omega t} \quad (4.6)$$

where $\omega_{i,e}^2$ takes into account the interactions up to a cut-off distance. If it is assumed that there are N_l dipole chains per unit area each containing N_d nanodots, the dielectric function of the nanodot layer is

$$\frac{\varepsilon_i(\omega)}{\varepsilon_0} = 1 + \chi_e = 1 + N_l N_d \frac{n_e e^2}{\varepsilon_0 m^*} p_{i,m}(\omega). \quad (4.7)$$

Since a positive imaginary part of the dielectric function represents the absorption of energy from the incident EM wave, a polarisation dependent absorption spectrum whose energy profile is described by Eq. (4.8) is obtained

$$\varepsilon_i'' = N_l N_d \frac{n_e e^2}{m^*} \frac{\omega\Gamma}{(\omega_{i,e}^2 - \omega^2)^2 + \Gamma^2\omega^2}. \quad (4.8)$$

For comparison with experiment the Ag NPs were modelled as cylinders having an aspect ratio $R/h = 2$ and a radius $R = 8$ nm. It is assumed that $m^* = 8.7 \times 10^{-31}$ kg [135], the carrier density is 5.85×10^{22} cm⁻³ [136] and an inter-particle center-to-center distance of 22 nm. Figure 4.5 shows the absorption spectra for polarisation along and perpendicular to the chain. The simulation reproduces qualitatively the measured PTS. In particular, a reasonable energy splitting and a smaller negative peak amplitude is obtained. The model developed here suggests that for $kd \gg 3R$ the interaction becomes negligible, excluding any strong inter-array interaction and the presence of retardation effects.

Using the three layer model of Chapter 2 the RAS features can be finally derived from the same microscopic picture assuming the dots were embedded in an effective

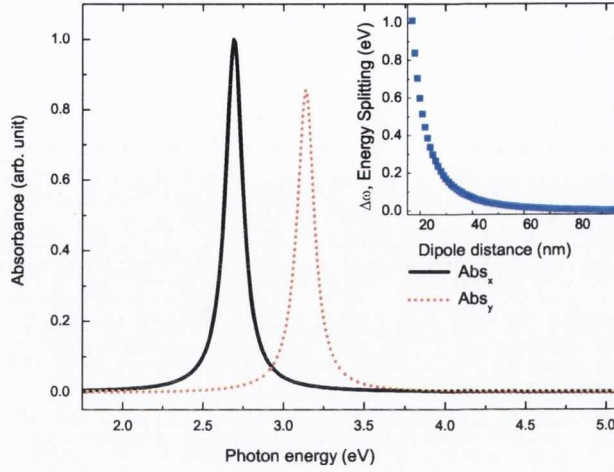


Figure 4.5: Simulation of the absorption spectra. $R=8$ nm, $h = 4$ nm, $d = 22$ nm, $\omega_0 = 2.8$ eV were the parameters used. A clear shift in the two resonances is visible. The dependence of the energy splitting for polarisation along and perpendicular to the NP chain, as a function of the dipole distance, is shown in the inset.

refractive index material $n = (1 + n_b)/2$, where the arrays are assumed not to interact. In this way the model provides a useful tool for understanding the RAS features measured in Section 4.4. The increase in the RAS intensity with the thickness can be understood as an increase in the thickness of Ag, hence an increase in d in the three layer model. For high deposition angles the peak shift also increases with the deposited thickness. This behaviour is attributed to an increase in the coupling between each oscillator due to the increase in island size: from Eq. (4.5)

$$\Delta\omega \propto \omega_{cp}^2 \propto n_e. \quad (4.9)$$

The main limitation of the model is that ω_0 is unknown. However, from the discussion above, it is related to ω_x and ω_y by

$$\omega_0 \doteq \omega_x + \frac{2}{3} \times \Delta\omega. \quad (4.10)$$

The extracted peak positions show that ω_x decreases and the peak splitting, $\Delta\omega$, increases with coverage, indicating that ω_0 is only slowly varying and can be correctly treated as a fitting parameter as shown in the next section.

4.6 The origin of the peak broadening

The position of the resonance peaks has been discussed in Section 4.4 as a function of deposition angle and deposited thickness. The other key feature of any plasmonic resonance study is the width of the peaks. Narrow resonances are necessary to improve the sensitivity of a plasmon-based biosensor and to provide information on the morphological dispersion of the system.

The coupled oscillator model of the previous section will be used here to extract quantitative information on the broadening of the peak. The full classical model of Chapter 1 will be finally utilised to justify more rigorously the effect of the peak broadening due to morphological dispersion. Combining Eq. (4.8) and Eq. (2.3), a fitting of the experimental RAS signal can be obtained by allowing the amplitude of the minor peak to vary. The RAS is then given by

$$\frac{\Delta r}{r}(B, K, V, \Gamma, \omega_0) = B \frac{[\varepsilon_x''(V, \Gamma, \omega_0) - K\varepsilon_y''(V, \Gamma, \omega_0)]}{\varepsilon_b - 1} \quad (4.11)$$

where B is the positive peak amplitude, K is a unitless factor which allows the minor peak amplitude to be adjusted, and V is the NP volume for cylindrical islands of aspect ratio 2. The advantage of using Eq. (4.11) rather than the full model of Chapter 1 is that the fitted Γ parameter is directly related to the Gaussian broadening of the peaks and is adjusted independently on the other parameters. The parameter values obtained by using this simple five parameter fit are given in Table 4.1 for the 6° off-cut samples. The values of peak height and width, particle volume and resonance frequency appear quite reasonable, given the approximations of the model.

The results from RAS analysis of samples produced using deposition angles of 2° and 6° and their fits according to Eq. (4.11) are shown in Figure 4.6, where both peak shifts and broadening are clearly seen and well reproduced by Eq. (4.11). The Lorentzian nature of the model results in some excess intensity in the wings of the peaks, as is to be expected if the data are inhomogeneously broadened by dispersion in particle size.

Varying the deposition angle alters the width of the peak for consistent Ag coverages. In particular, from Table 4.1 a larger dispersion in particle size is obtained for smaller angles of deposition. This can be related to shadowing effects. With increasing coverage the height of a NP can increase to a value that, for very shallow angles of

Dep. angle(°)	R	d	B(10 ⁻³)	K	V(nm ³)	Γ(eV)	ω ₀ (eV)
2	6.9 ± 2.9	24 ± 3	372 ± 12	0.51	931 ± 29	0.88	3.10
3	7.9 ± 3	21 ± 5	331 ± 10	0.55	760 ± 21	0.75	3.03
6	7.6 ± 1.9	23 ± 6	259 ± 6	0.63	807 ± 12	0.61	2.92
12	6.6 ± 1.6	21 ± 5	171 ± 5	0.68	690 ± 13	0.60	2.93

Table 4.1: Mean particle radius and interparticle distance for the 6° miscut sample, as determined by SEM, together with fitted parameters using Eq. (4.11), for different angles of deposition. Errors not shown explicitly are ±0.01.

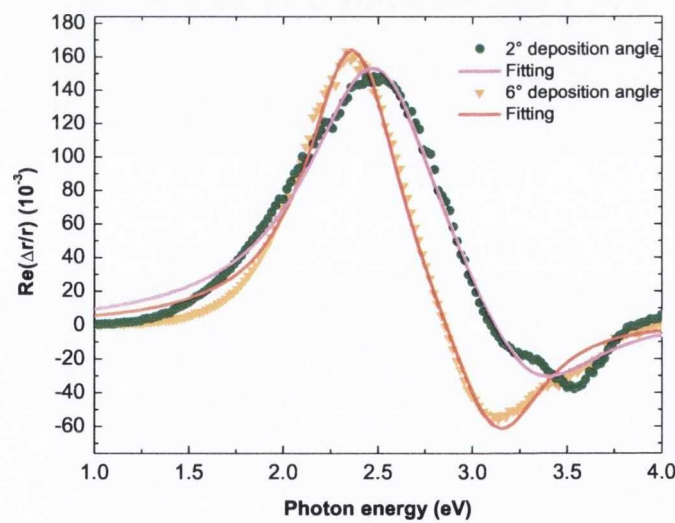


Figure 4.6: Fits using Eq. (4.11) of the RAS spectra for the 6° miscut sample, at 2° and 6° deposition angle.

deposition, begins to shadow the NP on the adjacent step, which then stops growing. Figure 4.7 (A) shows a schematic of the shadowing effect and Figure 4.7 (B) an SEM image for 4 nm coverage and a 2° deposition angle, where arrays of small islands can be seen behind the arrays of larger islands.

The dependance of the peak width on the angle of deposition is shown in Figure 4.8, where larger angles are shown to produce narrower resonance peaks. Furthermore, a linear correlation (see Figure 4.8) between the fitted Γ parameter value and the dispersion of the island size, as determined by SEM analysis, can be observed and the Γ parameter can then be used as a direct semi-quantitative measure of the broadening.

The correlation between the fitted Γ value and the dispersion in particle size allows the Γ value, together with the peak amplitude, B , to be used as a direct guide to optimize growth parameters. Figure 4.9 shows the fitted Γ value, as a function of deposition angle, for different coverages: similar trends are observed for all coverages. The trend of increased width with coverage indicates that the inhomogeneous dispersion is the dominant contribution to the Γ value, as the larger islands produced at higher coverage will reduce the intrinsic decay rate. It is clear that a more homogeneous distribution of particle size is obtained at higher deposition angles, but the decrease in peak amplitude that accompanies this (Table 4.1) indicates increased growth on the terrace. The optimum conditions are a trade-off between these competing effects and, for this 6° miscut sample, the optimum deposition angle is found to be $\sim 6^\circ$.

This result shows not only the semi-quantitative agreement between the coupled oscillator model and the RAS measurements, but also offers the possibility of monitoring, *in situ*, the sample morphology on a macroscopic length scale via the fitted peak width and amplitude.

The broadening of the peaks due to morphological dispersion can be also demonstrated more rigorously with the model of Chapter 1. The correlation between the statistical distribution of NP size and peak broadening can be explained using the three-layer model and Eq. (1.42). In Figure 4.8 it is shown experimentally a linear dependency of the RAS broadening with the SEM morphology. In the coupled oscillator model such broadening was simulated by introducing an effective dispersion parameter Γ which leads to a broadening of the peak. An alternative approach consists in convoluting the morphological Gaussian distributions with the $\text{Re}[\Delta r/r]$ profiles obtained for the different morphological parameters. Generally speaking, if $\text{Re}[\Delta r/r(X)]$ is a

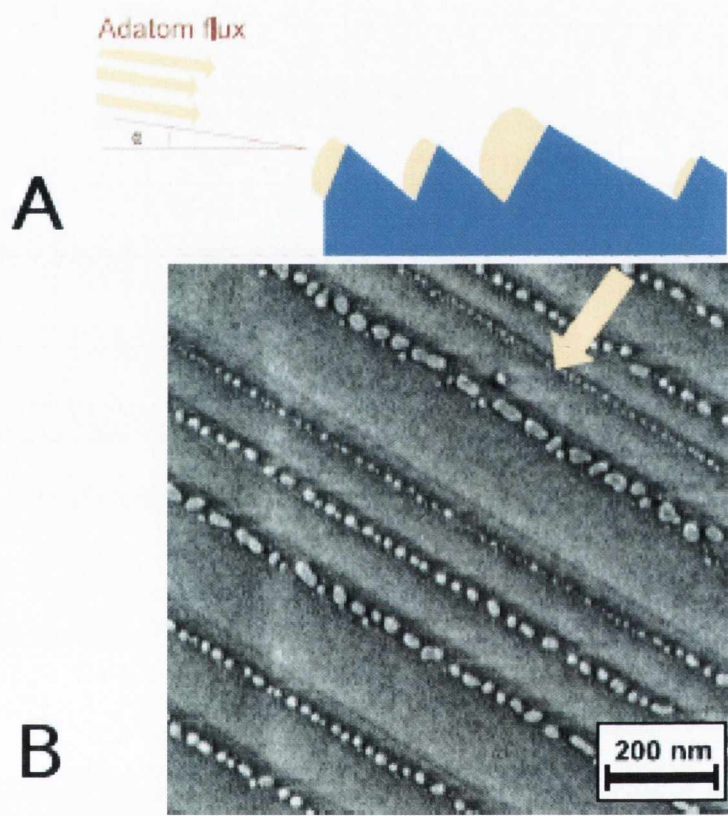


Figure 4.7: Effects of shadowing on NP array formation for the 6° miscut. (A) Sketch of the shadowing effect: the bigger islands shadow the islands behind, increasing the inhomogeneity in the shape distribution. (B) SEM image for a 2° deposition angle. The arrow indicates the flux direction.

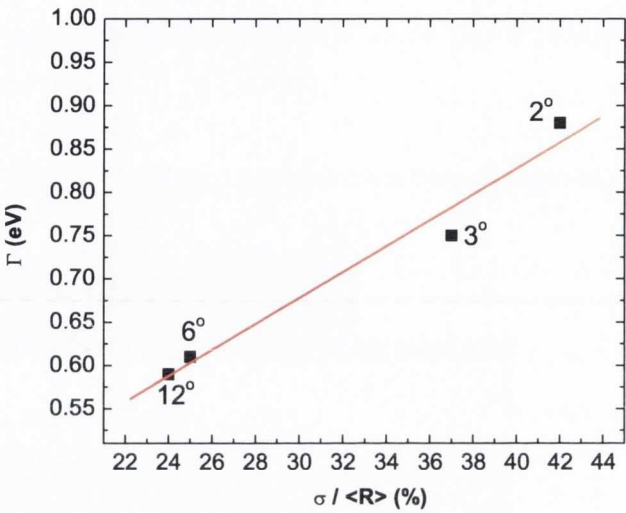


Figure 4.8: Plot of fitted Γ value as a function of the percentage dispersion in the island size, determined by SEM, showing the strong correlation.

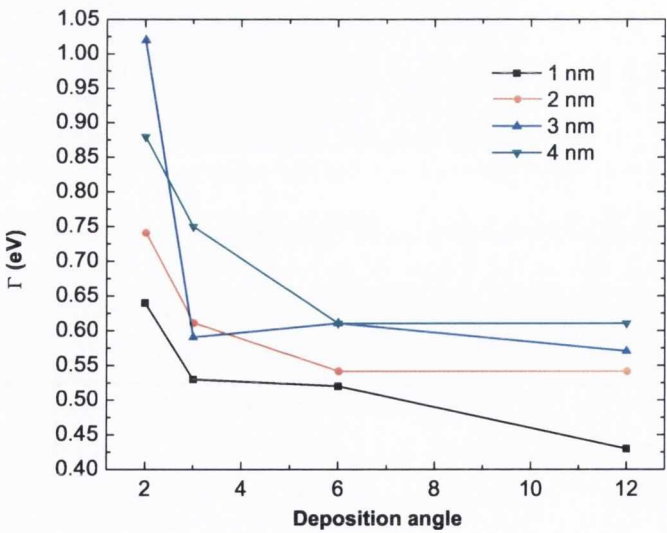


Figure 4.9: Plot of the fitted Γ value, as a function of deposition angle, for different coverages.

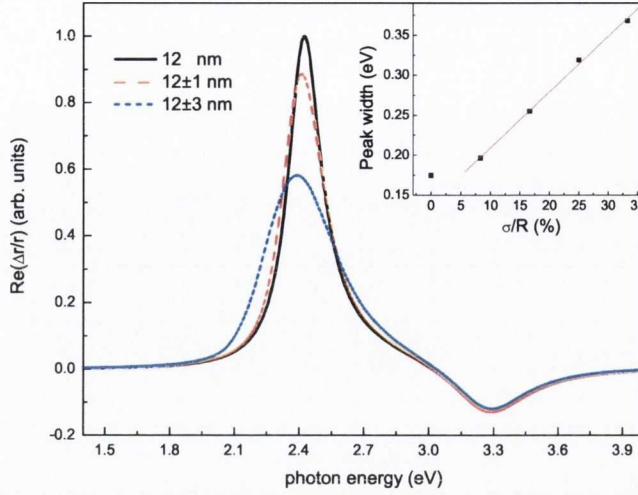


Figure 4.10: Simulated RAS spectra for interacting spheres in the monodispersed case with $R = 12$ nm and for a spherical ensemble with $R = 12 \pm 1$ nm and 12 ± 3 nm. Inset: the Gaussian width of the positive peak vs relative standard deviation, showing an almost linear trend. The spectra were calculated using the model developed in chapter 1.

function of a random variable X , which follows a Gaussian distribution with average value $\langle X \rangle$ and standard deviation σ , we expect a broadening of the measured peaks. In this case the effective RAS signal can be written as

$$\text{Re}\left[\frac{\Delta r}{r}\right] = \frac{1}{\sigma\sqrt{2\pi}} \int \text{Re}\left[\frac{\Delta r}{r}(X)\right] \exp\left[-(X - \langle X \rangle)^2 / 2\sigma^2\right] dX. \quad (4.12)$$

Where the spectra depend on other independent random variables, the integral for each of them can be calculated independently due to linearity of the integral operator. As a representative example to clarify the effects of morphological distribution, we consider interacting sphere of average radius $R = 12$ nm placed along an array at a fixed interparticle gap of 6 nm, similar to the experimental results. An interarray distance of 80 nm was chosen and fixed during the simulation. As the NP radius increases, the volume and thus the coupling along the arrays increases, producing a red shift of the positive peak but leaving the negative peak almost unchanged. In order to clearly show the effect of peak broadening in the simulation, the NP interaction was increased by doubling the size of the β parameter. Figure 4.10 shows the modelled RAS spectra

for monodispersed spheres and after Gaussian convolution with standard deviations of 1 nm and 3 nm.

In the presence of morphological dispersion, the RAS peaks appear broadened. This is particularly evident for the positive peak, as it is the one most sensitive to changes in the interaction volume. The inset in Figure 4.10 shows that the peak broadens almost linearly with an increase in the standard deviation as has been observed experimentally in Figure 4.8. Furthermore, as the negative peak shows much less broadening, the relative height between the positive and the negative peaks is modified with respect to the monodispersed case. This analysis only accounts for the NP size distribution, but in the grown arrays there is dispersion in shape, NP spacing and row spacing, which leads to additional broadening that also affects the second peak.

We therefore expect pronounced broadening in the measured RAS spectra, with a proportional trend between NP morphological dispersion and the peak width. It has thus been demonstrated theoretically that RAS not only measures the resonance energy of tunable Ag NP arrays during growth, but it can also monitor the overall order of the surface through the Gaussian broadening of the positive peak.

4.7 Exposure of the sample to atmosphere

Figure 4.3 suggests that the peak position can be modified by increasing the deposited thickness. This behaviour was explained using the coupled oscillator model by stronger NP coupling interactions due to increasing NP volume. As the measurements can be performed *in situ* on the same substrate and the deposition can be interrupted, structures with a particular resonance frequency can be obtained. However, the RAS profile changes immediately after venting the growth chamber, complicating the exact tunability of the resonant structure.

As a representative example, Figure 4.11 shows the measured SEM image and RAS spectra of one of the samples studied. Silver was deposited at 6° deposition angle onto a 81 ± 17 nm template periodicity for 30 minutes at a rate of 2.6 nm/min. SEM of Figure 4.11 shows the highly ordered structures already reported in Section 4.4. The surface is decorated with chains of Ag NPs aligned along the step edge. The NPs appear slightly elongated with principal axes of 29.4 ± 7 nm and 20.0 ± 3.4 nm along

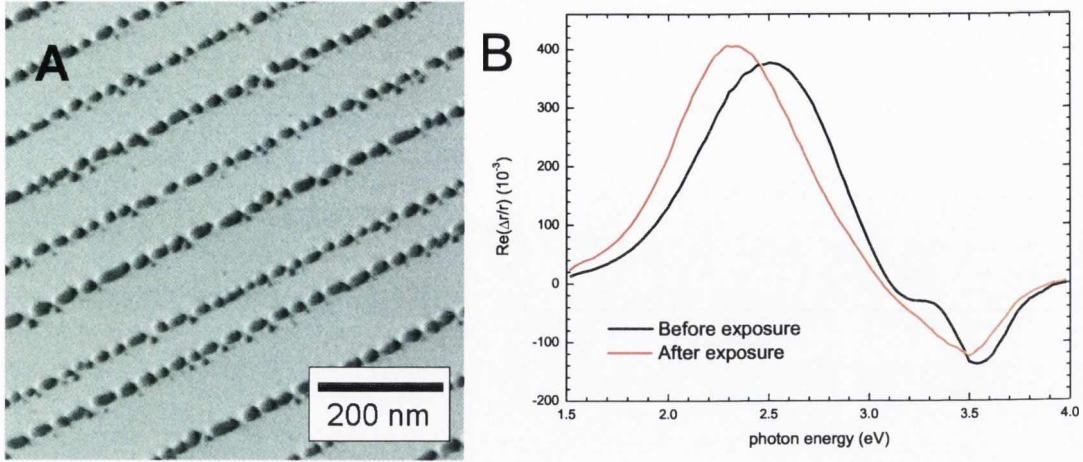


Figure 4.11: (A) SEM image of NP arrays grown at tilted angle of incidence. The substrate was a 6° off-cut substrate annealed for 24 hours at 1400° . Ag was deposited at 6° for 30 minutes. (B) RAS spectra before and immediately after exposure to atmosphere.

and perpendicular to the array respectively and a center to center distance of $l_x = 36.4 \pm 7.7$ nm. RAS spectra were taken *in situ* after deposition and immediately after exposure of the sample to atmosphere. As for the *in situ* measurements, the double peak feature due to LPRs is observed. After exposure of the sample to atmosphere the positive peak red shifts by 0.14 eV and the negative one smooths and red shifts.

This behaviour is consistent with modifications of the dielectric environment surrounding the particles, from vacuum to a material with higher refractive index. According to literature sulphur is the most likely material to interact with silver, turning the outer layer of the NP into Ag_2S . Figure 4.12 reports the measured [137] real and imaginary parts of the dielectric function of Ag_2S produced by a native tarnished layer, confirming effectively that $\epsilon'_s > \epsilon_m$. As already discussed in Chapter 1, a red shift is then expected. In order to obtain more quantitative information, the RAS spectra have been then simulated with the model of Chapter 1 using the in-plane morphology measured by SEM, an out-of-plane radius of 7 nm and the measured dielectric function for Ag_2S . From Figure 4.13, a red-shift of both the positive and negative peak is observed. In particular, the red shift of 0.14 eV measured after exposure of the samples to atmosphere corresponds in our model to a thickness $s_x = 0.6$ nm, i.e. around two monolayers. This approach could be extended further to monitor the chemical growth

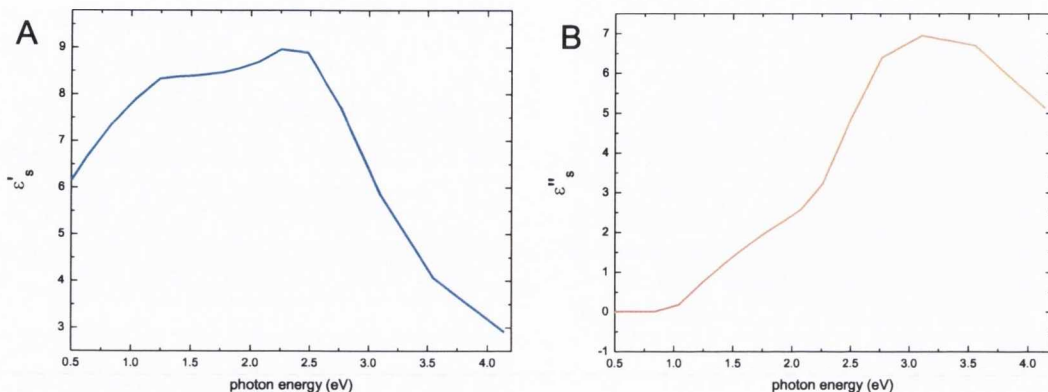


Figure 4.12: Measured [137] real (A) and imaginary (B) part of the dielectric function of a native Ag_2S layer.

of a dielectric shell *in situ*, where the dielectric shell formed could produce a desired shift in the resonance position. Moreover, as all the Ag samples measured in this report undergo similar changes due to atmospheric exposure, the modifications in the optical spectra can be predicted and structures with a particular resonance frequency can be tuned using the *in situ* capability RAS naturally provides.

Finally, during the deposition, two negative peaks can be clearly distinguished and the negative shoulder disappears after exposure of the sample to atmosphere. This feature can be attributed to quadrupolar resonances associated with sharp structures, being rounded away by tarnishing [128, 129].

4.8 Dependency of the optical properties on the initial template periodicity

Experiment

To produce Ag NPs, three 6° off-cut Al_2O_3 stepped substrates with 50 nm, 80 nm and 140 nm periodicity were produced by high temperature annealing at different temperatures. The three substrates were loaded at the same time into the UHV chamber and

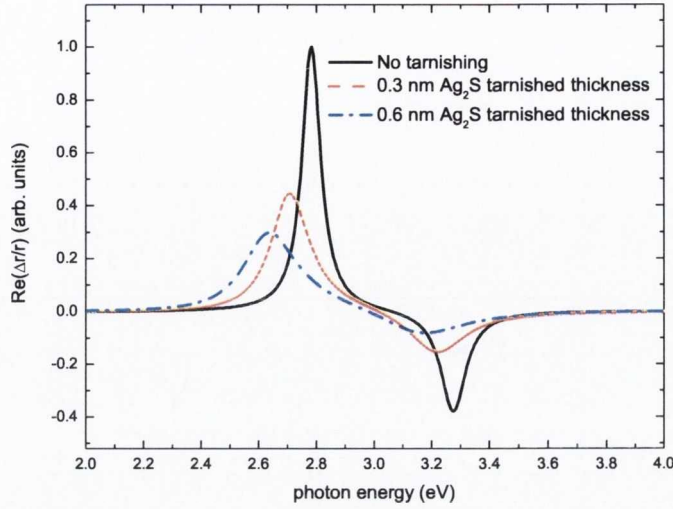


Figure 4.13: Simulated RAS spectra for different tarnishing thickness. The peaks redshift and broaden when a dielectric shell is formed.

exposed for 30 minutes at a rate of 2.6 nm/min to a collimated Ag beam tilted by 6° with respect to the average surface orientation. According to Section 4.6, this angle was chosen in order to minimise the morphological dispersion. SEM was used to characterise the NP morphology *ex situ* (see Figure 4.14). The NPs appear ordered, aligned and elongated along the chain axis. As the deposition angle is equal to the template off-cut there are no NPs present in the middle of terraces. The measured NP radii R_i along the $i = (x, y)$ direction, the center to center distance l_i , the NP edge separation along the array axis and the average number of particles N per unit area are presented in Table 4.2 for the three initial templates. As earlier, the indexes x and y signify the in-plane directions along the chain of NPs and perpendicular to it, respectively. The small separation (< 8 nm) between particles ensures the strong coupling required for waveguiding purposes and for electric field enhancement in between the adjacent NPs. For larger periodicity we observe an increase in the shape anisotropy R_x/R_y and the average NP dimensions, and yet an almost constant interparticle separation. For a given Ag coverage, this can be explained in terms of nucleation sites determining the interparticle separation and center to center distance. Greater periodicities l_y produce larger facets and the initial adatoms nucleate further away from each other as a consequence of the longer diffusion length, resulting in larger center to center distances

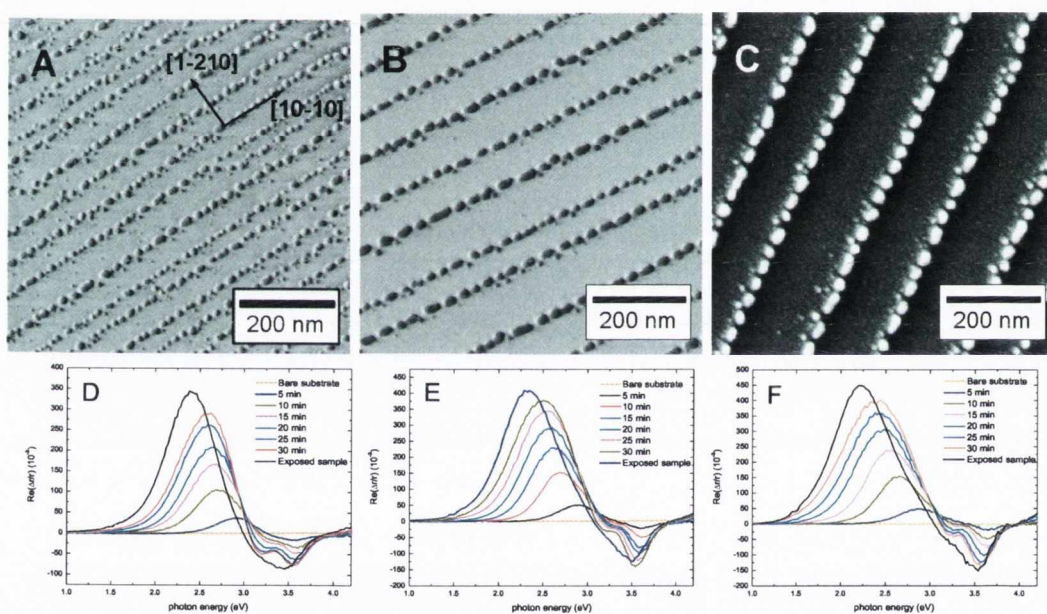


Figure 4.14: SEM images of the Ag NP arrays grown at glancing angle deposition for (A) 50 nm, (B) 80 nm and (C) 140 nm template periodicity. The *in situ* RAS spectra measured during growth interruptions and after exposure of the sample to the atmosphere are reported in (D), (E) and (F) respectively.

Table 4.2: Average interparticle center to center distance l_i , average separation along the axis, NP radii R_i , and number of NPs per unit area N , obtained for templates with different periodicities after Ag glancing angle deposition. The statistics were obtained though analysis of the SEM images.

	50 nm	80 nm	140 nm
Ann. T. (°C)	1362	1410	1457
$l_x(\text{nm})$	23 ± 5	36 ± 8	42 ± 11
$l_y \text{ (nm)}$	49 ± 9	81 ± 17	141 ± 35
NP separation (nm)	6	7	5
$R_x(\text{nm})$	8.6 ± 2.4	14.5 ± 3.5	18.4 ± 11.5
$R_y \text{ (nm)}$	8.0 ± 1.3	10.0 ± 2.0	12.0 ± 2.3
$N \text{ (part/m}^2\text{)}$	8.9×10^{14}	3.4×10^{14}	1.7×10^{14}

l_x . At the same time the lower facet density accompanying larger periodicities requires larger NPs to accommodate the same amount of deposited material, resulting then in an almost constant gap between the NPs. Furthermore, larger facets allow the lateral dimension of the NPs to increase. The morphology of the system, namely island anisotropy, interparticle distance and separation between the rows of NPs can then be changed by simple modifications of both template annealing and NP deposition parameters.

The increase in NP dimensions is accompanied by a decrease in the average particles per unit areas and the filling factor f will depend on the sample periodicity. For this reason we will refer simpler to the deposition time rather than NP height in the following discussion. In order to obtain information on the out-of-plane morphology, sections of the array formed on the 80 nm periodicity template have been investigated using TEM. A comparison of the array with a bare substrate of comparable step height is shown in the inset in Figure 4.15 (A). The height of the Ag NPs was determined to be $h = 13 \pm 4 \text{ nm}$. Examination of the images indicates that the Ag clusters are polycrystalline. An amorphous layer was observed between the Al_2O_3 substrate and

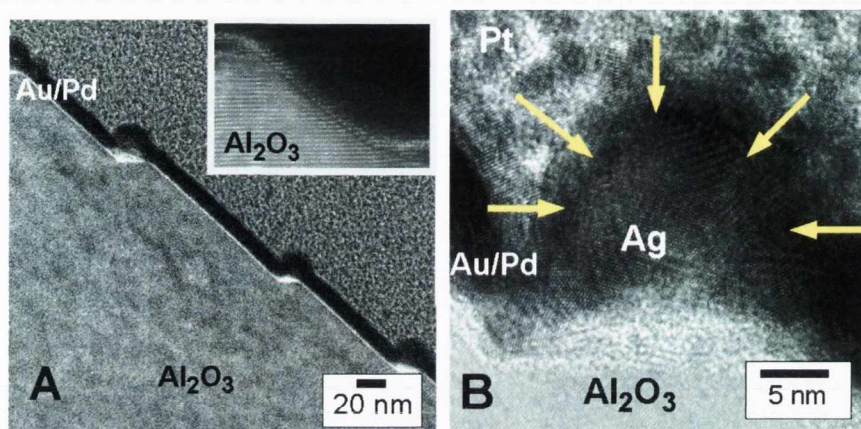


Figure 4.15: TEM section of a 80 nm periodicity substrate with Ag NPs deposited at glancing angle. (A) Low magnification and (B) high magnification. A Au/Pd layer was deposited by sputtering to protect the surface during the FIB section preparation. The arrows in (B) define the surface of the Ag NP. Inset of Figure A: substrate with similar periodicity before Ag deposition.

the deposited Ag. Through elemental analysis this layer was determined to be bonded carbon present already before the substrate annealing process. However, the Ag NPs appear to be directly in contact with the substrate surface, in contrast to previous results on similar structures [65].

We have thus demonstrated that the morphology of the NP layer can be tailored by glancing angle deposition on stepped templates with different periodicities and consequent changes in the optical properties are expected. RAS spectra were recorded during deposition at growth interruptions. The bare substrate did not show any distinctive features. After Ag deposition, the usual two peak features were measured. In particular, the peak height increases with the deposited thickness and the peak positions red shift.

The combination of RAS and low angle deposition hence provides a tool where the morphology can be tailored by the growth process and the optical behaviour monitored at the same time. Figure 4.16 shows the spectra obtained after exposure of the sample to atmosphere, confirming the dependency of the key spectral features on the initial template morphology. A linear red shift of the positive peak with increasing template periodicity is observed, accompanied by a blue shift of the negative one. The shifts can be explained qualitatively by the combination of an increased aspect ratio of the

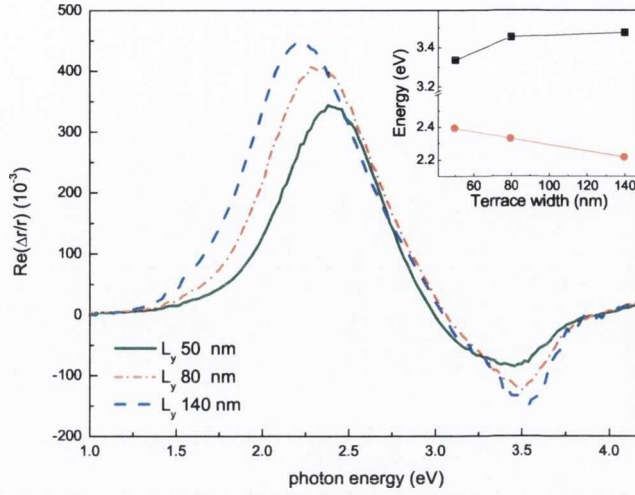


Figure 4.16: RAS spectra obtained after exposure of the samples to atmosphere, for different template periodicity l_y and a Ag deposited layer of average thickness 0.7 nm. (Inset) Energy of the positive (circles) and negative (squares) peak as a function of the periodicity l_y . A linear red shift for the positive peak and a blue shift of the negative one can be observed as the periodicity of the template is increased.

isolated NP together with an increase in the NP coupling due to their larger volume (see Table 4.2). At resonance, a polarization of almost 50% of the total reflected light is reached, confirming the strong dichroic response obtained with a Ag layer of average thickness only 0.7 nm.

Theory

In order to completely understand the optical features of the NP arrays grown on different template periodicities the coupled oscillator model presented in Section 4.5 is not suitable due to the great oversimplifications used. The full treatment of Chapter 1 is required to understand the effects of island anisotropy, of the image charges and NP interaction.

The main limitation of this approach in the present case is that the NPs grown in the present case lack in-plane rotational symmetry. However, an effective distance D^* for the image charge can be obtained by approximating the NPs as oblate spheroidal

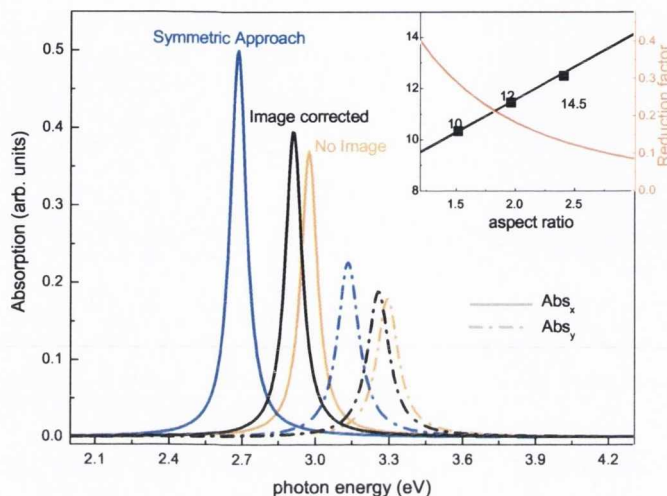


Figure 4.17: Simulation of the effects of the image charge on the absorption peaks of isolated Ag ellipsoids supported on a Al_2O_3 substrate: when no image charge is considered (orange), when the image charge is placed symmetrically underneath the NP (blue), and when a corrected image charge position is used with an in-plane average radius of $\bar{R} = (R_x + R_y)/2$ (black). If the image charge is placed symmetrically underneath the NP, the absorption peaks in the x and y direction red shift. The introduction of an effective distance for the position of the image charge reduces the red shift by a factor ~ 0.2 . Inset: effective distance D^* and reduction factor in the shift of the NP, using the corrected approach, as a function of the aspect ratio ($\bar{R}/R_z$). The reduction factor in the limiting cases of an average in-plane radius of $\bar{R} = 10$ nm or 14.5 nm is ~ 0.1 and ~ 0.3 respectively.

particles with average in-plane radius $\bar{R} = (R_x + R_y)/2$. In this way it is possible to correctly place the image charges and calculate the value of the β_i coefficient. The effects of the self-image charge of an isolated Ag NP are shown in Figure 4.17 for a NP whose morphology resembles that of the 81 nm periodicity template. As already discussed, the self-image charge red shifts the in-plane absorption peaks for both the x and y axes. The error in the shift of the resonance due to the planar isotropy assumed for the determination of D^* are estimated to be smaller than 10% (<0.03 eV).

With the corrections in the image-charge effects the dependency of the RAS spectra on the initial template periodicity can also be modelled, as shown in Figure 4.18. The in-plane morphology is taken from the SEM analysis of Table 4.2 and a tarnished layer with $s_x = 0.6$ nm is assumed for all the samples. NP out-of-plane radii of 6 nm, 7 nm

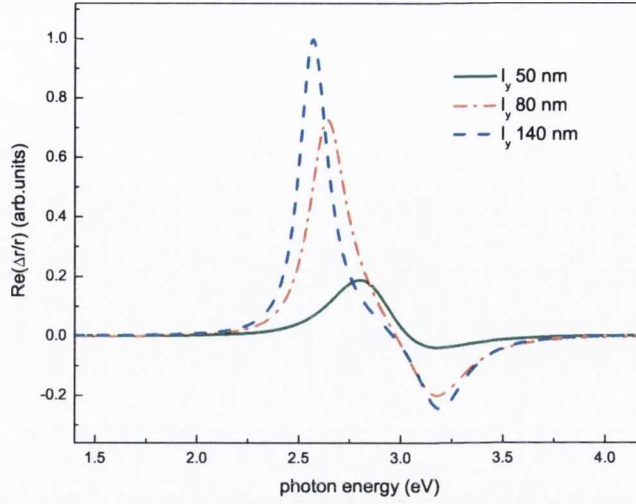


Figure 4.18: Simulated RAS spectra of Ag NP arrays with different periodicities l_y . The in-plane morphological parameters were obtained from SEM analysis (4.2), and $s_x = 0.6$ nm. Out-of-plane R_z values of 6 nm, 7 nm and 8 nm were assumed for the 50 nm, 80 nm and 140 nm, respectively. Semi-quantitative agreement with 4.16 can be seen.

and 8 nm were used for the 50 nm, 81 nm and 140 nm periodicity, respectively. The R_z value of 7 nm for the 81 nm substrate was based on the height $h = 2R_z = 13 \pm 4$ nm measured by TEM. The other heights are consistent with scaling this value using the morphology and the NP densities measured by SEM. The trend in Figure 4.18 resembles the one measured experimentally: the positive peak red shifts and the negative one slightly blue shifts with increasing periodicity.

This model produces then semi-quantitative agreement with the experimental trends observed. However, quantitative fitting of the peak positions cannot be obtained in the present case. Never the less, the model utilised here provides the main physical insights of the measured optical features. First, a physical origin for the production of the resonance has been introduced in a formal way. Second, the effects of image charges and the exact origin of the dichroic response has been addressed in a more rigorous, albeit incomplete, fashion. The presence of the steps, the tilting of the NPs with respect to the optical surface, the hemispherical shape of the NPs and the exact effects of morphological distributions cannot still be fully taken into account with the present model. The simulation parameters suggest that the shift between the in-plane

resonances can be inferred to be an interplay between NP elongation along the array axis and the interparticle interaction, whose effects are comparable in size. As they both affect the RAS spectra in similar ways, care will be required in developing more quantitative models of the optical response. However, this offers advantages for varying the optical properties of the arrays as the positive peak position can be tuned over an even larger energy range (in the present case up to 0.6 eV, corresponding to ~ 100 nm in the visible region of the spectrum), thus increasing the versatility of the glancing angle deposition technique. The model can be considered as an approximate guide for the factors governing the optical behaviour of NP arrays. The *in situ* optical monitoring, which RAS provides, will then allow the necessary refinements of growth and template parameters required to produce the desired resonant structure.

4.9 Conclusions

The possibility of growing ordered chains of Ag NP on a faceted Al_2O_3 template using glancing angle deposition has been demonstrated. The samples showed a strong optical anisotropy which has been measured *via* PTS and RAS, the equivalence between these two measurement techniques being demonstrated. RAS spectra were measured *in situ* during the growth as a function of the deposited thickness, deposition angle and initial template periodicity.

The double peak RAS signal is attributed to plasmon resonances along and perpendicular to the chain axes. In particular, the peak intensity increases linearly with the deposited thickness and the peak positions are a function of thickness and deposition angle.

A model based on the interaction of point dipoles placed on a 1D infinite array provides a qualitative understanding of the optical behaviour of the Ag NP chains. Comparison with SEM results showed that semi-quantitative information could be obtained by a simple adaptation of the model to allow for the effect of island anisotropy. The model provides a quantitative direct measurement of the broadening of the resonance peaks, due to morphological dispersion. An optimum deposition angle can then be found in order to minimise the peak width. The optimal deposition conditions can be obtained as a trade-off between the competing effects of large island shadowing at

small deposition angles and isotropic growth on the terrace at larger ones. For a 6° miscut sample at lower coverages, an optimum deposition angle of $\approx 6^\circ$ is indicated.

The model of Chapter 1 was also utilised to address the optical signature of the samples grown. In particular, changes due to exposure of the sample to atmosphere has been explained by the creation of a tarnished Ag_2S layer covering the NPs.

The dependency of glancing angle deposition on the initial template periodicity has been investigated. The templates have been prepared by annealing $\alpha\text{-Al}_2\text{O}_3$ in atmosphere at different temperatures. NP arrays with long range order and good uniformity over the entire substrates have been formed subsequently. RAS has been used *in situ* to monitor the evolution of the optical dichroic response of the NP array with deposition time and the consequent increase in NP size. It has been shown that different substrate periodicities tailor different NP morphologies leading to consistent changes in the RAS properties of the array. In this way, tunability of the optical properties of the NP arrays over wider energy range has been obtained. The model developed in Chapter 1 has been used to provide a semi-quantitative explanation of the optical behaviour of the samples.

RAS has proved to be a very promising *in situ* growth monitoring technique when combined with glancing angle deposition. RAS can provide not only the resonance peak energies and spectral features for anisotropic arrays of plasmonic NPs, but can also be used as a powerful tool for monitoring their order. In particular, information can be provided reproducibly, reliably and without the need for microscopy techniques, which are time-consuming and can require the exposure of the samples to atmospheric contaminants. The models provides then guidance regarding the physical origin of the large optical anisotropies in the experimental data and fine tuning of the resonant features is obtained using the *in situ* monitoring capability that RAS provides, helping to form structures with engineered spectral features.

Chapter 5

Ellipsometric Investigation of the Out-of-Plane Optical Response

A fact is a simple statement that everyone believes. It is innocent, unless found guilty. A hypothesis is a novel suggestion that no one wants to believe. It is guilty, until found effective.

E. Teller

In the previous chapter the possibility of growing NP arrays and tuning their in-plane optical properties has been shown. The structures possessed two distinct resonances related to the oscillatory motion along and perpendicular to the array, in accordance with previous literature. In contrast, it is difficult to obtain information on the characteristics the out-of-plane LPRs in NP arrays and plasmonic materials in general. The lack of investigation is due to inherited difficulty in using any widely

available spectrometer to measure the out-of-plane component and the impossibility of extracting this signal using RAS. Spectroscopic Ellipsometry (SE) can overcome this limitation as it monitors changes in the polarization state of linearly polarized beam reflected at oblique angles of incidence[89]. It is therefore capable of investigating the full optical behaviour of a plasmonic sample in the far field and recording the spectra with a better sensitivity compared to absorption spectroscopy, since it monitors only relative changes in the polarization state of the incoming light. The major complication with any SE analysis is that the recorded data must be modelled and the model compared afterwards with the experiment. An analysis of plasmonic structures is further complicated by the presence of the substrate which modifies the overall optical response.

In this chapter a comparison between RAS and SE is shown, and the equivalence of the two techniques in measuring the in-plane effective dielectric function of the layer is demonstrated. More importantly, we report how a quantity, the anisotropic surface excess function (ASEF), can be extracted directly from the measured signal, whose properties depend only on the optical properties of the nanocluster layer. The validity of the approach used in this framework is discussed together with the advantages that it naturally provides. Finally, the dipolar model developed in Chapter 1 is used to reproduce the measured response. A route to probe also the out-of-plane resonances is then outlined.

5.1 The Anisotropic Surface Excess Function

The possibility of analysing the optical properties of layers on top of a surface through SE is not trivial as explained in Chapter 1. We report here an alternative way which, to our knowledge, has never been applied to plasmonic structures.¹

In order to analyse the surface contribution we limit the films thickness d to values which are small compared to the wavelength. The reflectivity of the sample can be addressed with the 3 layers model. We further impose a fully isotropic substrate dielectric function and we impose that bulk and surface optical axis are aligned with

¹The discussion of this section has been taken from [138].

the axis of symmetry of the spectrometer. Let ε_b and ε_L be the dielectric function of the bulk and of the anisotropic layer respectively. Vacuum is considered as the dielectric medium surrounding the system and $\varepsilon_m = 1$ is assumed throughout the chapter. The electric field of s-polarised light is sent parallel to the y axis and the surface is perpendicular to the z direction. If Θ is the angle of incidence, the reflectance between two isotropic media (i) and (j) is

$$r_{(ij)} = \frac{C_{(i)} - C_{(j)}}{C_{(i)} + C_{(j)}}. \quad (5.1)$$

The following relations are hold in case of s-polarisation

$$\begin{aligned} C_{(i)} &= \varepsilon_{y(i)}^{1/2} \cos \Theta_{(i)} = n_{(i)}, \\ \varepsilon_{y(i)}^{1/2} \sin \Theta_{(i)} &= \varepsilon_{y(j)}^{1/2} \sin \Theta_{(j)} \end{aligned} \quad (5.2)$$

and p-polarisation respectively

$$\begin{aligned} C_{(i)} &= \varepsilon_{x(i)}^{-1/2} \cos \Theta_{(i)}, \\ n_{(i)} &= \varepsilon_{x(i)} \cos \Theta_{(i)}, \\ \varepsilon_{z(i)}^{1/2} \sin \Theta_{(i)} &= \varepsilon_{z(j)}^{1/2} \sin \Theta_{(j)}. \end{aligned} \quad (5.3)$$

The last relations in Eq. (5.2) and Eq. (5.3) represent the common Snell law and transmission law of an incoming light beam respectively.

When a multi-layered system is considered, multiple reflections at the various interfaces have to be considered and the overall reflectance is

$$r_{(012)} = \frac{r_{(01)} + Z r_{(12)}}{1 + Z r_{(12)} r_{(01)}}, \quad (5.4)$$

with

$$Z = \exp[i(2\omega d/c)n_{(1)}]. \quad (5.5)$$

The change in reflectivity δr due to the presence of a film with respect to the simple substrate can be written as

$$\begin{aligned} \frac{\delta r}{r} &= \frac{r_{(012)} - r_{(02)}}{r_{(02)}} \\ &= -2C_{(0)}(Z - 1)[C_{(2)}^2 - C_{(1)}^2] \times \\ &\quad \{(Z + 1)[C_{(0)}^2 C_{(1)} - C_{(2)}^2 C_{(1)}] + (Z - 1)[C_{(0)} C_{(2)}^2 + C_{(1)}^2 C_{(2)} - C_{(1)}^2 C_{(0)} - C_{(0)}^2 C_{(2)}]\}^{-1}. \end{aligned} \quad (5.6)$$

After a Taylor expansion of Eq. (5.5), the following relations for s and p-polarised light are then obtained:

$$\frac{\delta r_s}{r_s} \approx \frac{-i2\omega \cos \Theta}{c(\varepsilon_b - 1)} \Delta \varepsilon_y \quad (5.7)$$

$$\frac{\delta r_p}{r_p} \approx \frac{i2\omega \cos \Theta}{c(\varepsilon_b - 1)(\sin^2 \Theta - \varepsilon_b \cos^2 \Theta)} \times [(\varepsilon_b - \sin^2 \Theta) \Delta \varepsilon_x - (\varepsilon_b \sin^2 \Theta) \Delta \frac{1}{\varepsilon_z}], \quad (5.8)$$

with

$$\begin{aligned} \Delta \varepsilon &= \varepsilon_{L,i} - \varepsilon_b \\ \Delta \frac{1}{\varepsilon_{L,i}} &= \frac{1}{\varepsilon_{L,i}} - \frac{1}{\varepsilon_b}. \end{aligned} \quad (5.9)$$

In SE the optical properties are measured as a complex reflectance ratio $\rho = r_p/r_s$ and the pseudo-dielectric function is calculated using Eq. (2.7). From Eq. (5.8) the presence of an isotropic film produces a change in the reflectance ratio which is

$$\begin{aligned} \frac{\rho}{\rho_b} &\approx 1 - \frac{i2\omega \cos \Theta}{c(\varepsilon_b - 1)(\sin^2 \Theta - \varepsilon_b \cos^2 \Theta)} \\ &\times [(\varepsilon_b \sin^2 \Theta)(\Delta \varepsilon_x + \varepsilon_b \Delta \frac{1}{\varepsilon_z}) + (\sin^2 \Theta - \varepsilon_b \cos^2 \Theta) \Delta(\varepsilon_x - \varepsilon_y)]. \end{aligned} \quad (5.10)$$

Combining Eq. (2.7) with the inverted Eq. (5.10) relation, an expression for the direct calculation of the surface response without fitting procedure can be obtained. Within this approach, previous work defining a surface excess function [138–140] is adapted to make the anisotropic response explicit. The anisotropic surface excess function (ASEF) is then given by

$$\xi_j = \frac{i\lambda(\varepsilon_b - 1)}{4\pi\varepsilon_b \sqrt{\varepsilon_b - \sin^2 \Theta}} (< \varepsilon_j > - \varepsilon_b) \quad (5.11)$$

and it can be modelled using [138]

$$\xi_j = d[(\Delta \varepsilon_j + \varepsilon_b \Delta \frac{1}{\varepsilon_z}) + (\frac{1}{\varepsilon_b} - \frac{\cos^2 \Theta}{\sin^2 \Theta})(\Delta \varepsilon_j - \Delta \varepsilon_k)]. \quad (5.12)$$

where $j, k = (x, y)$.

The quantity ξ_j was already obtained by Plieth *et al* [139] in the mid 70s but the complex integrals are averaged over the whole anisotropic layer of thickness d in the present case. The introduction of ASEF directly from the experiment incredibly simplifies the development of theoretical models as the effect of the substrate is completely removed. Through Eq. (5.11) and (5.12) the following conclusions can be obtained:

- The modelled quantity ξ_j scales with the thickness of the anisotropic layer d . So, as for the surface dielectric anisotropy in RAS measurements, without any information about the thickness of the anisotropic layer only relative results can be correctly compared with the theory.
- The contribution of bulk and surface can be simply summed together in the thin film approximation utilised here.
- The i factor in Eq. (5.11) suggests that the overall response of the system, expressed by the pseudo- dielectric function $\langle \varepsilon \rangle$, involves a mixing between real and imaginary parts of the bulk and the surface respectively.
- Once the thickness d has been evaluated, the ASEF becomes a function dependent only on the dielectric properties of the anisotropic layer $\Delta\varepsilon$ and $\Delta\frac{1}{\varepsilon}$ and microscopic models can be applied to simulate the optical response of the surface layer alone.
- Using ASEF the value of ξ_j can be expressed simply as the sum of ε_L along the three orthogonal directions. However, measuring the in-plane anisotropy for both azimuthal positions we obtain two measured values for the three unknowns $\varepsilon_{L,x}$, $\varepsilon_{L,y}$ and $\varepsilon_{L,z}$. Generally speaking, the problem of over-estimation of ξ_j can be reduced by using additional measurements such as RAS which will measure the difference $(\varepsilon_{L,x} - \varepsilon_{L,y})$ and hence a full derivation of ε_L can be obtained. In the present case the effective dielectric function ε_L possesses only LPRs and each resonance will be directly referred to a particular resonance direction.

Equation (5.11) is a particularly convenient formula which allows to directly relate the optical properties of the layer to the SE measurements and offer some insights into the effects of a surface. In the rest of the chapter, the ASEF will be extracted from the raw ellipsometric measurements and the results reproduced afterwards using the model of Chapter 1.

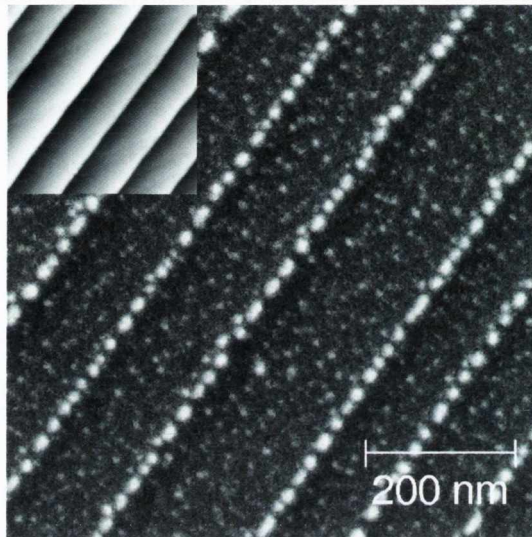


Figure 5.1: 700x700 nm² SEM image of Ag NP arrays grown at glancing angle of 6° for 20 minutes on a faceted Al₂O₃ template. Inset: AFM image with the same dimension of the substrate prior to deposition.

5.2 Experiment

To produce NP arrays, a substrate off-cut 3° was prepared by annealing as described in Chapter 3. After annealing at 1450°C for 24 hours the surface was measured with AFM in tapping mode and showed the typical quasi-periodic pattern of facets and terraces. The periodicity was measured to be $l_y = 120 \pm 35$ nm. The template was subsequently loaded in the UHV chamber and exposed for 20 minutes to a collimated Ag flux inclined at 6° with a rate at normal incidence of 0.2 nm/min. The morphology is shown in Figure 5.1. As already observed in the previous chapter, the stepped surface is decorated by rows of elongated NPs aligned along the array axis x . Statistics of the semi-axes R_j with $j = (x, y)$, the number of particles per unit area N and the center-to-center interparticle distance l_j have been extracted from the SEM images and presented in Table 5.1 along with the standard deviations. As the deposition angle is larger than the off-cut angle of the substrate, small clusters with radius less than 2 nm, i.e. almost ten times smaller than the NPs on the facets, appear deposited isotropically on the terraces, consistent with the results of Chapter 4. Because of their small volume and their isotropic morphological distribution on the substrate they will lead to a reduction

N (NPs/ μm^{-2})	l_y (nm)	l_x (nm)	R_x (nm)	R_y (nm)
347 ± 133	120 ± 35	24 ± 6	9.3 ± 2.3	7.7 ± 1.4

Table 5.1: Morphology parameters of the sample measured with SEM and AFM.

in the RAS measured intensity and, as no optical plasmonic response can be attributed to such clusters, they will be disregarded in the modelling.

For optical characterisation of the sample grown, both SE and RAS measurements have been performed immediately after exposure of the sample to atmosphere. During SE measurements two measurement configurations were utilised: in the parallel measurement configuration the plane of incidence was along the array chain, i.e. $E_s \parallel y$. In the perpendicular measurement configuration, after a $\theta = 90^\circ$ azimuthal rotation of the sample, the sample was scanned in the orthogonal direction $E_s \parallel x$. An angle of incidence of $\Phi = 61^\circ$ has been chosen as it is close to the measured Brewster angle of the Al_2O_3 substrate and r_s is expected to be minimised. A sketch of the parallel measurement configuration is presented in Figure 5.2.

The pseudo bulk dielectric function $\langle \varepsilon_j \rangle$ of the sample can be determined directly from SE measurements, for both the parallel and perpendicular measurement configurations (see Figure 5.3 (A) and (B)). The asymptotic behaviour of the NP layer on top of the substrate follows that of the bare Al_2O_3 dielectric function. The plasmonic resonances appear in the visible range, departing from the optical behaviour of the simple substrate only in the center of the measurement range. The real part $\text{Re}[\langle \varepsilon_j \rangle]$ of the pseudo-dielectric function appears to be the simple sum of the substrate and LPRs, whose position and intensity depend on the measurement configuration. A comparison of $\langle \varepsilon_j \rangle$ with the measured RAS spectra of Figure 5.3 (C) and similar previous results [30, 33, 75] suggests that the positive peaks can be attributed to in-plane plasmonic resonances parallel (x resonance, 2.18 eV in the present case) and perpendicular (y resonance, 3.24 eV) to the array axis.

The measured ellipsometry spectra can be compared to the RAS measurements. The pseudo-dielectric function is the dielectric response of the solid phase of a two phase system, consisting of the solid and ambient, where a sharp interface is assumed.

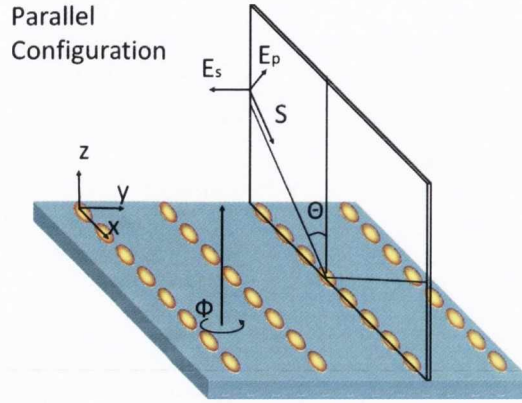


Figure 5.2: Sketch of the SE measurement of Ag NP arrays in the parallel configuration. The sample presents 3 axes of symmetry, along the chain (x), perpendicular (y) and out-of-plane (z). Light was sent (Poynting vector $\mathbf{S}$) at an angle of incidence Θ with respect to the normal and the s and p components of the incident electric field are outlined. In this configuration, the out-of-plane resonance and the resonance along the axes is probed, while an azimuthal rotation of the substrate by $\Phi = 90^\circ$ allows the resonance perpendicular to the array axis to be measured.

For these samples the solid phase comprises the substrate and NP layer. The standard anisotropic two-phase reflectance formula [141] can be simply adapted to allow the RAS response to be extracted from SE measurements:

$$\frac{\Delta r}{r} = \frac{1}{\sqrt{\langle \bar{\epsilon} \rangle}} \frac{\langle \epsilon_x \rangle - \langle \epsilon_y \rangle}{\langle \bar{\epsilon} \rangle - 1} \quad (5.13)$$

where $\langle \bar{\epsilon} \rangle = (\langle \epsilon_x \rangle + \langle \epsilon_y \rangle)/2$. The comparison between measured RAS and the RAS response extracted from ellipsometry is shown in Figure 5.3 (C). The agreement is very good, allowing for a small scaling factor associated with the different experimental geometries. The real parts of RAS and SE thus provide equivalent information on the in-plane reflection properties of Ag NPs. In addition, the out-of-plane optical response is clearly revealed by the SE measurements.

5.3 Discussion

Comparison of the SE and RAS results in Figure 5.3 can be used to identify the x and y resonances, which then allow the minimum in $\text{Re}[\langle \epsilon_j \rangle]$ to be related to the z

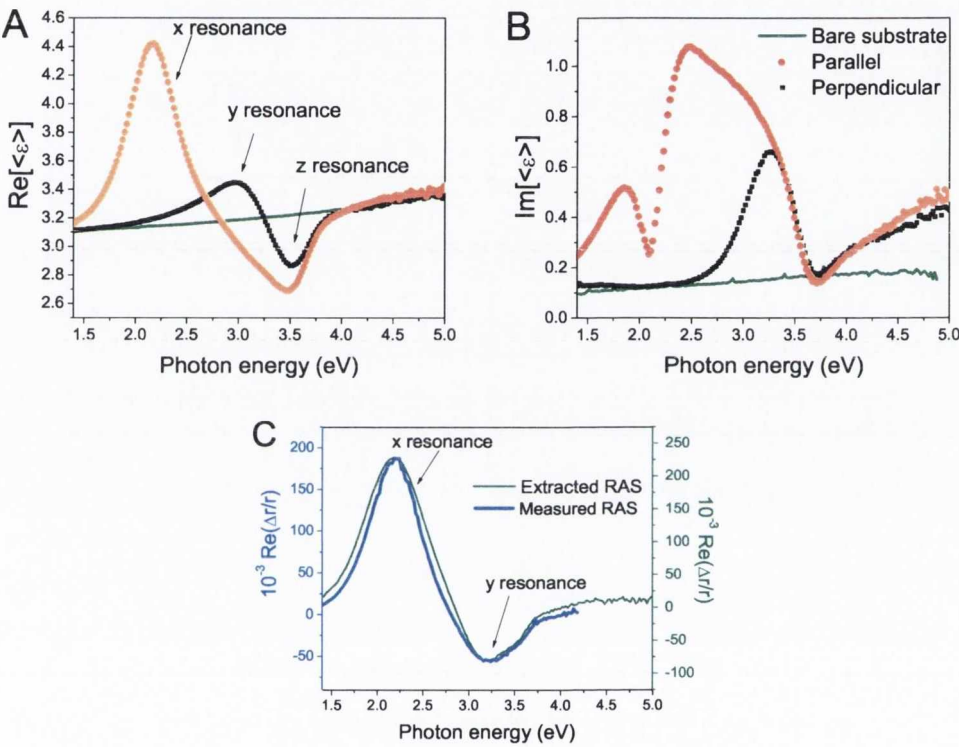


Figure 5.3: Extracted real(A) and imaginary (B) pseudo-dielectric function extracted from the ellipsometry measurements. (C) Comparison between the measured RAS (orange) and the in-plane response extracted from ellipsometry dielectric functions (green). The two spectra match very well, allowing for a small experimental scaling factor.

resonance. The peaks in Figure 5.3 (A) show that $\text{Re}[\langle \varepsilon_j \rangle]$ is associated with the absorptive response of the NP layer and there appears to be a simple additivity of the substrate dielectric function ε_b and NP layer dielectric function $\varepsilon_{L,j}$. These features can be explained using the ASEF.

The thin film approximation holds provided that

$$d \ll \frac{\lambda}{4\pi\sqrt{\varepsilon_{L,j} - \sin^2\theta}}. \quad (5.14)$$

In the spectral region of interest it appears that this approximation can be usefully applied for films of average thickness less than 10 nm, provided $\varepsilon_{L,j}$ is not too large. The average individual NP was estimated ~ 10 nm from Section 4.8, resulting in an average layer thickness of 1 nm, for a filling factor of 0.1. For such thin layers, the ASEF offers a simplified approach to interpreting SE measurements. However, the isotropy of the substrate assumed to derive Eq. (5.11) is not strictly correct in these experiments. Al_2O_3 is a well known birefringent crystal, but, as its ordinary and extraordinary refractive indexes are very similar[142], we did not detect any change when ASEF was calculated using the two values: the ordinary refractive index is assumed in the remainder of the paper. The imaginary part of the ASEF extracted in the present case is shown in Figure 5.4 (A). Three resonances can be observed and correspond, as previously mentioned, to resonances along the three main directions of the NP layer.

In order to reproduce the signal obtained, the dipolar model of Chapter 1 was finally used to calculate the effective dielectric function of the NP ensemble. The in-plane and out-of-plane components become respectively (we report here the final formula for self consistency):

$$\varepsilon_{L,i} = 1 + \frac{N\alpha_j}{1 + \alpha_j\beta_j} \quad (5.15)$$

$$\frac{1}{\varepsilon_{L,z}} = 1 - \frac{N\alpha_z}{1 + \alpha_z\beta_z}. \quad (5.16)$$

It is important to note the negative sign in Eq. (5.16) due to the boundary conditions of the out-of-plane component of the incident electric field in the Maxwell equations [143], which accounts for the minimum in the optical response in Figure 5.3 (A), being assigned effectively to the out-of-plane resonance. The ASEF has been modelled using infinite arrays of identical ellipsoids with radii $R_x = 9.3$ nm, $R_y = 7.7$ nm and $R_z =$

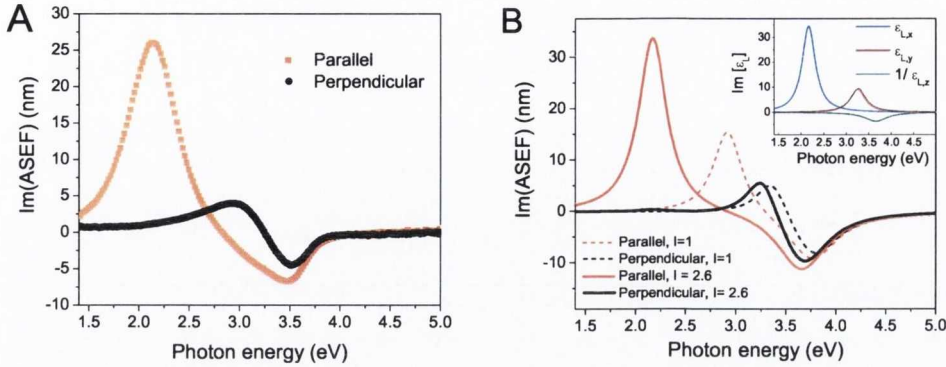


Figure 5.4: (A) Imaginary part of the ASEF obtained from Eq. (5.11). (B) Imaginary part of the simulated ASEF for different scaling factor I of the interaction coefficients. The morphological parameters used were extracted from SEM analysis and are listed in Table 4.2. Additional parameters used are $R_z = 5$ nm, and $A = 0.5$. A clear correspondence between experiment and theory can be seen. In the inset, the NP layer effective dielectric function ϵ_L is shown for $I = 2.6$.

5 nm, and center to center interparticle distances of $l_x = 23$ nm and $l_y = 120$ nm, in accordance with the statistical analysis obtained with AFM and SEM (Table 5.1). Finally, the A coefficient of Eq. (1.10) was assumed $= 0.5$. Figure 5.4 (B) shows the resulting ASEF simulated spectra when a scaling factor $I = 2.6$ in the β coefficient to reproduce the measured peak splitting and with $I = 1$. If such a scaling factor is introduced, the agreement between experiment and theory is good once the NP dispersion, which will broaden the peaks and decrease their intensities is considered.

The shape of the extracted ASEF is the same and the relative intensities match the experimental results. In particular, an increase can be noticed in the negative peak intensity of the ASEF with respect to $1/\epsilon_z$ (see inset) due to the $\epsilon_b \Delta \frac{1}{\epsilon_z}$ term in Eq. (5.12). Contributions to ξ_j mainly come from ϵ_j and $1/\epsilon_z$, as the second bracket in Eq. (5.12) is small for the particular experimental parameters used. The difference in the out-of-plane peak intensity between the calculated and measured ASEF in the parallel and perpendicular configurations is explained by the partial overlapping of the in-plane and out-of-plane peaks.

The introduction of ASEF thus allows the response of the plasmonic layer to be extracted directly from the SE measurements. This quantity can then be more simply modelled as the substrate does not have to be included. Similar results have been

obtained on substrates with different periodicities and off-cuts, and it appears that this formalism may be generally applicable for thin plasmonic films.

5.4 Conclusion

The full optical properties of Ag NP arrays grown at glancing angle was investigated by SE. RAS has been also measured and it is in agreement with the normal incidence response extracted directly from the SE measurements. For these thin layers it has been shown that an anisotropic surface excess function (ASEF) can be successfully extracted, which simplifies the development of theoretical models as the effect of the substrate is removed. A model based on dipolar interaction of supported ellipsoids has been utilised in order to reproduce the results obtained and the validity of the approach employed discussed.

Chapter 6

Deposition of Alternative Plasmonic Materials

Science is a differential equation
without known boundary conditions.

R. Verre

During the thesis Ag NP arrays have been grown using glancing angle deposition and their optical properties investigated in the far field, both in-plane and out-of-plane. The dependency of the optical properties upon changes of the different parameters governing the growth has been investigated, demonstrating the possibility of tuning the optical resonances over wide energy ranges. The resonance frequency $\omega_{res,i}$ of isolated NPs (without any coating dielectric shell) along the i -th direction is (see Section 1.2 for the derivation)

$$\omega_{res,i} = \sqrt{\frac{\omega_p^2}{\varepsilon_\infty + (\frac{L_i}{1-L_i})\varepsilon_m}} - \Gamma^2. \quad (6.1)$$

In case of interacting supported NPs Eq. (6.1) is still valid if an effective frequency dependent shape depolarization factor is introduced [66]:

$$L_i^* = L_i - \frac{\beta_i}{V}. \quad (6.2)$$

Using Eq. (6.2) the value of L is determined by the particular nanocomposite morphology, while changes in either ω_p or ε_∞ can produce additional shifts in the resonance frequency via Eq. (6.1). These values can be easily modified in semiconductors varying the doping concentration, but for noble metals they are constant: the material itself produces then the major constraint in the choice of a particular resonance position.

As glancing angle deposition utilises geometrical consideration for the production of NP arrays, it is a technique virtually independent from the deposited material. Rather than modifying the property of a material, structures resonating within larger ranges can be obtained by changing the deposited metal. The possibility of growing NP arrays made of Au and Cu is shown in this chapter and the possibility of tuning the positive peaks towards the NIR is demonstrated.

6.1 Au and Cu dielectric function

Prior to discussing the plasmonic properties of the NP arrays, the dielectric function of both Au and Cu must be introduced. As already mentioned in Section 1.1, these materials possess interband transition (IT) contributions and their dielectric properties will present additional features with respect to the simple free electron Drude response. Rather than computing the contribution of the IT contributions to the overall polarizability, tabulated values will be used in the simulations.

The experimentally measured [135] bulk dielectric functions of Au and Cu are shown in Figure 6.1. The IR response of these metals is characterised by a Drude-like tail and their imaginary parts present additional absorption peaks. In particular, two IT appear visible in the visible range for Au and 3 for Cu (see vertical lines in Figure 6.1 B).

The data shown in Figure 6.1 have been extracted from bulk measurements, and NP surface scattering has been disregarded. In Ag it was demonstrated[35] that the presence of the NP surface broadens the resonance profiles and these modifications were taken into consideration introducing an additional contribution to the scattering rate (see Eq. (1.10)). A similar correction can also be obtained for Cu and Au parametrising the bulk dielectric function and increasing the free electron scattering rate Γ by the same amount.

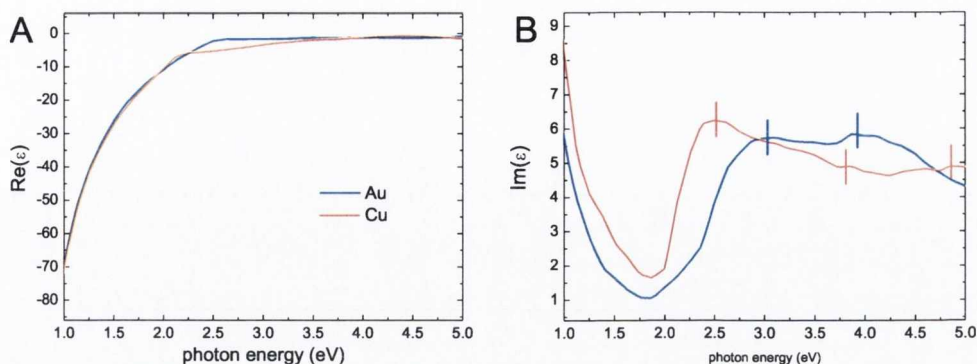


Figure 6.1: Real (A) and Imaginary (B) part of the bulk dielectric function for Au and Cu. The absorption peaks maxima are underlined by vertical lines in (B).

Generally speaking, the lack of structural periodicity in a confined system do not allow for the definition of a proper electronic wave function in the form of Bloch waves. The band structure of a quasi zero-dimensional NP changes with respect to the bulk counterpart and variations in position, intensity and broadening of the IT peaks are also expected. Unfortunately, the exact calculation of the dielectric function for a NP is impossible to be exactly evaluated. In the next paragraph the measured the dielectric function of a thin layer for both Cu and Au is extracted by SE and the optical response parametrised. The parametrised values for both free electrons and IT contributions will be referred to a thin film rather than to the bulk value. This will result in a closer fit between real NP dielectric function and extracted values due to the reduced dimensionality of the thin film if compared to the bulk counterpart.

Evaluation of Au and Cu thin film dielectric function

A thin layer of Au has been deposited in a UHV chamber (base pressure 3×10^{-10} mBar) on a flat Al_2O_3 substrate. Prior to deposition the substrate was heated at 600° in a O_2 reach atmosphere at a pressure of 3×10^{-5} mBar for 2 hours. The substrate was left to cool down and a Au film was deposited at room temperature at a rate of 1.2 nm/min. The deposition time was 16 minutes, correspondent to a nominal thickness of 19 nm. After exposure of the sample to atmosphere the sample was measured with ellipsometry at multiple angles of incidence of 67° , 70° and 73° . The layer thickness and

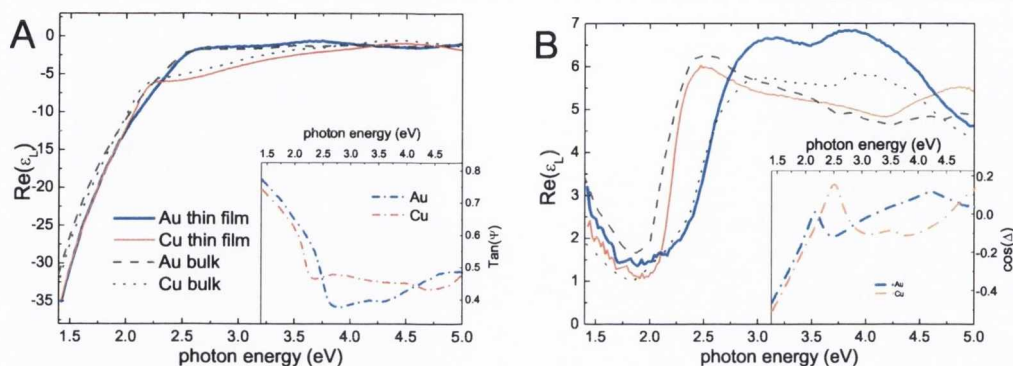


Figure 6.2: Real (A) and Imaginary (B) part of the measured Au (blue) and Cu (red) films dielectric functions compared with the tabulated values (gray). The curves were obtained by a point by point fitting procedure. Insets: measured $\tan \Psi$ (A) and $\cos \Delta$ (B) of the samples using a 70° incidence angle.

roughness were afterwards measured by X-ray diffraction in reflection mode. Values of 17.8 ± 0.6 nm and 1.4 ± 0.3 nm were obtained for the film thickness and roughness respectively. AFM scans of the surface confirmed a comparable roughness.

A similar procedure has been followed for the Cu thin film. Cu was deposited in a different UHV chamber provided by a Cu source. The chamber base pressure was 2×10^{-8} mBar and no preheating was performed. A Cu layer was deposited at a rate of 0.24 nm/min for 66 minutes, corresponding then to a thickness of 16 nm. After the ellipsometry scans, XRD and AFM have been performed and a thickness and roughness of 16.1 ± 0.6 nm and 1.8 ± 0.4 nm were measured respectively.

The dielectric functions of the two layers have been finally compared with the respective bulk dielectric values. The comparison has been realised with a point to point fit of $\tan \Psi \cos \Delta$ using roughness and layer thickness obtained by XRD. The results are shown in Figure 6.2. While the general shape of the dielectric function resembles the tabulated values, the position and the intensity of the various peaks do not match completely.

The thin layer dielectric functions have been parametrised. The values were obtained by fitting the multiple angle scans of the ellipsometry raw data till convergence. The multiple resonator Eq. (1.8) of Chapter 1 was first used in the fit. A resonator was introduced to describe the electron IR response and additional two and three resonators added to simulate to the ITs of gold and copper respectively. Unfortunately,

the equations utilised could not reproduce accurately the measured spectra and additional peaks were required to resemble the ellipsometry measurements more accurately. The introduction of these additional non-physical peaks would complicate the direct utilisation of the parametrised equation. However, substituting the lowest energy IT resonator with a 1D Van Hove singularity was found to produce a much closer resemblance of the measured peaks. Van Hove singularities are a discontinuity in the density of states and the wavevectors at which Van Hove singularities occur appear as critical points of the Brillouin zone. As IT absorption spectra can be represented by transition in the reciprocal space, strong absorption peaks appear in correspondence with such critical points as more states (infinite) are allowed. The finite intensity of the absorption profile are simply due to the losses inside the material. From a formal point of view, Van Hove singularities can be represented by points in the reciprocal space where

$$\nabla_{\mathbf{k}}(E_{i\mathbf{k}} - E_{f\mathbf{k}}) = 0 \quad (6.3)$$

with the indexes i and f correspond to initial and final transition states. The type of critical points, the singular behaviour and hence the imaginary part $\varepsilon''(\omega)$ of the dielectric function depend on the dimensionality of the system. For a 1D crystals there are two types of IB singularities, corresponding to a minimum and a maximum in the imaginary part of the dielectric function and the second one was utilised in the present case to reproduce the absorption peak. The dielectric functions utilised during the fitting procedure have the following analytical expression

$$\varepsilon(\omega) = \varepsilon_{\infty} - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma} + \exp(i\phi_{1D}) \frac{A_{1D}}{\sqrt{\omega_{0,1D} - \omega - i\Gamma_{1D}}} + \sum_{j=1}^M \exp(i\phi_j) \frac{A_j}{\omega_{0j}^2 - \omega^2 - i\omega\Gamma_j} \quad (6.4)$$

where $M = 1$ or 2 for gold and copper respectively. The exponential factors in Eq. (6.4) are required to ensure Kramer-Kroenig consistency of the relations and were fixed for simplicity to $\pi/2$.

The obtained fitted curves are shown in Figure 6.3 for both Au and Cu and the parameters are listed in Table 6.1. The curves appear to closely match in the vis-UV. The main difference is an underestimation in the dampening of the IR response. However, for typical NP dimensions produced by glancing angle deposition, the main contribution will be provided by surface scattering if $A = 0.3$ in Eq. (1.10) is used.

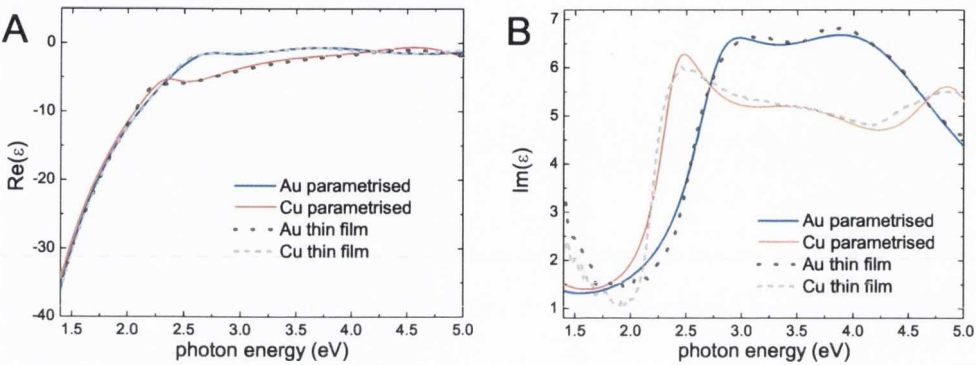


Figure 6.3: Real (A) and Imaginary (B) part of the fitted thin film dielectric function of Au and Cu using Eq. (6.4) with the parameters listed in Table 6.1.

	ϵ_{∞}	$\omega_p(\text{eV})$	$\Gamma(\text{eV})$	$A_{1D}(\text{eV}^2)$	$\omega_{0,1D}(\text{eV})$	$\Gamma_{1D}(\text{eV})$
Au	3.48	9.3	0.02	3.17	2.72	0.30
Cu	2.42	9.0	0.03	2.34	2.63	0.18
	$A_1(\text{eV}^2)$	$\omega_{0,1}(\text{eV})$	$\Gamma_1(\text{eV})$	$A_2(\text{eV}^2)$	$\omega_{0,2}(\text{eV})$	$\Gamma_2(\text{eV})$
Au	35	4.2	2.2	-	-	-
Cu	17	3.7	2.0	4.9	15.1	1.0

Table 6.1: Fitted parameters for the thin film dielectric function of Au and Cu. For the fitting, Eq. (6.4) was utilised.

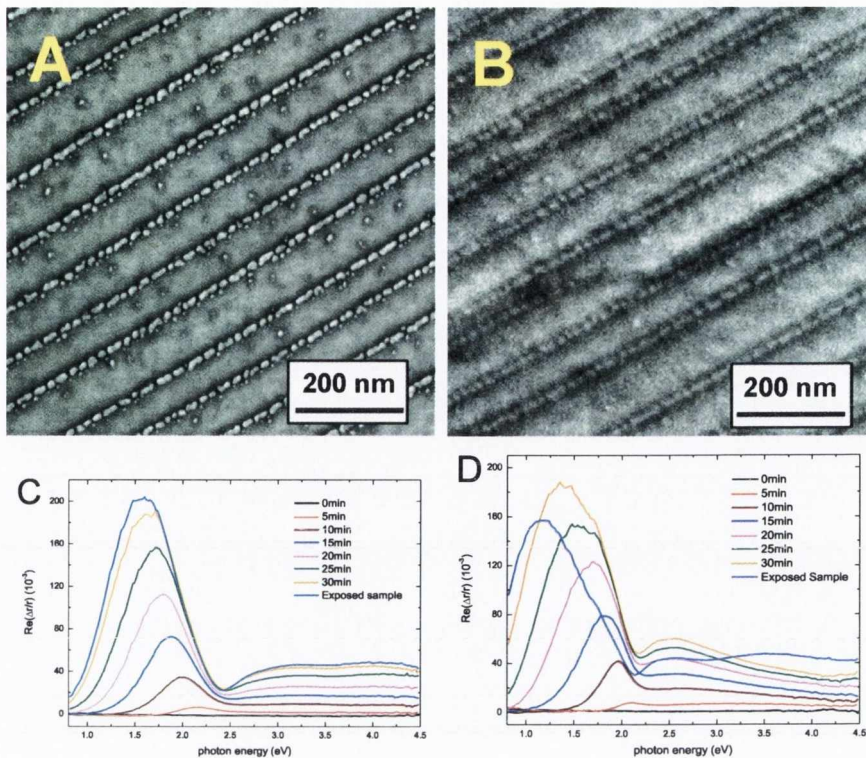


Figure 6.4: SEM images of Au (A) and Cu (B) NP arrays grown at glancing angle deposition on a 100 nm template periodicity. (C) and (D): Relative RAS spectra taken *in situ* at different deposition times and after exposure of the sample to atmosphere.

6.2 Au and Cu NP arrays: results and discussion

A stepped Al_2O_3 has been utilised as a template to produce Au and Cu NP arrays. The sample was annealed at 1440° for 24 hours and the periodicity was measured to be 95 ± 22 nm. The sample was then cut into two pieces, cleaned and each piece inserted into the UHV chamber loaded with a Knudsen cell filled by Au or Cu. The materials have been evaporated for 30 minutes on the sample inclined by 6° with respect to the adatom flux with a rate of 2.3 nm/min. Figure 6.4 shows the resulting morphologies obtained by SEM. The NP average dimensions are below lithographic resolution and the surface morphology remains unchanged throughout the entire sample of 5×5 mm² size. Furthermore, the requirement of interparticle distances being smaller than the average particle diameter is satisfied. As for Ag, also in this case the steps are decorated by NP arrays elongated along the chain axis, confirming glancing angle deposition is virtually

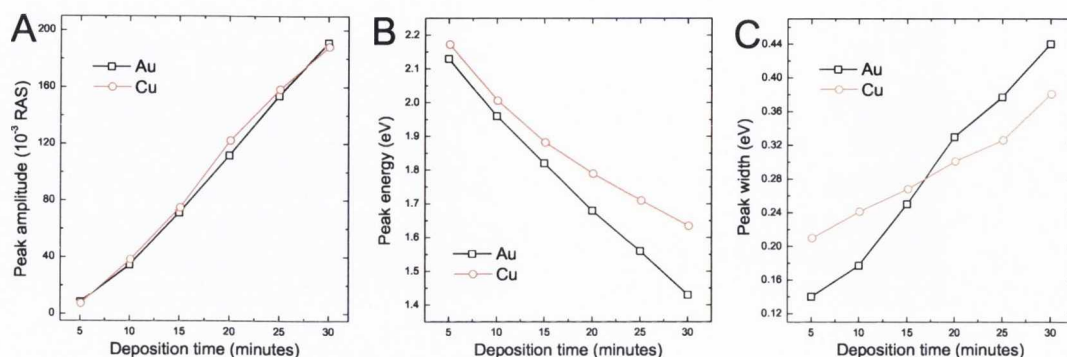


Figure 6.5: RAS intensity (A), peak position (B) and peak width (C) of the positive plasmonic peak for Au and Cu NP arrays as a function of the deposited time. An increase in intensity and width can be noticed with increase in the deposited thickness. At the same time the resonant position red shifts.

independent on the deposited material. An analysis of the in-plane morphological information extracted by SEM is reproduced in Table 6.2. Compared to Ag, the NP center to center distance for both Au and Cu is smaller, suggesting a smaller adatom diffusion constant for the latter.

RAS was measured as a function of the deposited thickness for both samples, the spectra presenting this time remarkable differences. In particular, the spectra show only positive peaks. The sharp resonances at low energies are related to plasmonic resonance along the array axis while a comparison with Figure 6.1 suggests that the additional positive features at higher energies are related to inter band contributions. The negative peaks related to transversal resonances are then completely screened in this case. The positive peak position, intensity and width for Au and Cu has been fitted by a Gaussian and the results shown in Figure 6.5.

As already discussed in Chapter 4, the peak intensities increase almost linearly with the deposited thickness corresponding to an increase in the deposited plasmonic materials. The width also increase and the behaviour is consistent with an increase in the morphological distribution of the sample as discussed in Section 4.6. Finally, the positive peaks shift in the IR upon increasing the deposition time, corresponding to an increase in NP shape anisotropic and interparticle coupling. If compared with Ag plasmonic response (see, for example, Figure 4.14), the peak positions are placed further in the IR, gaining a larger tunability in the choice of the resonant energy.

Table 6.2: Morphology of Au and Cu NP arrays as measured with SEM and AFM.

	N (NPs/ μm^{-2})	l_y (nm)	l_x (nm)	R_x (nm)	R_y (nm)
Au	421 $\pm$ 140	95 $\pm$ 22	25 $\pm$ 6	11 $\pm$ 3	7 $\pm$ 2
Cu	390 $\pm$ 130	95 $\pm$ 22	27 $\pm$ 6	12 $\pm$ 3	8 $\pm$ 1

The exposure of the sample to atmosphere produced spectral changes similar to the ones observed in silver in Section 4.7. The positive peaks red shift a small 0.04 eV for gold and of 0.26 eV for Cu. The larger shift of Cu confirms its instability to the atmosphere and capping would be necessary to preserve these structures from oxidation. After exposure of the samples to atmosphere the main peaks are present at 1.59 eV for Au and 1.16 eV for Cu.

The classical model of Chapter 1 has been finally used to simulate the measured optical spectra. The parametrised dielectric functions of Au and Cu and the morphology of the sample as extracted from SEM were used as input parameters. Figure 6.6 shows the normalised layer dielectric function $\varepsilon_{L,j}$ and the RAS simulated spectra using $R_z = 5$ nm and supposing no tarnished layer surrounding the NPs. As already mentioned, the peak relative to resonance perpendicular to the arrays is completely screened in the present case and the spectral RAS spectral shape resembles qualitatively the experimental one. However, as already observed in the previous chapters, the exact peak position cannot be reproduced with the current model without additional fitting parameters. Never the less, in the simulation shifts of the resonances towards the IR are obtained for both Au and Cu, if compared with Ag NP simulations. In addition, Cu positive resonance peak is placed further in the IR if compared with Au. The trend measured experimentally is thus confirmed. It appears clear that further refinements will be required to quantitatively reproduce the response of truncated ellipsoids supported on a stepped surface. However, the simulations reported here confirm experimental observations, at least for a qualitative understanding of the results.

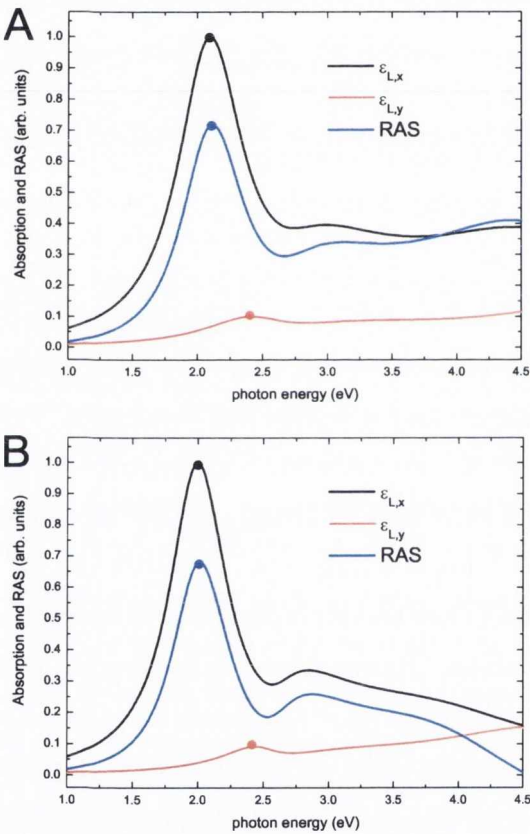


Figure 6.6: Simulated NP layer dielectric functions and RAS for Au (A) and Cu (B) NP arrays using the model of Chapter 1. The dots indicate the plasmonic resonances.

6.3 Conclusions

In order to extend the optical tunability of plasmonic structure obtained by glancing angle depositions, gold and copper NP arrays were produced and their optical properties measured *in situ* with RAS. The generality of glancing angle deposition technique has been then demonstrated and structures resonant in the NIR obtained. To simulate their optical response, the dielectric function of a thin film was measured and parametrised to account for the increase in the scattering rate due to NP confinement. With these changes, a qualitative match with the experimental data was obtained.

Chapter 7

Conclusions and Future Work

The science of today is the
technology of tomorrow

E. Teller

Plasmonics is a rapidly evolving field due to its potential applications, ranging from solar cell, biophysics to optoelectronic. For most applications the dispersion of the plasmonic metal nanoparticles (NPs) onto a substrate is required and standard production methods do not allow for their distribution in a ordered fashion. However, closely spaced and ordered NPs can provide advanced functionalities useful for different applications. The presence of hot spot phenomena described in Chapter 1 can produce enhancement effects, and coupling between NPs can increase the sensitivity of plasmonic-based optical sensors or it can allow for more pronounced scattering of light inside the absorbing medium of a solar cell. It appears thus necessary to develop novel production techniques capable of combining the high throughput of the typical colloidal preparations with the order of lithographic production methods.

This thesis demonstrates an alternative route with the required characteristics. The technique is based on evaporation of material at glancing angles onto a previously stepped template. The main capability of the glancing angle deposition is the ability to grow anisotropic structures of any evaporable material on a wide range of substrates,

restricted only by the requirement that the latter form ordered stepped morphologies. Self-assembly methods usually suffer of a lack of a precise control of the parameters affecting the growth. However *in situ* reflectance anisotropy spectroscopy (RAS) enables tailored growth to any resonance peak position required without the usual uncertainty if only post growth characterisation can be used.

A necessary requirement for the glancing angle deposition technique is the use of suitable textured templates. In order to obtain these substrates, we focused on c-plane α -alumina and its surface morphology upon annealing. Samples with different off-cut angles along the $[1\bar{2}10]$ direction were annealed at different temperatures. Combining these parameters, we proved the possibility of producing periodic stepped surfaces with tunable morphologies. In particular, annealing at higher temperatures resulted in increasing periodicity while higher off-cut resulted in higher steps.

The glancing angle deposition technique was developed to routinely grow NP arrays of different plasmonic materials such as silver, gold and copper. The deposition technique is mainly based on geometrical considerations and its independence on the material deposited was demonstrated. The nanostructures produced were characterized via optical spectroscopy in the far field and their strong dichroic response due to LPRs was shown. The possibility of monitoring their optical profile is obtained using the *in situ* capability RAS provides. Furthermore, RAS can also monitor the overall order of the surface through the Gaussian broadening of the plasmonic peaks.

The resulting LPRs have been investigated as a function of deposition time, angle and initial template periodicity in Chapter 4. Different NP dimensions and a large optical tunability were achieved by tweaking the various growth parameters. Figure 7.1 shows that Ag NP arrays grown at different deposition time and angles on different template periodicities and large shifts of the peak positions can be observed, especially for the positive RAS peak. At the same time an optimum deposition angle can be found in order to minimise the morphological dispersion and the resulting peak width.

Shifts up to ~ 0.6 eV for the main peak have been observed for Ag NP arrays. Larger shifts are limited by the electronic properties of the deposited material. However, using different plasmonic materials, tunabilities in a larger range of ~ 1.8 eV can be obtained. Figure 7.2 shows the normalised intensity RAS spectra for Ag, Cu, and Au NP arrays grown in similar conditions: NP arrays having their positive resonant energy lying between the 1.1 eV and 2.9 eV have been produced. The structures described in this

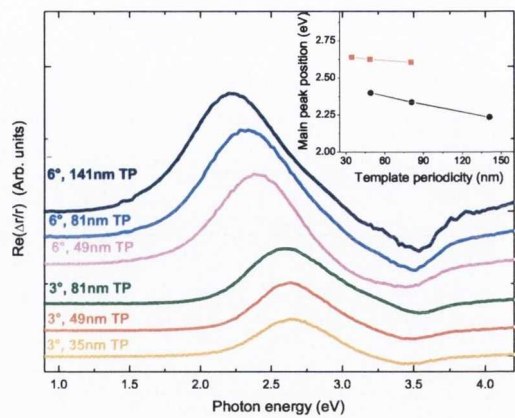


Figure 7.1: RAS spectra of Ag NP arrays after venting characterised by different template periodicities (TP) and deposition angles. 20 minutes (30 minutes) depositions were performed for the 3° (6°) deposition angles. (Inset) Resonance energy of the main peak for deposition of Ag at 3° (red line), 6° (black line) as a function of the template periodicity. The intensity of the curves were shifted for clarity.

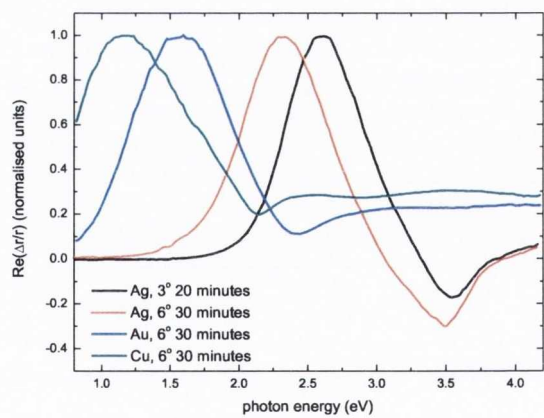


Figure 7.2: Normalised RAS spectra of various NP arrays of different plasmonic materials produced by glancing angle deposition . The legend indicates the corresponding material, deposition angle and deposition time.

thesis were grown at room temperature, however it is believed that high temperature deposition can further increase their tunability and improve their order.

Finally, the exact origin of the measured dichroic response has been addressed using a coupled dipolar model. The structures were modelled as interacting supported ellipsoids represented as point dipoles. The measured optical signals, the effects of the image charges and the exposure of the sample to atmosphere have been explained in this way. The gaussian broadening of the peak has also been discussed and attributed to the morphological dispersion of the plasmonic layer.

The plasmonic structures were further characterized by SE and an original route to investigate their out-of-plane optical response outlined in Chapter 5. From the raw experimental data, a quantity named anisotropic surface excess function was extracted. This function depends only on the characteristics of the surface layer and the theoretical model developed was applied to simulate their optical response.

7.1 Future work,

from fundamental studies to applications

This thesis presents a comprehensive study on the capability of glancing angle deposition in the production of anisotropic plasmonic structures. The optical properties have been fully investigated as a function of the different parameters involved and the origin of the resonances has been also addressed. With the background knowledge reported in this thesis we can now move forward towards applications and demonstrate the capabilities of the structures grown.

There are numerous possible applications for the structures produced. For example, the NP arrays can be tested as building blocks for optical biosensors. The dependency of the optical response of the system surrounded by different refractive index media can be investigated. Figure 7.3 shows preliminary results of the RAS spectra of a typical sample immersed in different solvents. A linear red shift of the main peak is observed with increases of the refractive index. This behaviour can be fully investigated first using homogeneous liquids and afterwards by functionalising the NP surface with

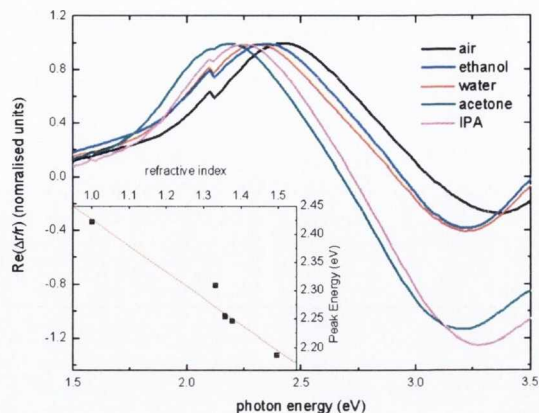


Figure 7.3: Normalised RAS spectra of Ag NP arrays immersed in different solvents. (inset) Positive peak position as a function of the refractive index of the liquid. A red shift with increases in the refractive index is observed.

organic molecules, linked to the particle surface by thiol (sulphur based) groups. The presence of the analyte will produce a changes in the refractive index surrounding the NPs and shift of the resonance peaks can be studied as a function of its concentration.

We also propose an investigation of the hot spot phenomenon for the structures grown. Using the COMSOL multiphysics package we can already simulate the optical behaviour of the structures grown and a mapping of the electric field in the NP interstitial space at resonance can be done. The effects of NP shape anisotropy and interparticle separation for the different metals will be addressed. After the completion of this study, Raman active molecules could be dispersed on the plasmonic substrates and increases in their Raman scattering cross section due to surface enhanced effects could be measured. It could be first tested for standard molecules such as Rodhamine G6 as a function of the molecule concentration. Similar enhancement effects can be studied for fluorescent dyes whose resonance frequency will be matched with the resonant frequency of the NP arrays and of the exciting laser.

The NP arrays can also be used as catalyst for the growth of anisotropic superimposed structures. For example, it has been reported that randomly placed gold NP on top of c-plane alumina can be used as catalysts for the growth of out-of-plane ZnO nanorods [144]. Glancing angle depositions can produce ordered gold NP arrays and hence anisotropic out-of-plane forests of ZnO nanorods can be produced in this

way. Such nanostructures are believed to possess an anisotropic photoemission spectrum and hence polarization-dependent light emitting diodes can be produced following this route.

Being highly independent of the deposited material, the glancing angle deposition can also be utilised for the growth of core shell structures. A magnetic or dielectric core can first be deposited and an outer plasmonic shell grown around this. A self-assembly growth of such hemi-shell plasmonic NP arrays has never been reported in literature. Heterostructure having a dielectric core have been demonstrated [145] to possess an increased refractive index sensitivity while magnetic core ones can be used as metamaterials or as structures with coupled plasmonic and magnetic properties, being optically active both in the radio frequency and visible range.

From the fundamental point of view, second harmonic generation investigations on Ag NP arrays have already been performed, but as the results require further clarification they have not been included in this thesis. A full study will be performed and the origin of the signal measured addressed.

The content of this thesis represents a knowledge pool for the applicability of glancing angle deposition technique in real world devices. At the same time the technique in combination with RAS is proved as a helpful tool to investigate the role of coupling between NPs, the effects of substrate, NP morphology and morphological disorder from a fundamental point of view.

Appendix: Obtaining the C coefficient

We report in this appendix the calculated analytical expressions for the different C_{int} and C_{im} coefficients if the identical particles are placed on a rectangular lattice. The $C_{int,i}$ are

$$C_{int,x} = \sum_{j,k \neq 0} \frac{3\cos^2(\arctan(\frac{jL_y}{kL_x})) - 1}{((kL_x)^2 + (jL_y)^2)^{3/2}} \quad (7.1)$$

$$C_{int,y} = \sum_{j,k \neq 0} \frac{3\cos^2(\arctan(\frac{kL_x}{jL_y})) - 1}{((kL_x)^2 + (jL_y)^2)^{3/2}} \quad (7.2)$$

$$C_{int,z} = \sum_{j,k} \frac{-1}{((kL_x)^2 + (jL_y)^2)^{3/2}} \quad (7.3)$$

while the imaginary ones are

$$C_{imm,x} = - \sum_{j,k} \frac{3\cos^2(\arctan(\frac{((2D^*)^2 + (jL_y)^2)^{1/2}}{kL_x})) - 1}{((kL_x)^2 + (jL_y)^2 + (2D^*)^2)^{3/2}} \quad (7.4)$$

$$C_{imm,y} = - \sum_{j,k} \frac{3\cos^2(\arctan(\frac{((2D^*)^2 + (kL_x)^2)^{1/2}}{jL_y})) - 1}{((kL_x)^2 + (jL_y)^2 + (2D^*)^2)^{3/2}} \quad (7.5)$$

$$C_{imm,z} = \sum_{j,k} \frac{3\cos^2(\arctan(\frac{(2D^*)}{((kL_x)^2 + (jL_y)^2)^{1/2}})) - 1}{((kL_x)^2 + (jL_y)^2 + (2D^*)^2)^{3/2}} \quad (7.6)$$

$$(7.7)$$

References

- [1] U. Kreibig and M. Vollmer. *Optical Properties of Metal Clusters*. Springer, Berlin, 1957.
- [2] V. Shalaev and S. Kawata. *Nanophotonics with Surface Plasmons*. Springer, Berlin, 2007.
- [3] L. Brongersma and P. Kik. *Surface Plasmon Nanophotonics*. Springer, Berlin, 2007.
- [4] G. Mie. Beitrage zur Optik trber Medien, speziell kolloidaler Metallosungen. *Annalen Physike*, 330:337–445, 1908.
- [5] C. Bohren and D. Huffman. *Absorption and scattering of light by small particles*. Wiley, New York, 1983.
- [6] T. W. Ebbesen, H. J. Lezec, H. F. Ghaemi, T. Thio, and P. A. Wolff. Extraordinary optical transmission through sub-wavelength hole arrays. *Nature*, 391: 667–669, 1998.
- [7] L. Haitao and L. Philippe. Microscopic theory of the extraordinary optical transmission. *Nature*, 452:728–731, 2008.
- [8] B. Lukyanchuk, N. I. Zheludev, S. A. Maier, N. J. Halas, H. Nordlander, Peter Giessen, and T. C. Chong. The Fano resonance in plasmonic nanostructures and metamaterials. *Nature Materials*, 9:707–715, 2010.

- [9] S. Maier, P. Kik, A. Atwater, and S. Meltzer. Local detection of electromagnetic energy transport below the diffraction limit in metal nanoparticle plasmon waveguides. *Nature Materials*, 2:229–232, 2003.
- [10] S. Nie and S. R. Emory. Probing Single Molecules and Single Nanoparticles by Surface-Enhanced Raman Scattering. *Science*, 275(5303):1102–1106, 1997.
- [11] S. Kim, J. Jin, Y. J. Kim, I. Y. Park, Y. Kim, and S. W. Kim. High-harmonic generation by resonant plasmon field enhancement. *Nature*, 453:757–760, 2008.
- [12] A. Kinkhabwala, Z. Yu, S. Fan, Y. Avlasevich, K. Mullen, and M. E. Large single-molecule fluorescence enhancements produced by a bowtie nanoantenna. *Nature Photonics*, 3:654 – 657, 2009.
- [13] Z. Nie, A. Petukhova, and E. Kumacheva. Properties and emerging applications of self-assembled structures made from inorganic nanoparticles. *Nature Nanotechnology*, 5:15 – 25, 2009.
- [14] X. Lu, M. Rycenga, S. E. Skrabalak, B. Wiley, and Y. Xia. Chemical Synthesis of Novel Plasmonic Nanoparticles. *Annual Review of Physical Chemistry*, 60(1): 167–192, 2009. PMID: 18976140.
- [15] M. Neouze and U. Schubert. Surface Modification and Functionalization of Metal and Metal Oxide Nanoparticles by Organic Ligands. *Monatshefte für Chemie / Chemical Monthly*, 139:183–195, 2008. 10.1007/s00706-007-0775-2.
- [16] F. Le, D. W. Brandl, Y. A. Urzhumov, H. Wang, J. Kundu, N. J. Halas, J. Aizpurua, and P. Nordlander. Metallic Nanoparticle Arrays: A Common Substrate for Both Surface-Enhanced Raman Scattering and Surface-Enhanced Infrared Absorption. *ACS Nano*, 2(4):707–718, 2008.
- [17] L. J. Sherry, R. Jin, C. A. Mirkin, G. C. Schatz, and R. P. Van Duyne. Localized Surface Plasmon Resonance Spectroscopy of Single Silver Triangular Nanoprisms. *Nano Letters*, 6(9):2060–2065, 2006.

- [18] V. Sharma, K. Park, and M. Srinivasarao. Colloidal dispersion of gold nanorods: Historical background, optical properties, seed-mediated synthesis, shape separation and self-assembly. *Materials Science and Engineering: R: Reports*, 65(1-3): 1 – 38, 2009.
- [19] F. Hao, C. L. Nehl, J. H. Hafner, and P. Nordlander. Plasmon Resonances of a Gold Nanostar. *Nano Letters*, 7(3):729–732, 2007.
- [20] randommmmm. <http://www.nanowerk.com/news/newsid=15712.php>, Internet Site.
- [21] J. Penninkhoff. *Tunable plasmon resonances in anisotropic metal nanostructures*. PhD thesis, Utrecht University, 2006.
- [22] S. A. Maier, M. L. Brongersma, P. G. Kik, and H. A. Atwater. Observation of near-field coupling in metal nanoparticle chains using far-field polarization spectroscopy. *Physical Review B*, 65(19):193408, 2002.
- [23] C. L. Haynes and R. P. Van Duyne. Dichroic Optical Properties of Extended Nanostructures Fabricated Using Angle-Resolved Nanosphere Lithography. *Nano Letter*, 3(7):939–943, 2003.
- [24] P. K. Jain and M. A. El-Sayed. Noble Metal Nanoparticle Pairs: Effect of Medium for Enhanced Nanosensing. *Nano Letters*, 8(12):4347–4352, 2008.
- [25] S. Zou and G. C. Schatz. Silver nanoparticle array structures that produce giant enhancements in electromagnetic fields. *Chemical Physical Letter*, 403(1-3):62 – 67, 2005.
- [26] A. Sundaramurthy, P. J. Schuck, N. R. Conley, D. P. Fromm, G. S. Kino, and W. E. Moerner. Toward Nanometer-Scale Optical Photolithography Utilizing the Near-Field of Bowtie Optical Nanoantennas. *Nano Letters*, 6(3):355–360, 2006.
- [27] A. N. Grigorenko, N. W. Roberts, M. R. Dickinson, and Y. Zhang. Nanometric optical tweezers based on nanostructured substrates. *Nature Photonics*, 2:365–370, 2008.

- [28] P. A. Atawer H.A. Plasmonics for improved photovoltaic devices. *Nature Materials*, 9:205–213, 2010.
- [29] A. Sugawara, T. Coyle, G. G. Hembree, and M. R. Scheinfein. Self-organized Fe nanowire arrays prepared by shadow deposition on NaCl(110) templates. *Applied Physics Letters*, 70(8):1043–1045, 1997.
- [30] S. Camelio, D. Babonneau, D. Lantiat, and L. Simonot. Self-organized growth and optical properties of silver nanoparticle chains and stripes. *EuroPhysical Letter*, 79(4):47002–47008, 2007.
- [31] F. Cuccureddu, S. Murphy, I. Shvets, M. Porcu, and H. W. Zandbergen. Plasmon Resonance in Silver Nanoparticles Arrays Grown by Atomic Terrace Low-Angle Shadowing. *Nano Letter*, 8(10):3248–3256, 2008.
- [32] I. V. Shvets, H. C. Wu, V. Usov, F. Cuccureddu, S. K. Arora, and S. Murphy. Concept of a nanowire array magnetoresistance device. *Applied Physics Letter*, 92(2):023107–023109, 2008.
- [33] A. Toma, D. Chiappe, D. Massabo, C. Boragno, and F. B. de Mongeot. Self-organized metal nanowire arrays with tunable optical anisotropy. *Applied Physics Letter*, 93(16):163104–163106, 2008.
- [34] J. D. Jackson. *Classical electrodynamics 3rd edition*. JournalWiley, New York, 1992.
- [35] H. Hövel, S. Fritz, A. Hilger, U. Kreibig, and M. Vollmer. Width of cluster plasmon resonances: Bulk dielectric functions and chemical interface damping. *Physical Review B*, 48(24):18178–18188, 1993.
- [36] F. Bassani and G. Pastori Parravicini. *Electronic States and Optical Transitions in Solids*. Pergamon Press, Oxford, 1975.
- [37] K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. *The Journal of Physical Chemistry B*, 107(3):668–677, 2003.

- [38] T. Yamaguchi, S. Yoshida, and A. Kinbara. Optical effect of the substrate on the anomalous absorption of aggregated silver films. *Thin Solid Films*, 21(1):173 – 187, 1974.
- [39] N. Witkowski, Y. Borensztein, G. Baudot, V. Repain, Y. Girard, and S. Rousset. Combined scanning tunneling microscopy and reflectance anisotropy spectroscopy study of self-organized anisotropic cobalt nanodots on a vicinal Au(111) surface. *Physical Review B*, 70(8):085408, 2004.
- [40] A. Pinchuk, A. Hilger, and G. V. Plessen. Substrate effect on the optical response of silver nanoparticles. *Nanotechnology*, 15:1890–1903, 2004.
- [41] P. Bobbert and J. Vlieger. The polarizability of a spheroidal particle on a substrate. *Physica A: Statistical Mechanics and its Applications*, 147(1-2):115 – 141, 1987.
- [42] C. E. Roman-Velazquez, C. Noguez, and R. G. Barrera. Substrate effects on the optical properties of spheroidal nanoparticles. *Physical Review B*, 61(15):10427–10436, 2000.
- [43] C. Beitia, Y. Borensztein, R. Lazzari, J. Nieto, and R. G. Barrera. Substrate-induced multipolar resonances in supported free-electron metal spheres. *Physical Review B*, 60(8):6018–6022, 1999.
- [44] R. Lazzari, G. Renaud, C. Revenant, J. Jupille, and Y. Borensztein. Adhesion of growing nanoparticles at a glance: Surface differential reflectivity spectroscopy and grazing incidence small angle x-ray scattering. *Physical Review B*, 79(12):1–8, 2009.
- [45] R. Lazzari, S. Roux, I. Simonsen, J. Jupille, D. Bedeaux, and J. Vlieger. Multipolar plasmon resonances in supported silver particles: The case of Ag/ α -Al₂O₃(0001). *Physical Review B*, 65(23):235424–235433, 2002.
- [46] D. Bedeaux and J. Vlieger. *Optical Properties of Surfaces*. Imperial College Press, London, 2004.

- [47] M. Valamanesh, Y. Borensztein, C. Langlois, and E. Lacaze. Substrate Effect on the Plasmon Resonance of Supported Flat Silver Nanoparticles. *Journal Chemical Physical C*, 115:2914–2922, 2011.
- [48] R. Ruppin. Optical Absorption of Two Spheres. *Journal of the Physical Society of Japan*, 58(4):1446–1451, 1989.
- [49] A. F. Koenderink. Plasmon Nanoparticle Array Waveguides for Single Photon and Single Plasmon Sources. *Nano Letters*, 9(12):4228–4233, 2009.
- [50] H. Taflove and S. Hagness. *Computational electrodynamic: the finite difference time domain method*. Artech House, Boston, 2000.
- [51] C. Oubre and P. Nordlander. Finite-difference Time-domain Studies of the Optical Properties of Nanoshell Dimers. *The Journal of Physical Chemistry B*, 109(20):10042–10051, 2005.
- [52] D. W. Mackowski and M. I. Mishchenko. Calculation of the T matrix and the scattering matrix for ensembles of spheres. *Journal Optics Society American A*, 13(11):2266–2278, 1996.
- [53] B. Draine and P. Flatau. Discrete dipole approximation for scattering calculations. *Journal Optics Society American A*, 11:1491–1499, 1994.
- [54] B. Draine and P. Flatau. Discrete-dipole approximation for periodic targets: theory and tests. *Journal Optics Society American A*, 25:2593–2703, 2008.
- [55] M. Quinten, A. Leitner, J. R. Krenn, and F. R. Aussenegg. Electromagnetic energy transport via linear chains of silver nanoparticles. *Optics Letter*, 23(17):1331–1333, 1998.
- [56] E. C. Jelks, G. L. Kerber, and H. A. Wilcox. A simple method for fabricating lines of 0.15- μ m width using optical lithography. *Applied Physics Letters*, 34(1):28–30, 1979.
- [57] L. F. Johnson, K. A. Ingersoll, and G. W. Kammlott. An oblique shadow deposition technique for altering the profile of grating relief patterns on surfaces. *Applied Physics Letters*, 34(9):578–580, 1979.

- [58] A. Sugawara, G. Hembree, and M. R. Scheinfein. Self-organized mesoscopic magnetic structures. *Journal Applied Physics*, 82(11):5662–5669, 1997.
- [59] T. Kitahara, A. Sugawara, H. Sano, and G. Mizutani. Anisotropic optical second-harmonic generation from the Au nanowire array on the NaCl(1 1 0) template. *Applied Surface Science*, 219(3-4):271 – 275, 2003.
- [60] M. Huth, K. Ritley, J. Oster, H. Dosch, and H. Adrian. Highly Ordered Fe and Nb Stripe Arrays on Facetted α -Al₂O₃ (10 $\bar{1}$ 0). *Advanced Functional Materials*, 12(5):333–338, 2002.
- [61] A. Westphalen, H. Zabel, and K. Theis-Brhl. Magnetic nanowires on faceted sapphire surfaces. *Thin Solid Films*, 449(1-2):207 – 214, 2004.
- [62] C. Teichert, J. Barthel, H. P. Oepen, and J. Kirschner. Fabrication of nanomagnet arrays by shadow deposition on self-organized semiconductor substrates. *Applied Physics Letters*, 74(4):588–590, 1999.
- [63] E. T. T. Jones, O. M. Chyan, and M. S. Wrighton. Preparation and characterization of molecule-based transistors with a 50-nanometer source-drain separation with use of shadow deposition techniques. Toward faster, more sensitive molecule-based devices. *Journal of the American Chemical Society*, 109(18):5526–5528, 1987.
- [64] W. L. Chan and E. Chason. Making waves: Kinetic processes controlling surface evolution during low energy ion sputtering. *Journal Applied Physics*, 101(12):121301-121347, 2007.
- [65] T. Oates, A. Keller, S. Facsko, and A. Micklich. Aligned Silver Nanoparticles on Rippled Silicon Templates Exhibiting Anisotropic Plasmon Absorption. *Plasmonics*, 2(2):47–50, 2007.
- [66] S. Camelio, D. Babonneau, D. Lantiat, L. Simonot, and F. Pailloux. Anisotropic optical properties of silver nanoparticle arrays on rippled dielectric surfaces produced by low-energy ion erosion. *Physical Review B*, 80(15):155434–155444, 2009.

- [67] M. Buljan, J. Grenzer, A. Keller, N. Radić, V. Valeš, S. Bernstorff, T. Cornelius, H. T. Metzger, and V. Holý. Growth of spatially ordered Ge nanoclusters in an amorphous matrix on rippled substrates. *Physical Review B*, 82(12):125316–125320, 2010.
- [68] Y. Lu, G. L. Liu, J. Kim, Y. X. Mejia, and L. P. Lee. Nanophotonic Crescent Moon Structures with Sharp Edge for Ultrasensitive Biomolecular Detection by Local Electromagnetic Field Enhancement Effect. *Nano Letters*, 5(1):119–124, 2005.
- [69] S. Shumaker-Parry, H. Rochholz, and M. Kreiter. Fabrication of Crescent-Shaped Optical Antennas. *Advanced Materials*, 17(17):2131–2134, 2005.
- [70] M. G. Ancona, S. E. Kooi, W. Kruppa, A. W. Snow, E. E. Foos, L. J. Whitman, D. Park, and L. Shirey. Patterning of Narrow Au Nanocluster Lines Using V2O5 Nanowire Masks and Ion-Beam Milling. *Nano Letters*, 3(2):135–138, 2003.
- [71] X.-M. Yan, S. Kwon, A. M. Contreras, J. Bokor, and G. A. Somorjai. Fabrication of Large Number Density Platinum Nanowire Arrays by Size Reduction Lithography and Nanoimprint Lithography. *Nano Letters*, 5(4):745–748, 2005.
- [72] H. A. Becerril and A. T. Woolley. DNA Shadow Nanolithography. *Small*, 3(9):1534–1538, 2007.
- [73] E. P. D. Poortere, H. L. Stormer, L. M. Huang, S. J. Wind, S. O'Brien, M. Huang, and J. Hone. Single-walled carbon nanotubes as shadow masks for nanogap fabrication. *Applied Physics Letters*, 88(14):143124, 2006.
- [74] D. Chiappe, A. Toma, Z. Zhang, C. Boragno, and F. B. de Mongeot. Amplified nanopatterning by self-organized shadow mask ion lithography. *Applied Physics Letters*, 97(5):053102–053104, 2010.
- [75] E. Fort, C. Ricolleau, and J. Sau-Pueyo. Dichroic Thin Films of Silver Nanoparticle Chain Arrays on Facetted Alumina Templates. *Nano Letter*, 3(1):65–67, 2003.

- [76] T. Oates, A. Keller, S. Noda, and S. Facsko. Self-organized metallic nanoparticle and nanowire arrays from ion-sputtered silicon templates. *Applied Physics Letter*, 93(6):063106–063108, 2008.
- [77] M. Cardona, F. H. Pollak, and K. L. Shaklee. Electroreflectance In Semiconductors. *Journal Physical Society Jap.*, S 21:89, 1966.
- [78] J. D. McIntyre and D. E. Aspnes. Differential Reflection Spectroscopy Of Very Thin Surface Films. *Surface Science*, 24:417, 1971.
- [79] D. E. Aspnes and A. A. Studna. Anisotropies in the above-band-gap optical spectra of cubic semiconductors. *Physical Review Letter*, 54(17):1956, 1985.
- [80] V. I. Berkovits, I. V. Makarenko, T. A. Minashvili, and V. I. Safarov. Optical transitions on GaAs(110) surface. *Solid State Communications*, 56(5):449, 1985.
- [81] P. Weightman, D. S. Martin, R. J. Cole, and T. Farrell. Reflection anisotropy spectroscopy. *Report Progress Physical*, 68(6):1251–1341, 2005.
- [82] D.E.Aspnes. Above-bandgap optical anisotropies in cubic semiconductors: A visible-near ultraviolet probe of surfaces. *Journal Vacuum Science Technol. B*, 3 (5):1498–1506, 1985.
- [83] D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez. Application of reflectance difference spectroscopy to molecular-beam epitaxy growth of GaAs and AlAs. *Journal Vacuum Science Technol. A*, 6(3):1327–1334, 1988.
- [84] A. Salvati and P. Chiaradia. Analysis of reflectometers for surface anisotropy. *Applied Optics*, 39(31):5821–5830, 2000.
- [85] J. F. McGilp. Optical characterisation of semiconductor surfaces and interfaces. *Progress in Surface Science*, 49(1):1 – 106, 1995.
- [86] Y. Borensztein, W. L. Mochan, J. Tarriba, R. G. Barrera, and A. Tadjeddine. Large anisotropy in the optical reflectance of Ag(110) single crystals: Experiment and theory. *Physical Review Letter*, 71(14):2334–2336, 1993.

- [87] P. Hofmann, K. C. Rose, V. Fernandez, A. M. Bradshaw, and W. Richter. Study of Surface States on Cu(110) Using Optical Reflectance Anisotropy. *Physical Review Letter*, 75(10):2039–2042, 1995.
- [88] K. Fleischer, S. Chandola, T. Herrmann, N. Esser, W. Richter, and J. F. McGilp. Free-electron response in reflectance anisotropy spectra. *Physical Review B*, 74(19):195432–195441, 2006.
- [89] R. Azzam and N. Bashara. *Ellipsometry and polarized light*. North Holland, 1977.
- [90] G. Binnig, C. F. Quate, and C. Gerber. Atomic Force Microscope. *Physical Review Letter*, 56(9):930–933, 1986.
- [91] D. Sarid. *Scanning force microscopy: with applications to electric, magnetic, and atomic forces*. Oxford University Press, 1994.
- [92] J. Goldstein, D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer, and R. Michael. *Scanning Electron Microscopy and X-ray Microanalysis, III edition*. Kluwer Academic/Plenum Publishers, New York, 2003.
- [93] A. Marmier and S. C. Parker. Ab initio morphology and surface thermodynamics of α -Al₂O₃. *Physical Review B*, 69(11):115409–115417, 2004.
- [94] M. Kitayama and A. M. Glaeser. The Wulff Shape of Alumina: III, Undoped Alumina. *Journal of the American Ceramic Society*, 85(3):611–622, 2002.
- [95] J.-H. Choi*, D.-Y. Kim*, B. J. Hockey, S. M. Wiederhorn*, C. A. Handwerker, J. E. Blendell, W. C. Carter, and A. R. Roosen. Equilibrium Shape of Internal Cavities in Sapphire. *Journal of the American Ceramic Society*, 80(1):62–68, 1997.
- [96] J. Toofan and P. R. Watson. The termination of the α -Al₂O₃ (0001) surface: a LEED crystallography determination. *Surface Science*, 401(2):162 – 172, 1998.
- [97] D. Dovinos, D. Hasko, and Z. Helin. Coulomb blockade in a silicon-on-sapphire nanowire. *Microelectronic Engineering*, 53(1-4):199 – 202, 2000.

- [98] S. Nakamura, M. Senoh, and T. Mukai. High-power InGaN/GaN double-heterostructure violet light emitting diodes. *Applied Physics Letters*, 62(19): 2390–2392, 1993.
- [99] Y. Chen, D. M. Bagnall, H. jun Koh, K. tae Park, K. Hiraga, Z. Zhu, and T. Yao. Plasma assisted molecular beam epitaxy of ZnO on c -plane sapphire: Growth and characterization. *Journal of Applied Physics*, 84(7):3912–3918, 1998.
- [100] T. J. Minvielle, R. L. White, M. L. Hildner, and R. J. Wilson. Temperature dependence of the epitaxial growth of Pt on basal-plane sapphire. *Surface Science*, 366(3):L755 – L759, 1996.
- [101] M. Yoshimoto, K. Yoshida, H. Maruta, Y. Hishitani, H. Koinuma, S. Nishio, M. Kakihana, and T. Tachibana. Epitaxial diamond growth on sapphire in an oxidizing environment. *Nature*, 399:340–342, 1999.
- [102] N. Sbai, J. Perrire, W. Seiler, and E. Millon. Epitaxial growth of titanium oxide thin films on c-cut and α -cut sapphire substrates. *Surface Science*, 601(23):5649 – 5658, 2007.
- [103] T. Tsukamoto and T. Ogino. Morphology of Graphene on Step-Controlled Sapphire Surfaces. *Journal of Applied Physics*, 2:1–3, 2009.
- [104] H. Ago, K. Imamoto, N. Ishigami, R. Ohdo, K. ichi Ikeda, and M. Tsuji. Competition and cooperation between lattice-oriented growth and step-templated growth of aligned carbon nanotubes on sapphire. *Applied Physics Letters*, 90(12):123112, 2007.
- [105] A. Wang, J. P. M. II, P. Finlayson, J. Li, K. Brabant, H. Tang, C. Black, T. Cao, X. Liang, S. O. Salley, G. W. Auner, and K. S. Ng. Short-and long-term neural biocompatibility of heparin coated sapphire implants. *Materials Science and Engineering: C*, 27(2):237 – 243, 2007. Symposium A: Advanced Biomaterials International Conference on Materials for Advanced Technologies (ICMAT 2005).
- [106] S. A. Chambers, T. Droubay, D. R. Jennison, and T. R. Mattsson. Laminar Growth of Ultrathin Metal Films on Metal Oxides: Co on Hydroxylated -Al₂O₃(0001). *Science*, 297(5582):827–831, 2002.

- [107] D. Cherns and Y. Sun. Defect reduction by epitaxial lateral overgrowth of nanorods in ZnO/(0001) sapphire films. *Applied Physics Letters*, 92(5):051909–051911, 2008.
- [108] T. Oto, R. G. Banal, K. Kataoka, M. Funato, and Y. Kawakami. 100 mW deep-ultraviolet emission from aluminium-nitride-based quantum wells pumped by an electron beam. *Nature Photonics*, 4:767–770, 2010.
- [109] M. Mezger, H. Schröder, H. Reichert, S. Schramm, J. S. Okasinski, S. Schder, V. Honkimäki, M. Deutsch, B. M. Ocko, J. Ralston, M. Rohwerder, M. Stratmann, and H. Dosch. Molecular Layering of Fluorinated Ionic Liquids at a Charged Sapphire (0001) Surface. *Science*, 322(5900):424–428, 2008.
- [110] A. H. Heuer, C. L. Jia, and K. P. D. Lagerlöf. The Core Structure of Basal Dislocations in Deformed Sapphire (α -Al₂O₃). *Science*, 330(6008):1227–1231, 2010.
- [111] S. H. Oh, M. F. Chisholm, Y. Kauffmann, W. D. Kaplan, W. Luo, M. Rhle, and C. Scheu. Oscillatory Mass Transport in Vapor-Liquid-Solid Growth of Sapphire Nanowires. *Science*, 330(6003):489–493, 2010.
- [112] M. Baram, D. Chatain, and W. D. Kaplan. Nanometer-Thick Equilibrium Films: The Interface Between Thermodynamics and Atomistics. *Science*, 332(6026):206–209, 2011.
- [113] J. R. Heffelfinger, M. W. Bench, and C. B. Carter. Steps and the structure of the (0001) α -alumina surface. *Surface Science*, 370(1):188–200, 1997.
- [114] L. P. Van, O. Kurnosikov, and J. Cousty. Evolution of steps on vicinal (0001) surfaces of α -alumina. *Surface Science*, 411(3):263, 1998.
- [115] P. R. Ribic and G. Bratina. Behavior of the (0 0 0 1) surface of sapphire upon high-temperature annealing. *Surface Science*, 601(1):44–49, 2007.
- [116] S. Curiotto and D. Chatain. Surface morphology and composition of c-, a- and m-sapphire surfaces in O₂ and H₂ environments. *Surface Science*, 603(17):2688–2697, 2009.

- [117] O. Kurnosikov. About anisotropy of atomic-scale height step on (0001) sapphire surface. *Surface Science*, 459(3):256–264, 2000.
- [118] E. Tune. Nanostructured sapphire vicinal surfaces as templates for the growth of self-organized oxide nanostructures. *Applied Surface Science*, 256(3):924 – 928, 2009.
- [119] L. P. Van, J. Cousty, and C. Lubin. Step heights and terrace terminations of a vicinal (0 0 0 1) α -alumina surface annealed in UHV. *Surface Science*, 549(2): 157 – 164, 2004.
- [120] F. Cuccureddu, S. Murphy, I. Shvets, M. Porcu, H. Zandbergen, N. Sidorov, and S. Bozhko. Surface morphology of c-plane sapphire (α -alumina) produced by high temperature anneal. *Surface Science*, 604(15-16):1294 – 1299, 2010.
- [121] R. Bachelet, F. Valle, I. C. Infante, F. Sanchez, and J. Fontcuberta. Step formation, faceting, and bunching in atomically flat SrTiO₃ (110) surfaces. *Applied Physics Letters*, 91(25):251904, 2007.
- [122] D. R. Giese, F. J. Lamelas, H. A. Owen, R. Plass, and M. Gajdardziska-Josifovska. Atomic force microscopy and scanning electron microscopy study of MgO(110) surface faceting. *Surface Science*, 457(3):326 – 336, 2000.
- [123] J. Heffelfinger and B. Carter. Mechanisms of surface faceting and coarsening. *Surface Science*, 389(1-3):188 – 200, 1997.
- [124] C. Herring. Some Theorems on the Free Energies of Crystal Surfaces. *Physical Review*, 82(1):87–93, 1951.
- [125] V. Marchenko. Theory of equilibrium shape of crystals. *Sov. Physical JEPT*, 54 (3):605–606, 1981.
- [126] H.-C. Jeong and E. D. Williams. Steps on surfaces: experiment and theory. *Surface Science Reports*, 34(6-8):171 – 294, 1999.
- [127] N. Ravishankar and C. Carter. Bunching of Surface Steps and Facet Formation on Alumina Surface. *Journal of Material Research*, 17:98–106, 2002.

- [128] J. M. Flores-Camacho, L. D. Sun, N. Saucedo-Zeni, G. Weidlinger, M. Hohage, and P. Zeppenfeld. Optical anisotropies of metal clusters supported on a birefringent substrate. *Physical Review B*, 78(7):075416–075424, 2008.
- [129] R. Lazzari, S. Roux, I. Simonsen, J. Jupille, D. Bedeaux, and J. Vlieger. Multipolar plasmon resonances in supported silver particles: The case of $Ag/\alpha - Al_2O_3(0001)$. *Physical Review B*, 65(23):235424–235437, 2002.
- [130] A. Marnier and S. Parker. Ab initio morphology and surface thermodynamics of $\alpha - Al_2O_3$. *Physical Review B*, 69(11):115409–115419, 2004.
- [131] N. Esser, A. M. Frisch, A. Röseler, S. Schintke, C. Goletti, and B. O. Fimland. Optical resonances of indium islands on GaAs(001) observed by reflectance anisotropy spectroscopy. *Physics Review B*, 67(12):125306, 2003.
- [132] S. Chandola, J. Jacob, K. Fleischer, P. Vogt, W. Richter, and J. F. McGilp. Optical and electronic properties of Ag nanodots on Si(111). *Journal Physical C*, 18(30):6979–6986, 2006.
- [133] N. Witkowski, Y. Borensztein, G. Baudot, V. Repain, Y. Girard, and S. Rousset. Combined scanning tunneling microscopy and reflectance anisotropy spectroscopy study of self-organized anisotropic cobalt nanodots on a vicinal Au(111) surface. *Physical Review B*, 70(8):085408–085413, 2004.
- [134] M. L. Brongersma, J. W. Hartman, and H. A. Atwater. Electromagnetic energy transfer and switching in nanoparticle chain arrays below the diffraction limit. *Physical Review B*, 62(24):R16356–R16359, 2000.
- [135] P. B. Johnson and R. W. Christy. Optical Constants of the Noble Metals. *Physical Review B*, 6(12):4370–4379, 1972.
- [136] C. Kittel. *Introduction to solid state physics*. Wiley, New York, 1986.
- [137] J. Bennett, S. L., and E. Ashley. Optical Constants of Silver Sulfide Tarnish Films. *Journal Optics Society American*, 60(2):224–232, 1970.

- [138] M. Kelly, S. Zollner, and M. Cardon. Modelling the optical response of surfaces measured by spectroscopic ellipsometry: application to Si and Ge. *Surface Science*, 285(3):282 – 294, 1993.
- [139] W. J. Plieth and K. Naegele. ber die bestimmung der optischen konstanten donnster oberflschichten und das problem der schichtdicke. *Surface Science*, 64(2):484 – 496, 1977.
- [140] P. V. Santos, B. Koopmans, N. Esser, W. G. Schmidt, and F. Bechstedt. Optical Properties of Ordered As Layers on InP(110) Surfaces. *Physical Review Letter*, 77(4):759–762, 1996.
- [141] D. E. Aspnes. Analysis of modulation spectra of stratified media. *Journal Optics Society American*, 63(11):1380–1390, 1973.
- [142] E. Palik. *Handbook of optical constants of solids III*. Elsevier, 1998.
- [143] T. Yamaguchi, S. Yoshida, and A. Kinbara. Anomalous optical absorption of aggregated silver films. *Thin Solid Films*, 18(1):63 – 70, 1973.
- [144] X. Wang, C. J. Summers, and Z. L. Wang. Large-Scale Hexagonal-Patterned Growth of Aligned ZnO Nanorods for Nano-optoelectronics and Nanosensor Arrays. *Nano Letter*, 4(3):423, 2004.
- [145] P. K. Jain and M. A. El-Sayed. Surface Plasmon Resonance Sensitivity of Metal Nanostructures: Physical Basis and Universal Scaling in Metal Nanoshells. *The Journal of Physical Chemistry C*, 111(47):17451–17454, 2007.

Be the change you want to see in the world.

Mohandas Karamchand Gandhi

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how it is working and helping me whenever I needed it. Thanks to Sumesh for the fun during the desperate moments when we were struggling to produce Ni NW arrays. A long time ago but thank you for the help. Thanks to Chris for the measurements with the RAS that does not work... .. at normal incidence and thanks to prof. McGilp for the patience, the help, the corrections and the suggestions you always gave me. This thesis would have not been so good without all of you. Thanks to Victor, this splendid and rough man who had the patience of standing me during the painful first year of my PhD. You are a great man. Thanks to Cormac, my brother of Si annealing and Ag NW contacts. And great, great, we are finishing finally! Thanks to Ciaran for correcting my thesis, Floriano for his previous work. I would like you to read this thesis and accept that, even if I am not a great scientist, it could be definitively worse. I was in the middle of your fight and I did not want to damage anybody. Thank you. Thanks to Han Chun, Rafa for the laugh we have for our (mine I would say) incapacibilities, thanks to Paul, Elisabetta, Brendon for help, meal, positive attitude, the English corrections and so forth. Thanks to Mohamed Abid, who showed me first how a real scientist works and helped me a lot. Thanks to John McCunniffe, thanks to amazing Lina la misuratrice della generazione di seconde armoniche (suona bene in Italiano, no?). Thanks to Savas. However it ended up I will remember the cheers to Igor we did together, I hope you are fine. Thanks to Sergej, Olaf, Sundar, Barry and Brendon the cyclist. Thanks to Oral for teaching me so much and for pushing forward my work and helping me in these last months.

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This is not enough. The thanks are much longer, so sit down if you want to read them all. I believe the quality of someone's life is made by the people you meet on your way. I learnt it here, in this city where everything is so precarious. I learnt what love is, what friendship really is, without any hypocrisy thought surrounding it. And I need to thank you all, friends of the past four years. Thank you for the moments we spent together. If you would have not been here, I would have probably not stand a chance to live in this cold city and I would have left long time ago. Thanks for the magic, amazing, beautiful moments we spent together. Thank you all. Thanks to the Erasmus group of the first year. Thanks for showing me the city, accepting me. I remember a day dancing on a roof on top of Mountjoy square and feeling so alive. Thanks to Stefania, Irene, Elisabetta and Gilberto above all of them. Thanks to Daniel, my bro. I am finally finishing as well. It has been beautiful everyday we spent together, never a problem, never a discussion, always everything so smooth. I hope all the best in your life: great philosopher, you deserve it. I remember the morning of my birthday, in our house, listening to DB and feeling this deep connection. Thanks to Cinzia, grazie di avermi fatto conoscere l'amore per la prima volta in vita mia, quello vero dico. Ti ricordo ancora con dolcezza e sono contento di sapere che la strada che stai percorrendo sia quella che volevi percorrere. Prosegui il tuo cammino e danza a piedi scalza la musica che ti piace tanto. "E' così bello!". Thanks to the Haddington girls, Sara and and Sara. Thanks to Denise, amiga de un Cluedo y des pues amiga por siempre. Amiga de furgoneta, de aventuras, de sonries y de royar. Gracias por las vacaciones en Londres y el buen sentimiento che existaria por siempre. Quando yo terminare' aquy nos encontramos securamente! Grazie a Marietto e a Sciupatiello, che pazza coppia che siete! E grazie per la sorpresa di essere tornati a trovarmi il giorno del mio compleanno...

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Grazie Giulio...

These are some of the people that come into my mind when I think about the last four years. About the adventures, the problems, the experiences. Some might say "they are too many people to share real feeling with all of them." I want to answer to these sceptics "they are just too many only if you have a small heart".

I ignore completely where some of them are now, what happened to them. My memory and my heart will always carry them with me thou.

With all of you I have shared adventures, thoughts. All of you made me grow. If now I watch at the mirror and I can see a man it is because of the time spent together. Thanks for teaching me and growing together.

"Live your life with courage and you will see that it will be an amazing adventure." This is what I used to say.

"I cannot have fears, preoccupations: wherever we will be, whatever we will do, we will always be part of each other. No regret. Only joy." This is what I say today.

Sorrisi.

It has been an amazing adventure indeed.

Thank you.