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Controllable growth of metallic nano-helices at room temperature conditions

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We report on a method to produce multiple-pitch, regularly shaped, aligned, and freestanding metallic nano-helices at room temperature. This method overcomes the limitations of the standard glancing angle deposition approach through a heat-management technique devoid of active substrate cooling and is even applicable for metals with low melting point, that is, high surface adatom diffusion. The structural quality and optical activity response of these metal nano-helices are comparable to state of the art helices produced by employing substrates cooled down to cryogenic temperatures. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4904091>]

Complex metallic artificial nano-structures such as helices represent unique and interesting materials for photonic and magneto-optical applications due to their enhanced chiral response at optical frequencies.^{1,2} The quest to achieve helical nano-structures from noble metals has been attempted in a variety of chemical and physical approaches.^{3,4} These include, for example, the use of helical nano-templates (e.g., DNA) and their decoration with Au nano-particles by appropriate chemical procedures.³ This approach, however, is limited by the template geometry and resulting overall structures are not electrically conducting, due to the separation between the individual Au nano-particles. An alternative technique is glancing angle deposition (GLAD) which allows large area patterning of helical nanostructures and helical films.⁴ This technique is based on the evaporation of materials on rotating substrates at extremely oblique angles. GLAD is successful when growing regularly shaped nano-structures made from different dielectric⁵ and semiconductor⁴ materials. As it is, this technique is not suitable for producing well-defined, free-standing nano-structures from individual metals due to the high surface-atom mobility (diffusion) of these materials.⁶ Previous attempts^{6–8} have resulted in helically shaped structures that are fully agglomerated and irregularly shaped, making them difficult to use for electromagnetic applications in the optical range.⁹ A possible way to achieve regular GLAD nano-structures made from metals was proposed already for quite some time,¹⁰ which employs the active cool down of the substrate to cryogenic temperature during the metal evaporation. However, this advanced modification has limitations. First, by actively cooling down the substrate to cryogenic temperatures, the achieved metallic nano-structures were reported to achieve heights only up to ~100 nm.¹¹ Longer, metallic nano-helices are not reported in the literature which could be due to the progressive degradation of the nano-structures attributed to a temperature rise during growth.¹² Second, it is technologically challenging and costly to realise permanent active cooling of a rotating

substrate with cryogenic liquids during metal evaporation.^{10,11} We report on a method without active cooling to produce multiple-pitch, regularly shaped, aligned, and freestanding metallic nano-helices. Our alternative technique uses the GLAD technique combined with an easily implementable heat-management system. The growth occurs without active substrate cooling which minimizes the temperature rise along the structures during the growth phase. We show how with the usage of this combined technique arrays of uniform metallic nano-helices with heights of several 100 nm are achieved. We emphasize that the growth of the nano-structures is undertaken at room temperature conditions, thus, maintaining the advantageous technological simplicity of standard GLAD. A key application of helical thin films is the enhancement of chiral effects in molecular sensing.² A metric for this is the optical activity (OA), which is the interaction of the nano-structures with circularly polarized light.¹³ OA leads, amongst others, to a difference in the absorption depending on both the handedness of the chiral nano-structures and that of the light. This absorption difference is called circular dichroism (CD) and serves to assess the structural uniformity of any chiral structure. CD measurements performed on the nano-helix arrays fabricated here show a similar quality in comparison to those produced with substrate cooling¹¹ and demonstrates the high structural homogeneity achieved by our room-temperature technique.

The GLAD approach⁴ was used and combined with a substrate heat-management system to grow the metallic nano-helices. In the present case, the substrate is pre-structured with a square array (pitch 150 nm) of Ag-dots (50 nm height and 50 nm diameter) which were defined on the substrate by standard electron-beam lithography. The bottom layer (heat-sink layer) is an 80 nm thick Ag layer deposited on the prestructured substrate. The top layer (200 nm thick) consists of polymethyl-metacrylate (PMMA) resist. Areas of nano-helix arrays are defined by exposing and developing the PMMA. The GLAD was carried out at 10⁻⁶ Torr in an electron-beam-evaporator with source-substrate distance of about 60 cm. In addition, metallic nano-helices can be grown on transparent substrates. In this case, the heat-sink layer is a transparent ITO film deposited on SiO₂ instead of the Ag film.¹⁴

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The key to control of the metal-nanostructure growth using GLAD is the reduction of the incoming ad-atom surface-diffusion which increases with the growth temperature, T_g , and is inversely correlated with the deposition rate r .¹² That is, the surface diffusion length considerably decreases under the conditions of higher deposition rates and lower growth temperatures.¹² It should be also noted that during the growth process, no thermal equilibrium is established between the nano-structures and the substrate as T_g is persistently greater than the substrate temperature T_{subs} . The heat-management process, see Figure 1(a), is controlled by two thin films. The bottom film (heat-sink layer) is a high thermal-conductivity κ material (Ag, Au, diamond, graphene, etc.), which enables an efficient heat transfer from the nano-structures (dashed arrows) to the substrate underneath. The top-layer (heat-shield) has a very low κ (UV photo- or polymethyl-metacrylate resist) and covers the substrate except the area where the desired nano-structures are to be fabricated. Its main function is to avoid heat transfer to the high κ layer from the areas where nano-structures are undesired. Figures 1(b)–1(e) are scanning-electron-microscopy images of arrays of nano-helices made from nickel and silver using our technique. Silver and nickel were chosen as test metals as they have significantly different surface adatom diffusion¹² and optical properties in the visible range.¹⁵ Structurally well-defined and freestanding nano-helices with uniform pitch and diameter are shown in Figures 1(b) and 1(e) proving the superiority of our procedure over the standard GLAD procedures at room temperature.^{6–8} We note that Ni nano-helices are more easily engineered than Ag nano-helices in agreement to the lower adatom mobility of Ni,¹² this is why uniform Ni nano-structures with heights larger than 500 nm are achievable with our method.¹⁴ To evaluate the actual heat-sink/shield performance, we have simultaneously grown samples with and without the heat-managing technique. Figure 2 shows two Ni and Ag samples simultaneously produced on dotted substrates with, see Figs. 2(a) and

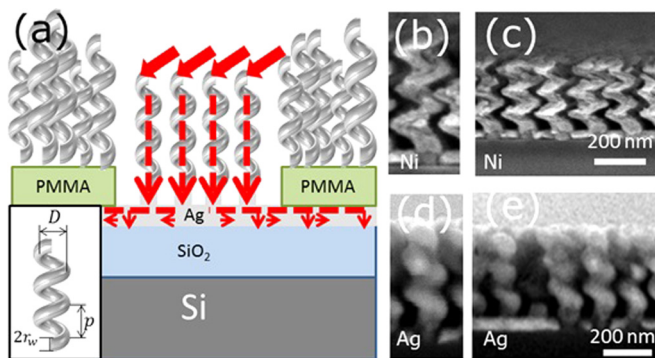


FIG. 1. (a) Heat-transfer process for an incoming particle flux. Inset: schematic of a three turn nano-helix with the pitch p , diameter D , and wire radius r_w . (b) and (c) Scanning electron micrograph showing the side-view of Ni nano-helices ($p = 75$ nm, $D = 85$ nm) grown using our heat-management technique. In (c), an enlarged view is provided demonstrating the highly uniform pitch and diameter. The nano-helices are free-standing and well-structured on the nano-scale. The substrate rotation-speed was 0.3 rpm, the deposition rate $r = 1.5$ nm s^{-1} , and the glancing angle $\sim 88^\circ$. (d) and (e) Ag nano-helices ($p = 75$ nm, $D = 80$ nm), again showing the same highly uniform pitch and diameter. The same deposition parameters as in the Ni case were used. The wire radius of both Ni and Ag samples is ~ 70 nm, and is mainly determined by the seed spacing⁴ (150 nm in our case).

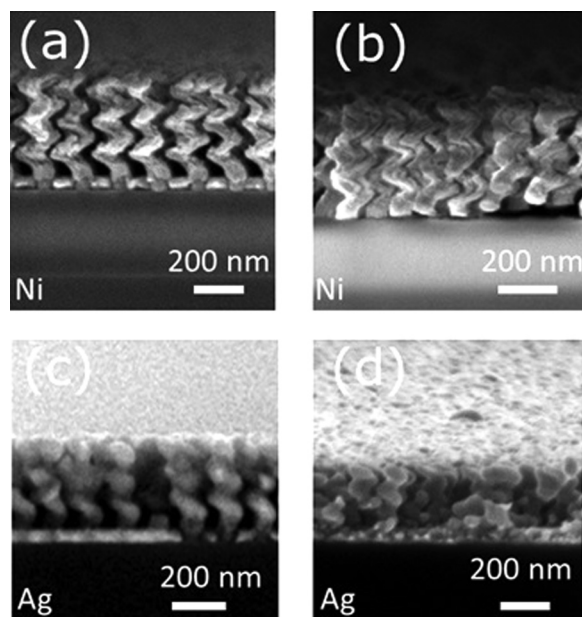


FIG. 2. (a) Nickel nano-helices made with pre-patterned substrate (dots) and the bi-layer heat-sink introduced in this work. (b) Nickel nano-helices made by prior art (pre-patterned substrate without heat-sink at room temperature): they are agglomerated and are not free-standing. (c) Ag nano-helices made with pre-patterned substrate (dots) and the bi-layer heat-sink introduced in this work. (d) Ag nano-helices made by prior art (pre-patterned substrate without heat-sink at room-temperature): the structures are fully agglomerated. Note that both set of samples, cf. (a) and (b), and (c) and (d), were fabricated simultaneously, that is, during the same growth process.

2(c), and without, see Figs. 2(b) and 2(d), heat-sink/shield layers, respectively. The metallic nano-structures become thicker, more deformed, and agglomerated when our heat-management system is not introduced.

The Standard Zone Model (SZM)¹⁶ can be used to qualitatively assess the heat-management technique introduced here. This model relates the morphology of physically evaporated films with one key processing factor: the reduced temperature T_g/T_m , where T_m is the melting temperature of the material in consideration (in our case, 1728 K for Ni and 1234 K for Ag). We note that this homologous temperature is directly related to the thermally induced surface diffusion (adatom mobility) of the materials.¹⁶ The uniformly structured and well separated Ni nano-helices grown using the heat-management system proposed here, see Figure 2(a), imply that they were grown within the zone 1 of the SZM. This gives an estimation of the maximum temperature reached during their growth of $T_g \sim 0.2 T_m = 350$ K. Meanwhile, the thicker and collapsed Ni nano-helices produced with no heat-management as presented in Figure 2(b) suggest that their growth fell well into the zone 2 of the SZM, with a temperature estimate of at least $T_g \sim 0.3 T_m = 520$ K. Consequently, the reduction of the growth temperature due to the heat-management system in the Ni case can be assessed to be more than 170 K. A similar analysis is applied to the Ag case, see Figures 2(c) and 2(d), which is known to be one of the more problematic metals for GLAD due to its low T_m (Ref. 17) (thus, larger adatom diffusion^{12,16}). In this case, the growth temperature reached with heat-management is estimated to be $T_g \sim 0.2 T_m = 300$ K and without heat-management $T_g \sim 0.25 T_m = 370$ K, giving an overall reduction of ~ 70 K. The results achieved with both metals

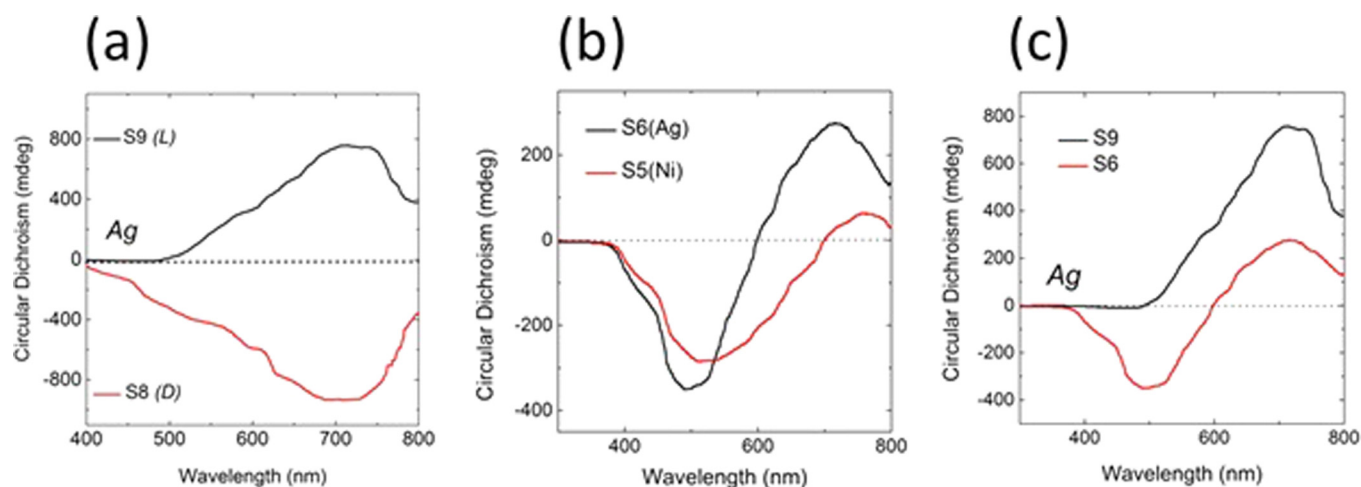


FIG. 3. Circular dichroism for arrays of Ag and Ni nano-helices. (a) Ag nano-helices with similar p and D (127 nm and 72 nm, respectively; cf. Table S1 (Ref. 14)) but different height and opposite helicity (D , L). (b) Ag and Ni nano-helices with similar structural parameters and the same helicity (L). (c) Comparing data from graphs in (a) and (b), it is shown that the circular dichroism can be deliberately tuned by the metal of choice and the actual helical structure.

explicitly show that the key parameter to be reduced in GLAD depositions is the growth temperature T_g rather than just the substrate temperature T_s . This is achieved with an efficient heat extraction during growth,^{16,18} which subsequently can be done by lowering the substrate temperature T_s (as done in Refs. 10 and 11) and/or by using materials with high thermal conductivity, as demonstrated in our study.

In addition, the nano-helices produced here are of similar structural quality as the ones reported to be grown with active substrate cooling with cryogenic liquids.¹¹ Not only that but also their overall average height (about 300 nm) is three times longer than previously reported samples,¹¹ and they have an excellent uniformity along their entire length (pitch variance is smaller than 7%, Table S1 (Ref. 14)). This structural homogeneity is confirmed with the circular dichroism measurements. Figure 3(a) shows the CD (RHC–LHC) of samples S8 and S9 (Table S1). These are Ag nano-helices with opposite helicity ($S8 = D$, $S9 = L$) but the same diameter (about 72 nm (Ref. 14)). It is observed that the CD response is inverted due to the differing helicity and the absolute value is similar to that reported in metal nano-helix structures produced with cryogenic liquid substrate-cooling.¹¹ A maximum CD difference can be observed at ~ 720 nm for both samples which is due to the fact that optical activity effects emerge at a wavelength related to the helix diameter.¹³ Figure 3(b) shows the CD of samples S5 (Ni) and S6 (Ag), both being left-handed (L). Although they show a qualitatively similar dependence on the wavelength, cf. occurring minima and maxima in Figure 3(b), the CD effects are weaker in the Ni sample, which is attributed to a stronger interband activity in Ni than in Ag for our experimental wavelengths.¹⁵ Comparison of the CD response of Ag and Ni nano-helices, see Figure 3(c), demonstrates clearly that the chiroptical activity of our metallic nano-helices can be deliberately tailored by choice of the helix growth material, and by the helix structural parameters pitch, diameter, and number of turns.

In conclusion, we have fabricated regular arrays of free-standing and structurally well-defined metallic nano-helices at room temperature by overcoming the standard GLAD

limitations through a simple heat-management technique. The purpose of this technique is to reduce the growth temperature T_g of the nanostructures by tuning the thermal conductivity of the supporting material on which the nanostructures are grown, rather than by reducing the entire substrate temperature.

According to our electron micrographs and optical activity measurements, this method offers, both, a significantly higher simplicity over the state-of-the-art cryogenic techniques, and allows longer nano-helices to be created, even for the case of metals with high surface adatom diffusion and medium-high melting temperatures such as Ag. Our method is compatible with and complements other existing advanced GLAD approaches generating scope to the growth of metal nano-helices across the entire range of metals known. The availability of multiple pitch and uniform metallic nano-helices make these structures ideal candidates to explore chiroptical phenomena and to use them in a broad range of optical, optoelectronic, and/or optomagnetic applications.

Additional figures on grown Ni and Ag nanohelices addressing height and growth on ITO substrates, a table summarising the structural parameters (pitch, diameter, turn-number) of different metal nanohelices produced and details on optical activity measurements. This material is available free of charge via the Internet at www.aip.org/pubservs/.

V.K. supervised the project and the associated studies. J.M.C. grew the nano-helices. Optical measurements were carried-out by J.M.C. and D.McC. under the support of J.F.D.

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