

Surface-plasmon-driven solution-phase growth of germanium nanostructures on lithographically-defined nanogap antenna arrays

R. O'Meara, B. R. Tak, K. Chumpol, N. Alattar, and R. G. Hobbs*

*Centre for Research on Adaptive Nanostructures and Nanodevices (CRANN) and the SFI Advanced Materials and Bio-Engineering Research Centre (AMBER), Dublin 2, Ireland;
School of Chemistry, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland,
D02 W9K7*

E-mail: hobbsr@tcd.ie

Phone: +353 (1)896 3035

Abstract

Low-temperature, spatially-selective fabrication of semiconductor nanostructures is essential for next-generation microelectronics, where back-end-of-line (BEOL) thermal budgets limit conventional high-temperature processing. Here, we demonstrate a plasmon-driven, solution-phase route to site-controlled growth of both crystalline and amorphous germanium nanostructures using lithographically defined Au nanoantennas and a diphenylgermane precursor. Resonant excitation at 785 nm of localized surface plasmon resonances (LSPRs) in Au nanogap antenna arrays can generate intense near-field photothermal heating, driving precursor decomposition and Ge nanostructure growth while avoiding global heating of the growth substrate. In this work, we demonstrate plasmon-driven growth of crystalline Ge nanowires at locations determined by lithographically-defined Au nanoantennas. Nanowire growth is demonstrated

on both bulk ITO/glass substrates and ultrathin 10-nm-thick SiN_x membranes to support characterization by transmission electron microscopy. The thermal conductivity of the substrates was found to dictate the optical power threshold required for catalytic nanowire growth. High-resolution TEM confirms the growth of single-crystalline Ge nanowires, while Raman spectroscopy also confirms the growth of Ge nanostructures. This approach may provide a low-thermal budget pathway for production of Ge photodetectors or other nanoelectronic devices directly onto BEOL metallization layers.

Introduction

The ability to fabricate semiconductor nanostructures and other quantum-confined materials at low temperatures with nanometre-scale positional control is critical for integrating functional components into advanced systems. Such methods enable applications across logic and memory devices, on-chip light sources and photodetectors for next-generation photonics, photocatalysis, and quantum technologies such as single-photon emitters.^{1–12} Furthermore, alignment of low-dimensional semiconductors, 0-d, 1-d and 2-d materials, within the hotspots of plasmonic nanocavities has been exploited to enhance light–matter interactions, thereby improving the efficiency and performance of nanoscale optoelectronic devices.^{1,2,13–16}

Plasmonic hotspots offer intense local electromagnetic fields that amplify optical transition rates, a key enabler for novel nanophotonic device architectures.^{1,17,18} Precise alignment of semiconductor nanostructures within these hotspots is therefore essential to fully leverage plasmon-enhanced responses in photodetectors and light-emitting devices.¹ Beyond field enhancement, plasmonic nanostructures can act as localized photothermal heaters^{19,20} or hot-carrier sources to drive the site-specific growth of nanomaterials on their surfaces. The use of plasmonic nanostructures to drive the local growth or modification of nanomaterials has been explored extensively for polymeric materials,^{18,21–29} while plasmon-driven growth of inorganic semiconductors is less widely reported.^{30–39} This plasmon-enabled growth approach

opens pathways to construct heterostructured nanomaterials with engineered composition and placement for applications in photonics, photocatalysis, and nanoelectronics.^{1,40}

Importantly, resonant excitation of plasmonic nanoantennas provides a route to locally heat materials on the nanoscale,^{28,41–43} which can support the growth of semiconductor nanostructures in controlled spatial configurations. This is particularly appealing for back-end-of-line (BEOL) semiconductor manufacturing, where global thermal budgets are restricted to avoid damage to front-end devices and interconnects.^{44,45}

Germanium has emerged as a promising material for BEOL-compatible photonics, thanks to its high carrier mobility and strong absorption at ~ 1550 nm making it well-suited for on-chip photodetectors in optical communications.⁴⁶ However, conventional growth of crystalline germanium nanostructures typically exceeds 400°C , rendering these approaches incompatible with BEOL processing.⁴⁷ In this context, plasmon-induced growth, where localized surface plasmon resonances (LSPRs) in nanoantennas are used to drive chemical reactions locally under optical excitation, offers a compelling solution for localized heating and position-controlled synthesis.

Although the concept of plasmon-driven growth dates back to the 2006 demonstration of plasmon-assisted CVD of PbO and TiO_2 ,³⁰ subsequent developments have extended the method to other semiconductor nanostructures including CeO_2 , ZnO, ZnS, TiO_2 , Ge nanowires, Si nanowires, and $\text{In}(\text{OH})_3$.^{31–34,36,37} The prior reports on plasmon-driven growth of Ge nanowires have relied on pyrophoric toxic gas-phase precursors such as germane or digermane,^{33,37} used a green laser excitation wavelength and utilized randomly dispersed Au nanoparticles prepared on substrates via dewetting of Au thin films or dispersion of colloidal nanoparticles. We propose therefore a refined approach: using lithographically-defined gold nanogap antennas, resonantly excited by a near-infrared 785-nm wavelength laser, to locally decompose a solution-phase diphenylgermane precursor, enabling spatially-controlled growth of germanium nanostructures. This solution-phase route with lithographically defined plasmonic nanoantennas avoids hazardous gaseous precursors, thus greatly simplifying the pre-

cursor delivery apparatus and enables precise antenna geometry and positioning. Moreover, we fabricate antennas on both bulk substrates and ultrathin SiN_x membranes that allow inspection of grown material via (scanning) transmission electron microscopy ((S)TEM).

Our strategy provides the foundation for a scalable platform to embed germanium photodetectors directly on BEOL metallization layers, as it demonstrates the ability to grow Ge nanostructures on lithographically-defined metal nanostructures in a metal-insulator-metal (MIM) type geometry. A similar MIM geometry with amorphous Ge and Au has previously been used to produce high-speed and high-bandwidth NIR photodetectors.⁴⁸ Modification of our plasmonic nanogap antennas to incorporate metal contact wiring to the antenna array similar to that reported by Yang et al.⁴⁹ could bring this process closer to resembling a real BEOL layout, thereby advancing integration of high-performance optical functionality into next-generation microelectronics.

Experimental Methods

Plasmonic nanoantenna arrays were prepared on 100-nm-thick tin-doped indium oxide (ITO) films on bulk glass substrates purchased from *Ossila Ltd.* and were cleaned using the following steps. First, the ITO/glass was cleaned by ultrasonication in 1% *Hellmanex III* surfactant solution for 5 min at 25 °C to remove particulate contaminants, followed by rinsing with deionised water and isopropyl alcohol (IPA). The substrates were then plasma-cleaned with an oxygen plasma using a *Diener PICO* low-pressure oxygen plasma cleaner for 5 min at 0.3 mbar O_2 pressure with a plasma power of 100 W to remove organic residues and aid wetting of PMMA resist. PMMA (2% 950k PMMA in anisole purchased from *Allresist GmbH*) was spin coated onto each substrate (2 krpm with an acceleration rate of 2 krpm/s for 60 s) to give a resist thickness of approximately 70 nm. After spin-coating, the substrates were baked at 180 °C for 2 min on a hot plate to remove any excess casing solvent and reduce stress in the resist film. Electron-beam lithography was performed using a *Zeiss SUPRA*

40 scanning electron microscope modified with a *Raith Elphy Quantum* pattern generator. The resist was exposed using an electron landing energy of 15 keV and an area dose of 1300 $\mu\text{C}/\text{cm}^2$. Following electron-beam exposure, the resist was developed in a solution of 1:3 methyl isobutyl ketone (MIBK):IPA solution at 0 °C for 30 s using a thermoelectric cold plate. Low temperature development was used for positive-tone lithographic processes as it improves both contrast and resolution. The developed sample was coated with metal using a *Temescal FC-2000* electron-beam evaporation system. A 1-nm-thick layer of Ti was first deposited at a rate of 0.2 Å/s as an adhesion layer, followed by a 20-nm-thick layer of Au deposited at a rate of 0.5 Å/s. This rate was used for Au as McPeak et al. found that Au films deposited at 0.5 Å/s had better optical properties in the NIR region than films deposited at higher deposition rates.⁵⁰ The EBL pattern was transferred to the substrates via a lift-off process by immersing the sample in n-methylpyrrolidone (NMP) at 60 °C for 45 min. The sample was then rinsed with acetone and IPA before being oxygen plasma-cleaned as above. Nanoantenna arrays were also prepared on 10-nm-thick SiN_x membranes purchased from *SiMPore Inc.* on 3 mm diameter Si frames. The substrates were first plasma-cleaned with an oxygen plasma as above. PMMA was spin coated onto each substrate at a rate of 5 krpm with an acceleration rate of 8 krpm/s for 60 s to give a resist thickness of approximately 70 nm. Higher spin speeds and acceleration rates are required for the small (3 mm diameter) chips in order to reduce edge-beading of the resist, and to yield a uniform resist film at the centre of the chip. The subsequent electron-beam exposure and metallization steps were the same as outlined for ITO/glass substrates above.

Ge nanostructure growth was achieved using diphenylgermane (DPG) purchased from *Fluorochem Ireland Ltd.* as the Ge precursor compound. Growth cells for laser exposure shown in figure 1a were prepared using a silicone isolator gasket (aperture diameter = 7 mm) that was placed directly onto the ITO glass substrate such that the nanoantenna arrays were located in the centre of the gasket aperture. The well formed by the gasket bound to the substrate by adhesive was filled with DPG and sealed with a glass cover slip, ensuring that

no air bubbles were present in the sealed cell. Care was taken to use a freshly opened bottle of DPG to minimize oxidation of the precursor prior to closure of the cell. Moreover, the time between cell preparation and laser exposure was kept as short as possible to minimize oxidation of DPG. DPG was observed to exhibit negligible absorbance at 785 nm indicating that direct decomposition of DPG in the laser path was unlikely. The measured spectrum of DPG, after subtraction of the spectrum of an empty cell, is shown in figure S6. Laser excitation for growth of Ge was provided by a 785 nm wavelength laser (*Stingray*, *Coherent Inc.* or *785 nm MatchBox*, *Integrated Optics, UAB*) focused via a 50 $\times$ objective lens with a NA of 0.53 giving a spot with a diameter (FWHM) of approximately 5 μm and 2 μm for each laser on the ITO surface, respectively. The laser spot diameter was observed to broaden by approximately 20% on passing through the DPG layer and SiN_x membrane in each case. Results shown in figures 2 and 3 were produced using the *Stingray* laser, while the results shown in figure 4 were produced using the *Matchbox* laser. Laser power was varied from 30-60 mW. Exposure times ranged from 1 s to 5 min. A photograph of the setup used for laser exposures and acquisition of optical spectra is shown in figure S7. Following laser exposure, the glass cover slip and silicone isolator were removed from the sample, and the sample was subsequently rinsed with acetone followed by IPA. For growth on SiN_x membranes, the silicone gasket was placed on a blank ITO/glass substrate and the 3 mm diameter chip containing the membrane was placed inside the 7 mm aperture of the gasket before filling the well with DPG and sealing with a cover slip as above.

Optical extinction spectra were obtained using a *CRAIC QDI1000* microspectrophotometer using a 15 $\times$ reflecting objective and a cooled CCD spectrometer (*Ocean Optics Inc.*) to collect spectra from 10 $\mu\text{m} \times 10 \mu\text{m}$ regions of the nanoantenna arrays. Raman spectra were obtained using a *Renishaw Qontor* Raman microscope employing a 785 nm laser for excitation and a 100 $\times$ objective lens using 50 acquisitions of 1 s duration. A *FEI Titan* TEM operating with an accelerating voltage of 300 kV was used to obtain high resolution TEM images of Ge grown on Au nanoantennas, and to probe the structure and elemental

composition of the grown Ge by energy-dispersive X-ray (EDX) analysis using a *Bruker 6-30 SDD*. Scanning electron microscopy was performed on a *Zeiss Ultra Plus* typically using a 5 keV electron landing energy and an in-lens secondary electron detector with EDX performed using an *Oxford Instruments INCA* EDX with 20 mm² detector.

Electromagnetic simulations were performed with the commercially available *Lumerical* FDTD solver from *ANSYS Inc.*. Values for the refractive index of Au were taken from Johnson and Christy.⁵¹ Values for the refractive index of Ti and SiO₂ were taken from Palik.⁵² Values for the refractive index of SiN_x and ITO were taken from Philipp et al.⁵³ and König et al., respectively.⁵⁴ The FDTD simulation unit cell is designed to match with the period of the nanoantennas fabricated using EBL *i.e.*, 400 nm in the *y*-direction for both bow-tie and nanodiamond structures, 400 nm in the *x*-direction for bow-tie nanoantennas, and 230 nm in the *x*-direction for a pair of nanodiamonds. To simulate individual nanoantennas, perfectly matched layers (PML) are used as boundary conditions. Symmetric and anti-symmetric boundary conditions were used in the FDTD simulations to account for the periodicity of the arrays while exploiting the symmetry of the nanoantennas to reduce the overall simulation time by a factor of 4. A total-field scattered-field (TFSF) source polarized in the *x*-direction was used as the light source. The source was specified to have a wavelength of 600-900 nm in all simulations for Au nanoantennas. A mesh size of 0.5 nm × 0.5 nm × 0.5 nm was used in the simulations.

Results and Discussion

In this work, we focus on the use of lithographically-defined plasmonic Au nanogap antennas to achieve plasmon-driven growth of Ge nanostructures. We select Au for the antenna material, as it is well established as a seed particle material for the growth of Ge nanowires via the vapour-liquid-solid (VLS) and solution-liquid solid (SLS) mechanisms.⁵⁵⁻⁵⁷ Given that Au is known to exhibit superior plasmonic performance in the near-infrared region of the

spectrum relative to the visible, we elected to use a 785 nm wavelength laser to stimulate growth.^{50,58,59} The selection of 785 nm, would also potentially aid characterization of the grown materials by surface-enhanced Raman spectroscopy where 785 nm is a commonly used excitation wavelength. Notably, prior reports of plasmon-driven Ge nanowire growth with gas-phase precursors utilized a 532 nm laser source rather than the 785 nm source used here. In this work, we decided to target the design of Au nanogap antennas resonant near 785 nm. Nanogap antennas, *e.g.* bow-tie nanoantennas, can offer increased quality factors for LSPRs relative to isolated particles, which we would expect to enhance light-matter interactions in our system. Moreover, nanogap antennas open up the opportunity to grow material in the nanogap thus generating a MIM-type geometry for optoelectronic device fabrication. We consider two nanogap antenna geometries, bow-tie nanoantenna arrays and nanodiamond chains as shown in Figure 1. As nanodiamond chains resemble back-to-back arrays of bow-tie antennas, this combination of nanogap antenna geometries allowed us to consider two significantly different array densities that would lead to differences in collective heating under resonant excitation. To allow illumination in a transmission configuration, we elected to use indium tin oxide (ITO) coated glass substrates, which would also provide an electrically conductive substrate that would minimize charge accumulation during fabrication of the antenna arrays by electron-beam lithography (EBL) as well as during inspection by scanning electron microscopy (SEM). Figure 1a shows a schematic of the experimental setup used to illuminate arrays of nanoantennas within a growth cell comprised of the ITO/glass substrate and a glass coverslip separated by a silicone gasket and loaded with the diphenylgermane precursor. Nanogap antennas were designed to exhibit LSPRs near 785 nm using a commercial FDTD solver (*Lumerical Inc.*). Simulation results indicated that bow-tie antennas based on equilateral triangles having side lengths of 85 nm and a central gap of 15 nm would return a resonance close to 785 nm, while nanodiamond chains composed of squares having a side length of 71 nm and a gap of 15 nm would similarly return a LSPR overlapping with the 785 nm laser wavelength. Figures 1b and 1c show

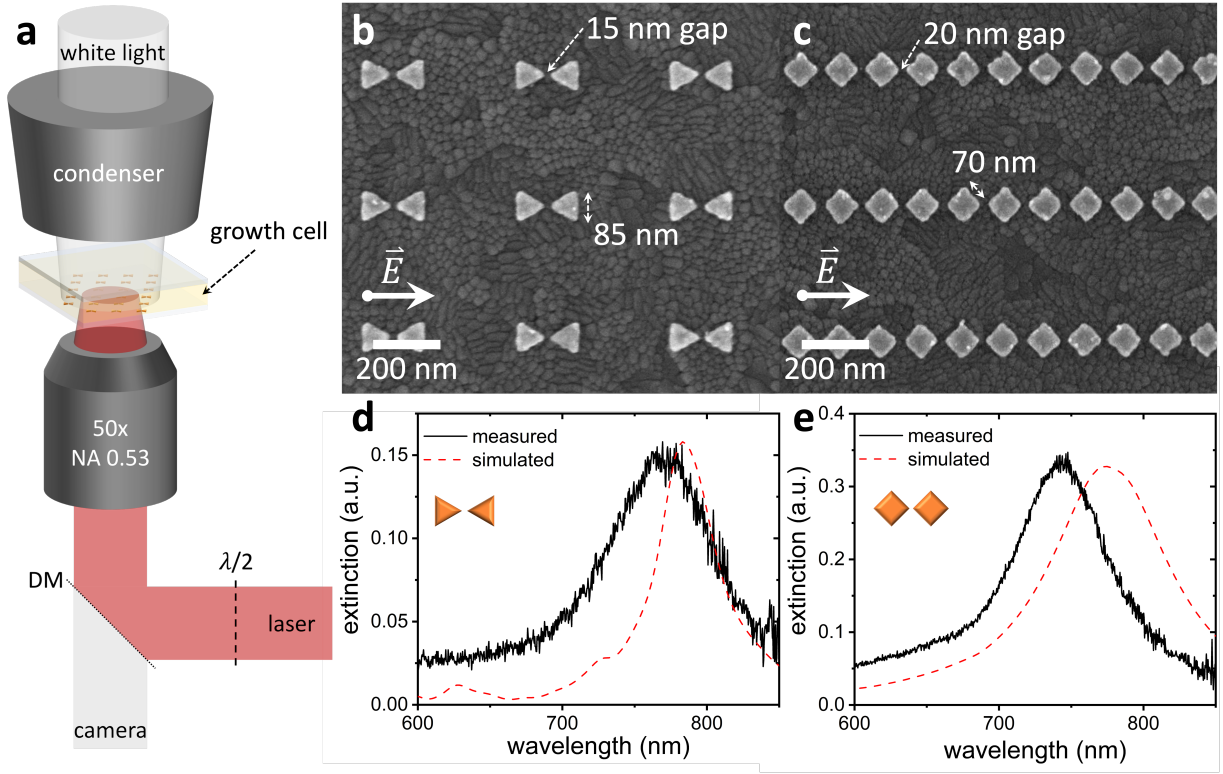


Figure 1: (a) Schematic of experimental setup used for plasmon-driven growth of Ge nanostructures. A linearly polarized (polarization controlled via half-wave plate ($\lambda/2$)) 785-nm wavelength laser illuminates the Au nanoantenna arrays via a dichroic mirror (DM) and a 50 $\times$ objective. The nanoantenna arrays are formed on ITO/glass or SiN_x membrane held in a growth cell filled with diphenylgermane precursor. (b) SEM image of plasmonic Au bow-tie antenna array on ITO/glass. Antenna dimensions designed for LSPR near 785 nm for polarization ($\vec{E}$) shown. (c) SEM image of Au nanodiamond array on ITO/glass. Nanodiamond dimensions and placement designed for LSPR near 785 nm and polarization shown. (d) Experimentally measured and simulated extinction spectra for an array of bow-tie antennas like those in (b). (e) Experimentally measured and simulated extinction spectra for an array of nanodiamond antennas like those in (c).

SEM images of bow-tie antennas and nanodiamond chains having dimensions close to the target dimensions. Measured side lengths for the bow-tie antennas were 86 ± 4 nm with a gap length of 16 ± 2 nm. Measured side lengths for the nanodiamond antennas were 70 ± 2 nm with a gap length of 20 ± 2 nm. Figures 1b and 1c also show the orientation of the linear polarization of the laser with respect to the antenna geometries, which was used for all experiments in this work. Figures 1d and 1e show the measured and simulated extinction spectra in air for the arrays shown in figures 1c and 1d, respectively. Comparison

of the measured spectra shows that the nanodiamond chains exhibit a significantly larger extinction, which is consistent with the higher density of antennas per unit area (6.25 bow-ties μm^{-2} and 21.74 nanodiamonds μm^{-2}). Notably, the peak in the measured spectrum for bow-tie arrays is at approximately 770 nm, while that for nanodiamond arrays is near 745 nm. These peak positions can be expected to red-shift by approximately 45 nm to near 815 nm and 790 nm, respectively, based on measured shifts for LSPR peaks in growth cells relative to air (see figure S2). After fabrication of the antenna arrays and confirmation of their extinction spectra, the arrays of antennas were used in experiments to optically stimulate the growth of Ge nanostructures.

Figure 2 shows examples of plasmon-driven growth of Ge nanomaterials on plasmonic Au nanodiamond arrays. While bow-tie antennas were also tested, growth was found to be limited to amorphous coatings on bow-ties for the range of exposure conditions used and as such, nanodiamond arrays were the primary focus for this work (examples of material grown on bow-tie antennas can be seen in figure S1). Figures 2a-2e show SEM images illustrating the progression in Ge-based material deposition with increasing laser exposure power. In figure 2a, deposited material is seen to completely coat the nanodiamond arrays within the elliptical laser spot for a laser power of 36 mW and an exposure time of 10 s. Figure 2b shows that with increased exposure time at a laser power of 36 mW, the deposited material at the very centre of the laser spot appears to diffuse radially outward leaving a void at the centre of the laser spot. Exposure with a higher laser power of 48 mW for 10 s leads to further deposition at the periphery of the laser spot resulting in the dark ring of material seen in figure 2c. Closer inspection of the central region enclosed by this ring reveals sub-100-nm diameter particles of material adhering to the plasmonic antennas (figure 2d), which may be the precursor to first stages of nanowire growth as observed in figure 2e. At a laser power of 60 mW and an exposure time of 10 s, extensive material growth is observed on the nanoantenna arrays as seen in the SEM image in figure 2e. Here, an area of approximately $10\text{ }\mu\text{m} \times 15\text{ }\mu\text{m}$ covered by Ge nanowires, microparticles and

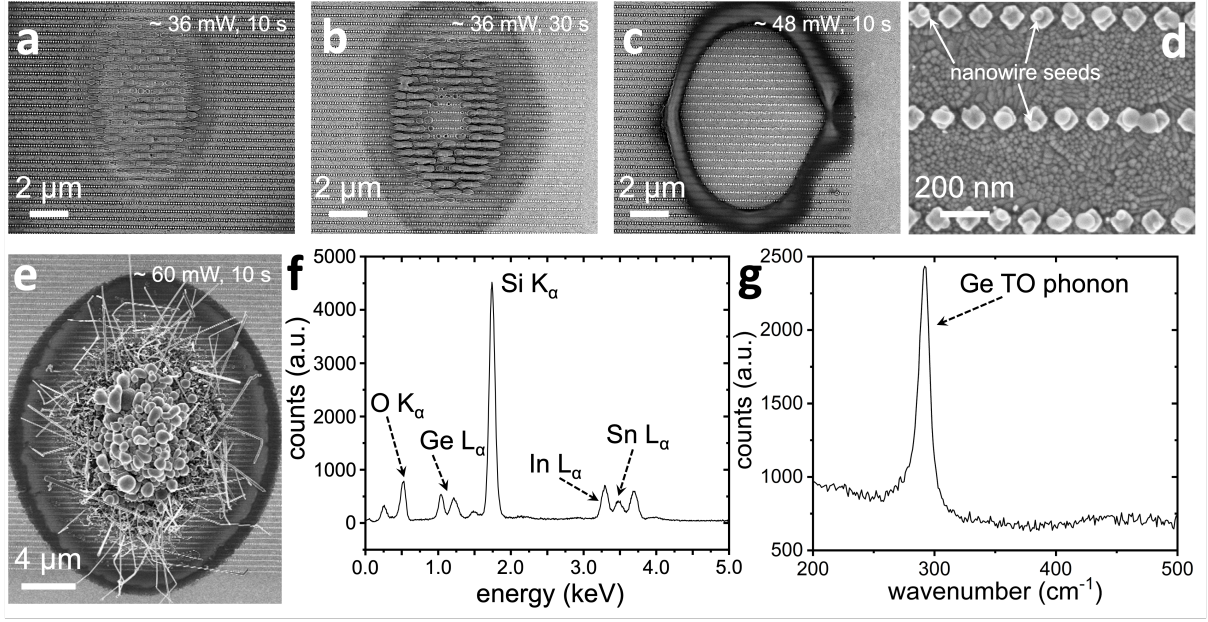


Figure 2: (a,b,c,e) SEM images of Ge-based material grown on Au nanodiamond arrays for a series of different laser powers and exposure times from 36 mW for 10 s in (a) to 60 mW for 10 s in (e). (d) High-magnification SEM image of region at the centre of image in (c) showing sub-100-nm particles that may represent seeds of nanowire growth. (f) EDX spectrum acquired from the material grown in (b) showing Ge peaks associated with the grown material and In, Si, Sn and O peaks associated with the ITO/glass substrate. (g) Raman spectrum of material formed in the centre of (e) showing the Ge transverse optical (TO) phonon mode close to 300 cm^{-1} consistent with the presence of crystalline Ge.

nanoparticles can be seen. It should be noted that exposures of bare regions of the substrate containing no antennas did not yield Ge deposition for the exposure conditions used here. Energy-dispersive X-ray (EDX) analysis and Raman spectroscopy were used to confirm the presence of Ge in the grown material. Figure 2f shows an example EDX spectrum acquired from the material grown in figure 2b and confirms the presence of Ge. Raman spectroscopy of the mass of grown material shown in figure 2g also confirms the presence of Ge and indicates the presence of crystalline Ge given the relative intensity and position of the Ge TO phonon peak in the Raman spectrum.⁶⁰ The large mass and distribution of morphologies of material grown at 60 mW relative to the other lower power exposures indicates that there is a mix of catalyzed nanowire growth and homogeneous pyrolytic growth taking place under these exposure conditions. This is consistent with previous reports of Au-catalyzed

solution-phase growth of Ge nanowires where homogeneous growth of amorphous material is notable at elevated temperatures.^{61,62} To allow further microstructural characterization of the grown material, we decided to fabricate Au nanodiamond arrays on ultrathin (10-nm thick) freestanding SiN_x membranes to allow plasmon-driven growth of Ge nanostructures on a substrate compatible with characterization by (S)TEM. Moreover, given the rapid growth of material with mixed morphologies seen in figure 2e, we sought to establish conditions required for the initiation of catalyzed Ge nanowire growth. Control of nanowire growth from nanogap antennas may open up opportunities to fabricate metal-semiconductor-metal structures that are attractive for future optoelectronic device production.

Figure 3 shows a summary of plasmon-driven Ge nanowire growth on Au nanodiamond arrays fabricated on 10-nm-thick SiN_x membranes. Electromagnetic simulations predicted that nanodiamond arrays with the dimensions shown in figure 3a would give an LSPR centred near 785 nm (dashed red trace figure 3b) in air. The larger diamond sizes relative to those on ITO/glass substrates shown in figure 1 are consistent with a lower effective refractive index expected for the near field of nanodiamonds on the 10-nm-thick membrane relative to the bulk substrate. Since the SiN_x membrane is so thin at 10 nm thickness, the effective refractive index of the medium surrounding the nanodiamonds on the SiN_x membranes is closer to that of air than for those prepared on ITO/glass. Consequently, larger diamonds are required to obtain an LSPR near 785 nm relative to those on an ITO/glass substrate. The solid black trace in figure 3b shows the measured extinction spectrum for the nanodiamond array in figure 3a. The measured spectrum shows a peak for the nanodiamond LSPR at approximately 720 nm, which could be expected to shift to near 770 nm in the growth cell based on measured shifts for LSPR peaks in growth cells relative to air (see figure S2). Additionally, smaller gap sizes were achievable by electron-beam lithography for nanodiamond arrays fabricated on SiN_x membranes compared to ITO/glass substrates, likely due to the reduced proximity effects generated by a freestanding membrane substrate.

Figures 3c-3e show the change in plasmon-driven growth of material produced as a func-

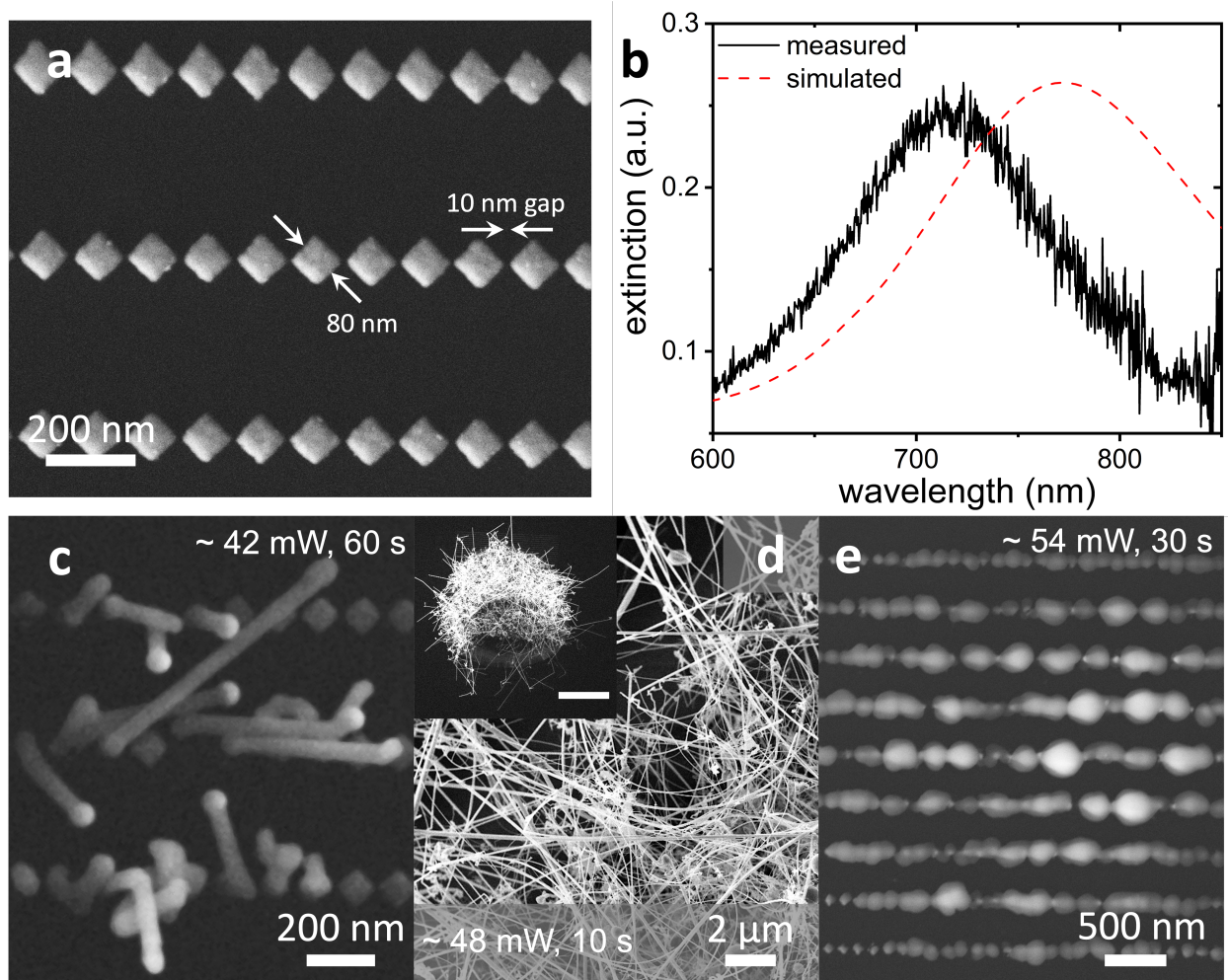


Figure 3: (a) SEM image of Au nanodiamond arrays fabricated on a 10-nm-thick SiN_x membrane. Arrays are composed of squares having an 80-nm-side length and gap width of 10 nm. (b) Experimentally measured (solid black trace) and simulated (dashed red trace) extinction spectra for a nanodiamond array on a 10-nm-thick SiN_x membrane in air. (c) SEM image of short nanowires grown during an exposure with laser power of 42 mW for 60 s. (d) SEM image of mesh of Ge nanowires and nanoparticles grown during a laser exposure at 48 mW for 10 s. Inset, a lower magnification SEM image of the mesh of nanowires (scale bar 10 μm). (e) SEM image of amorphous Ge grown on nanoantenna array during laser exposure at 54 mW for 30 s showing no nanowire growth.

tion of laser power used for excitation. It can be seen from figures 3c and 3d that nanowire growth is stimulated at lower incident laser powers for nanodiamond arrays on the SiN_x substrates (as low as 42 mW) than for those on ITO/glass substrates (60 mW). The lower laser power required for plasmon-driven growth on SiN_x relative to ITO/glass may be explained by the difference in thermal conductivity of the two substrates. Here, we assume

that the process of Ge nanowire growth follows a SLS mechanism as has been reported previously for metal-catalyzed solution-phase growth of Ge nanowires.^{61,63–65} SLS growth of Ge nanowires from Au seed particles requires the dissociation of the Ge precursor compound in solution or at the Au surface followed by diffusion of Ge into the Au seed yielding a liquid droplet at the eutectic composition and temperature (28 at. % Ge and approximately 360 °C from the bulk binary phase diagram of Au/Ge).^{61,66} Further saturation of the Au nanoparticle with Ge then leads to nucleation of solid Ge and subsequent nanowire growth from the liquid seed. The eutectic temperature for the binary system is also known to be size-dependent, with lower eutectic temperatures expected for nanoscale particles.⁶⁷ As such, a threshold temperature >300 °C may support nanowire growth. Photothermal heating of the plasmonic nanodiamond arrays and their surroundings is likely to be more pronounced for substrates having lower thermal conductivities. Given the thickness of the ITO layer (100 nm) in the ITO/glass substrate, the thermal conductivity of the substrate in that case is likely to be dominated by the properties of the bulk glass (thermal conductivity $\kappa_{\text{glass}} = 1.38 \text{ W m}^{-1} \text{ K}^{-1}$). The thermal conductivity of ultrathin 10-nm-thick SiN_x membranes has been reported to be $<1 \text{ W m}^{-1} \text{ K}^{-1}$.^{68,69} Furthermore, we may assume that the thermal conductivity of the liquid diphenylgermane is likely to be similar to other organic liquids *i.e.* $\kappa_{\text{liquid}} \approx 0.2 \text{ W m}^{-1} \text{ K}^{-1}$. Consequently, the thermal conductivities of the systems presented here are expected to be dominated by the substrate properties. Given the expected difference in thermal conductivities of the ITO/glass and SiN_x membrane substrates listed above, one could expect a higher threshold laser power will be required to achieve an equivalent temperature rise on the ITO/glass substrate when compared to the SiN_x membrane. Given the details of the Au/Ge eutectic point listed above, a local temperature increase of $\approx 340 \text{ °C}$ may be required to drive nanowire growth *i.e.* the temperature change required to heat from room temperature to the eutectic temperature of 360 °C. If we compare the laser power required to generated large-scale growth of nanowires, we find a laser power for ITO/glass substrates of 0.06 W (figure 2e), while that for the SiN_x membranes is 0.048 W

(figure 3d). The observed change in the required laser power increasing from 48 mW to 60 mW on changing from an ITO/glass substrate to a SiN_x membrane substrate is consistent with the plasmon-driven photothermal heating model described by Noel *et al.* (see supporting information for more details).³⁶

In figures 3c-3e, an apparent anomaly is observed in that nanowire growth is observed for 42 mW laser exposure and more extensive nanowire growth is observed at 48 mW, however, no nanowire growth is observed at a laser power of 54 mW. At higher laser powers, the growth of amorphous Ge appears to dominate. Additional TEM images and EDX characterization of amorphous material is included in figure S3. This observation may be rationalised by the fact that during the laser exposure, the formation of bubbles in the growth cell was observed (see figure S4). Bubble formation may arise due to diphenylgermane evaporation or decomposition as well as outgassing of air from solution,⁷⁰ and was more likely at high laser powers. The formation of bubbles would lead to local depletion of diphenylgermane concentrations on antennas as well as increased heating due to the creation of a void with lower thermal conductivity. Bubbles were only observed to form when the nanoantenna arrays were brought into the path of the laser beam, indicating that the temperatures needed for bubble formation were only achieved when antennas were illuminated. The increased heating (higher laser power, lower thermal conductivity within bubble) is likely to drive homogeneous nucleation of amorphous material as reported previously,^{61,62} while the lower precursor concentration in the bubble may prevent supersaturation of the Au nanostructures, which is required for SLS nanowire growth. Consequently, care must be taken to limit laser exposure to levels sufficient for nanowire growth, but below thresholds for bubble formation. Accordingly, in the remaining experiments we restricted laser exposure powers and times to initiate nanowire growth and form short nanowires at the locations of nanodiamond antennas.

As stated above, we sought to establish conditions required for the initiation of catalyzed Ge nanowire growth. By reducing the laser power and exposure time from that shown in figure 3c, we were able to achieve exposures where nanowire growth was just initiated as

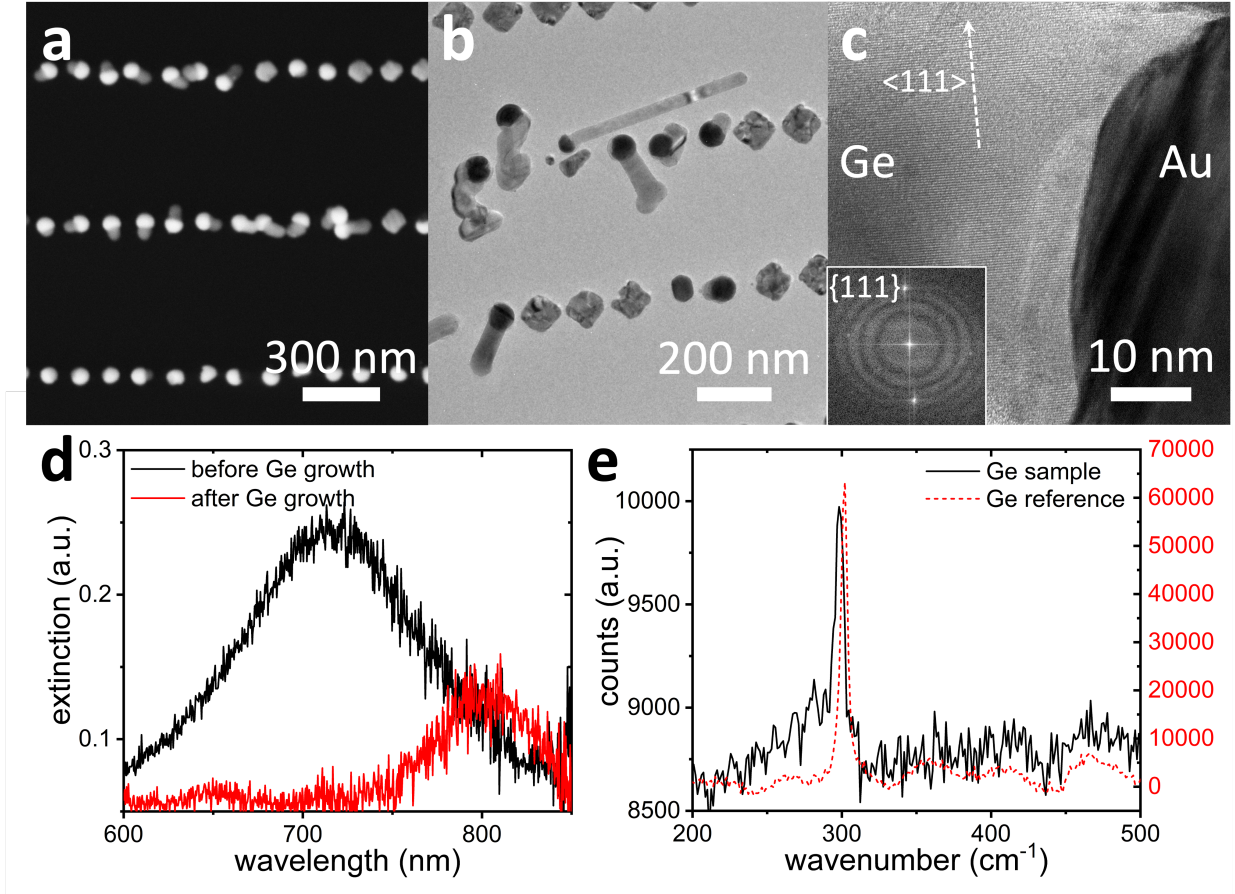


Figure 4: (a) SEM image of short Ge nanowires formed when growth is terminated after 20 s at a laser power of 40 mW. (b) Bright-field TEM image of similar nanowires to those presented in (a) (12 s growth at 40 mW). (c) High-resolution TEM image of Au-Ge interface for one of the nanowires in (b) showing the Ge lattice. Inset, Fourier transform of the HRTEM image of the Ge lattice showing the spatial frequencies consistent with the 111 lattice spacing. (d) Optical extinction spectra of the Au nanodiamond arrays before and after Ge growth for the sample shown in figure 3c. The LSPR peak is observed to decrease in amplitude and red-shift. (e) Raman spectrum of the short Ge nanowires shown in (a), solid black trace, and the reference spectrum of a 40-nm-thick single-crystal Ge thin film on SiO₂, dashed red trace.

shown in figures 4a and 4b. A high-resolution TEM image of a Ge nanowire is shown in figure 4c confirming the crystallinity of the grown nanowires. The Fourier transform shown in the inset of figure 4c was generated from the Ge nanowire region of the TEM image and confirms the single-crystal nature of the region imaged and the relative orientation of the crystal. Figure 4d shows the optical extinction spectra measured for an array of nanodiamond

antennas before and after Ge nanowire growth. The black trace shows the measured spectrum of the nanodiamond array in air before nanowire growth showing the LSPR peak near 715 nm. Following nanowire growth, the LSPR peak decreases in amplitude and shifts to 800 nm. The observed shift is consistent with the formation of a higher index material (Ge) on the antennas. However, the nanodiamond geometry also changes significantly during the growth process as the nanoparticles undergo a solid-to-liquid-to-solid phase change during nanowire growth. The observed reshaping of gold nanoantennas and the presence of Au and Ge in particles at the tips of nanowires seen in figures 4a and 4b (confirmed by EDX, figure S5) are again consistent with photothermal heating of nanoantennas to temperatures near the bulk Au-Ge eutectic temperature of 360 °C. Figure 4e shows a Raman spectrum (solid black trace) of the short Ge nanowires shown in figure 4a. The Raman spectrum of a 40-nm-thick crystalline Ge thin film (Ge on insulator wafer, 40 nm Ge on 145 nm SiO₂ on Si from *IQE Ltd.*) is also presented (dashed red trace). The TO phonon band for the single-crystalline Ge thin film has a peak at 302 cm⁻¹, while the TO phonon band of the short nanowires shown in figure 4a peaks at 298 cm⁻¹ and shows increased broadening consistent with previous reports for Raman spectroscopy of Ge nanocrystals.⁷¹⁻⁷⁴

In summary, we have demonstrated that lithographically defined plasmonic nanoantennas may be used for plasmon-driven, solution-phase growth of crystalline Ge nanostructures at lithographically-defined locations. Nanodiamond antenna arrays were observed to support catalytic growth of Ge nanowires while bow-tie nanoantenna arrays generated conformal amorphous coatings for the range of exposure conditions employed. Substrate thermal conductivity was identified as a key parameter controlling the nanowire nucleation threshold, with SiN_x membranes enabling plasmon-driven growth at lower incident laser powers. Inspection of grown material by TEM confirmed the production of single-crystalline Ge nanowires, while optical spectroscopy, EDX and Raman spectroscopy confirmed the changes in LSPR during the growth process and the production of Ge nanostructures, respectively. A photothermal growth mechanism based on the SLS mechanism was proposed based on exper-

imental observations. The transition from amorphous Ge deposition to crystalline nanowire growth at higher laser powers is consistent with prior reports of thermally-driven Ge nanowire growth. The observation of bubble formation on antenna arrays during laser exposure again supported the achievement of temperature levels needed to support SLS growth as did the observed reshaping of Au nanostructures during laser illumination and the presence of Au-Ge alloys in seed particles of nanowires observed by EDX. Hot-carrier effects cannot be ignored and may contribute in a plasmon-driven growth process. Further polarization-dependent and wavelength-dependent studies could help to elucidate any hot-carrier contribution to present system.

The scalable approach presented here opens a direct path to integrating Ge-based optoelectronic devices into BEOL architectures. Plasmon-driven growth of semiconductor nanostructures enables the generation of local temperatures that support the growth of crystalline semiconductor nanomaterials, while minimizing global heating of the entire substrate. In the present work, we have utilized a continuous-wave 785 nm wavelength laser to drive plasmon excitation and nanomaterial growth. Extension of this work to use low-duty-cycle pulsed laser sources having longer wavelengths would further support minimization of substrate heating. A low-duty-cycle pulsed illumination would allow the substrate to cool between pulses, while a longer wavelength *e.g.* $>1.1\text{ }\mu\text{m}$, would minimize absorption in a Si substrate for example. Consequently, plasmon-driven photothermal heating presents opportunities for localized heating, which is beneficial for the growth of materials in BEOL processes where high temperatures further down the device stack at transistor and via level can be detrimental to device performance. The nanomaterial growth demonstrated here may be further extended to growth on electrically contacted nanoantennas to enable direct fabrication of contacted semiconductor devices.

Acknowledgement

RGH and ROM acknowledge the support of Science Foundation Ireland (SFI) through The Advanced Materials and Bioengineering Research Centre (AMBER, grant 12/RC/2278_2) and the Royal Society-Science Foundation Ireland University Research Fellowship (15/RS-URF/3306). Access to electron microscopy and lithography equipment was provided through the Advanced Microscopy Laboratory at Trinity College Dublin. The authors acknowledge valuable discussions and technical support from Clive Downing, Dr. Raman Bekarevich and Dr. Riley Gatensby. In particular, the authors wish to acknowledge the support provided by Dr. Raman Bekarevich in acquiring some of the TEM images presented here.

Supporting Information Available

SEM images of material grown on bow-tie nanoantenna arrays, optical spectra before and after growth and TEM images of amorphous Ge material grown on nanodiamonds are included in the supporting information available online, as are additional details of the thermal model used to estimate the local temperature on nanoantenna arrays on different substrates.

References

- (1) Koenderink, A. F. Single-Photon Nanoantennas. *ACS Photonics* **2017**, *4*, 710–722.
- (2) Pfeiffer, M.; Lindfors, K.; Zhang, H.; Fenk, B.; Phillipp, F.; Atkinson, P.; Rastelli, A.; Schmidt, O. G.; Giessen, H.; Lippitz, M. Eleven Nanometer Alignment Precision of a Plasmonic Nanoantenna with a Self-Assembled GaAs Quantum Dot. *Nano Letters* **2014**, *14*, 197–201.
- (3) Nicoli, F.; Zhang, T.; Hübner, K.; Jin, B.; Selbach, F.; Acuna, G.; Argyropoulos, C.;

- Liedl, T.; Pilo-Pais, M. DNA-Mediated Self-Assembly of Plasmonic Antennas with a Single Quantum Dot in the Hot Spot. *Small* **2019**, *15*, 1804418.
- (4) Nazarov, A.; Bloom, Y.; Lubotzky, B.; Abudayyeh, H.; Mildner, A.; Baldessarini, L.; Shemla, Y.; Bowes, E. G.; Fleischer, M.; Hollingsworth, J. A.; Rapaport, R. Ultra-fast and Highly Collimated Radially Polarized Photons at Room Temperature from a Colloidal Quantum Dot Coupled to a Hybrid Nanoantenna. *ACS Photonics* **2024**, *11*, 4453–4460.
 - (5) Yuan, L.; Zhou, J.; Zhang, M.; Wen, X.; Martirez, J. M. P.; Robatjazi, H.; Zhou, L.; Carter, E. A.; Nordlander, P.; Halas, N. J. Plasmonic Photocatalysis with Chemically and Spatially Specific Antenna–Dual Reactor Complexes. *ACS Nano* **2022**, *16*, 17365–17375.
 - (6) Frisenda, R.; Navarro-Moratalla, E.; Gant, P.; Pérez De Lara, D.; Jarillo-Herrero, P.; Gorbachev, R. V.; Castellanos-Gomez, A. Recent progress in the assembly of nanodevices and van der Waals heterostructures by deterministic placement of 2D materials. *Chem. Soc. Rev.* **2018**, *47*, 53–68.
 - (7) Engel, M.; Farmer, D. B.; Azpiroz, J. T.; Seo, J.-W. T.; Kang, J.; Avouris, P.; Hersam, M. C.; Krupke, R.; Steiner, M. Graphene-enabled and directed nanomaterial placement from solution for large-scale device integration. *Nature Communications* **2018**, *9*, 4095.
 - (8) Chen, H.; Liu, H.; Zhang, Z.; Hu, K.; Fang, X. Nanostructured Photodetectors: From Ultraviolet to Terahertz. *Advanced Materials* **2016**, *28*, 403–433.
 - (9) Madigawa, A. A. et al. Assessing the Alignment Accuracy of State-of-the-Art Deterministic Fabrication Methods for Single Quantum Dot Devices. *ACS Photonics* **2024**, *11*, 1012–1023.

- (10) Fringes, S.; Schwemmer, C.; Rawlings, C. D.; Knoll, A. W. Deterministic Deposition of Nanoparticles with Sub-10 nm Resolution. *Nano Letters* **2019**, *19*, 8855–8861.
- (11) Chai, Z.; Childress, A.; Busnaina, A. A. Directed Assembly of Nanomaterials for Making Nanoscale Devices and Structures: Mechanisms and Applications. *ACS Nano* **2022**, *16*, 17641–17686.
- (12) Huang, H.; Tian, B.; Chen, Y.; Xia, X.; Cui, X.; Shao, L.; Chen, H.; Wang, J. Coherent Polaritons in WSe₂-Monolayer-Sandwiched Au-Nanodisk-on-Mirror Structures. *ACS Nano* **2025**, *19*, 25284–25294.
- (13) Bitton, O.; Haran, G. Plasmonic Cavities and Individual Quantum Emitters in the Strong Coupling Limit. *Accounts of Chemical Research* **2022**, *55*, 1659–1668.
- (14) Huang, J.; Hu, S.; Kos, D.; Xiong, Y.; Jakob, L. A.; Sánchez-Iglesias, A.; Guo, C.; Liz-Marzán, L. M.; Baumberg, J. J. Enhanced Photocurrent and Electrically Pumped Quantum Dot Emission from Single Plasmonic Nanoantennas. *ACS Nano* **2024**, *18*, 3323–3330.
- (15) Gupta, S. N.; Bitton, O.; Neuman, T.; Esteban, R.; Chuntanov, L.; Aizpurua, J.; Haran, G. Complex plasmon-exciton dynamics revealed through quantum dot light emission in a nanocavity. *Nature Communications* **2021**, *12*, 1310.
- (16) Santhosh, K.; Bitton, O.; Chuntanov, L.; Haran, G. Vacuum Rabi splitting in a plasmonic cavity at the single quantum emitter limit. *Nature Communications* **2016**, *7*, 11823.
- (17) Tame, M. S.; McEneaney, K. R.; Özdemir, c. K.; Lee, J.; Maier, S. A.; Kim, M. S. Quantum plasmonics. *Nature Physics* **2013**, *9*, 329–340.
- (18) Volpe, G.; Noack, M.; Aćimović, S. S.; Reinhardt, C.; Quidant, R. Near-Field Mapping

- of Plasmonic Antennas by Multiphoton Absorption in Poly(methyl methacrylate). *Nano Letters* **2012**, *12*, 4864–4868.
- (19) Cui, X.; Ruan, Q.; Zhuo, X.; Xia, X.; Hu, J.; Fu, R.; Li, Y.; Wang, J.; Xu, H. Photothermal nanomaterials: a powerful light-to-heat converter. *Chemical Reviews* **2023**, *123*, 6891–6952.
- (20) Jang, D.; Yu, S.; Chung, K.; Yoo, J.; Mota, F. M.; Wang, J.; Ahn, D. J.; Kim, S.; Kim, D. H. Direct deposition of anatase TiO₂ on thermally unstable gold nanobipyramid: Morphology-conserved plasmonic nanohybrid for combinational photothermal and photocatalytic cancer therapy. *Applied Materials Today* **2022**, *27*, 101472.
- (21) Ueno, K.; Juodkazis, S.; Shibuya, T.; Yokota, Y.; Mizeikis, V.; Sasaki, K.; Misawa, H. Nanoparticle Plasmon-Assisted Two-Photon Polymerization Induced by Incoherent Excitation Source. *Journal of the American Chemical Society* **2008**, *130*, 6928–6929.
- (22) Hobbs, R. G.; Putnam, W. P.; Fallahi, A.; Yang, Y.; Kärtner, F. X.; Berggren, K. K. Mapping Photoemission and Hot-Electron Emission from Plasmonic Nanoantennas. *Nano Letters* **2017**, *17*, 6069–6076.
- (23) Ding, T.; Mertens, J.; Lombardi, A.; Scherman, O. A.; Baumberg, J. J. Light-Directed Tuning of Plasmon Resonances via Plasmon-Induced Polymerization Using Hot Electrons. *ACS Photonics* **2017**, *4*, 1453–1458.
- (24) Deeb, C.; Ecoffet, C.; Bachelot, R.; Plain, J.; Bouhelier, A.; Soppera, O. Plasmon-Based Free-Radical Photopolymerization: Effect of Diffusion on Nanolithography Processes. *Journal of the American Chemical Society* **2011**, *133*, 10535–10542.
- (25) Shao, F.; Wang, W.; Yang, W.; Yang, Z.; Zhang, Y.; Lan, J.; Dieter Schlüter, A.; Zenobi, R. In-situ nanospectroscopic imaging of plasmon-induced two-dimensional [4+4]-cycloaddition polymerization on Au(111). *Nature Communications* **2021**, *12*, 4557.

- (26) Kameche, F.; Heni, W.; Telitel, S.; Vidal, L.; Marguet, S.; Douillard, L.; Fiorini-Debuisschert, C.; Bachelot, R.; Soppera, O. Probing Plasmon-Induced Chemical Mechanisms by Free-Radical Nanophotopolymerization. *The Journal of Physical Chemistry C* **2021**, *125*, 8719–8731.
- (27) Takahashi, Y.; Furukawa, Y.; Ishida, T.; Yamada, S. Site-selective nanoscale-polymerization of pyrrole on gold nanoparticles via plasmon induced charge separation. *Nanoscale* **2016**, *8*, 8520–8524.
- (28) Baffou, G.; Quidant, R. Nanoplasmonics for chemistry. *Chemical Society Reviews* **2014**, *43*, 3898–3907.
- (29) Jiang, H.; Gordon, R. Nonlinear Plasmonics: Four-photon Near-field Photolithography using Optical Antennas. *Plasmonics* **2013**, *8*, 1655–1665.
- (30) Boyd, D. A.; Greengard, L.; Brongersma, M.; El-Naggar, M. Y.; Goodwin, D. G. Plasmon-Assisted Chemical Vapor Deposition. *Nano Letters* **2006**, *6*, 2592–2597.
- (31) Kamarudheen, R.; Kumari, G.; Baldi, A. Plasmon-driven synthesis of individual metal@semiconductor core@shell nanoparticles. *Nature Communications* **2020**, *11*, 1–10.
- (32) Fujiwara, H.; Suzuki, T.; Pin, C.; Sasaki, K. Localized ZnO Growth on a Gold Nanoantenna by Plasmon-Assisted Hydrothermal Synthesis. *Nano Letters* **2020**, *20*, 389–394.
- (33) Cao, L.; Barsic, D. N.; Guichard, A. R.; Brongersma, M. L. Plasmon-Assisted Local Temperature Control to Pattern Individual Semiconductor Nanowires and Carbon Nanotubes. *Nano Letters* **2007**, *7*, 3523–3527.
- (34) Robert, H. M. L.; Kundrat, F.; Bermúdez-Ureña, E.; Rigneault, H.; Monneret, S.; Quidant, R.; Polleux, J.; Baffou, G. Light-Assisted Solvothermal Chemistry Using Plasmonic Nanoparticles. *ACS Omega* **2016**, *1*, 2–8.

- (35) Wu, B.; Liu, D.; Mubeen, S.; Chuong, T. T.; Moskovits, M.; Stucky, G. D. Anisotropic Growth of TiO₂ onto Gold Nanorods for Plasmon-Enhanced Hydrogen Production from Water Reduction. *Journal of the American Chemical Society* **2016**, *138*, 1114–1117.
- (36) Noel, L.; Khitous, A.; Molinaro, C.; Zan, H.-W.; Berling, D.; Grasset, F.; Soppera, O. Laser Direct Writing of Crystallized TiO₂ by Photothermal Effect Induced by Gold Nanoparticles. *Advanced Materials Technologies* **2024**, *9*, 2300407.
- (37) Di Martino, G.; Michaelis, F. B.; Salmon, A. R.; Hofmann, S.; Baumberg, J. J. Controlling Nanowire Growth by Light. *Nano Letters* **2015**, *15*, 7452–7457.
- (38) Alessandri, I.; Ferroni, M.; Depero, L. E. Plasmon-Assisted, Spatially Resolved Laser Generation of Transition Metal Oxides from Liquid Precursors. *The Journal of Physical Chemistry C* **2011**, *115*, 5174–5180.
- (39) Nishi, H.; Tatsuma, T. Accelerated site-selective photooxidation on Au nanoparticles via electrochemically-assisted plasmonic hole ejection. *Nanoscale* **2019**, *11*, 19455–19461.
- (40) Zhang, Z.; Zhang, C.; Zheng, H.; Xu, H. Plasmon-Driven Catalysis on Molecules and Nanomaterials. *Accounts of Chemical Research* **2019**, *52*, 2506–2515.
- (41) Baffou, G.; Cichos, F.; Quidant, R. Applications and challenges of thermoplasmonics. *Nature Materials* **2020**, *19*, 946–958.
- (42) Baffou, G.; Bordacchini, I.; Baldi, A.; Quidant, R. Simple experimental procedures to distinguish photothermal from hot-carrier processes in plasmonics. *Light: Science & Applications* **2020**, *9*, 108.
- (43) Baffou, G.; Quidant, R. Thermo-plasmonics: using metallic nanostructures as nano-sources of heat. *Laser & Photonics Reviews* **2013**, *7*, 171–187.

- (44) International Roadmap for Devices and Systems (IRDS) International Roadmap for Devices and Systems: 2023 Edition. <https://irds.ieee.org/roadmap-2023>, 2023; Accessed: 2025-07-31.
- (45) Zhu, J. et al. Low-thermal-budget synthesis of monolayer molybdenum disulfide for silicon back-end-of-line integration on a 200 mm platform. *Nature Nanotechnology* **2023**, *18*, 456–463.
- (46) Zhou, Z.-X.; Ye, M.-J.; Yu, M.-W.; Yang, J.-H.; Su, K.-L.; Yang, C.-C.; Lin, C.-Y.; Babicheva, V. E.; Timofeev, I. V.; Chen, K.-P. Germanium Metasurfaces with Lattice Kerker Effect in Near-Infrared Photodetectors. *ACS Nano* **2022**, *16*, 5994–6001.
- (47) Marzen, S.; Postelnicu, E.; Michel, J.; Wada, K.; Kimerling, L. C. High performance germanium on silicon photodiodes for back-end-of-line photonic integration. *Applied Physics Letters* **2023**, *123*, 111105.
- (48) Salamin, Y.; Ma, P.; Baeuerle, B.; Emboras, A.; Fedoryshyn, Y.; Heni, W.; Cheng, B.; Josten, A.; Leuthold, J. 100 GHz plasmonic photodetector. *ACS Photonics* **2018**, *5*, 3291–3297.
- (49) Yang, Y.; Turchetti, M.; Vasireddy, P.; Putnam, W. P.; Karnbach, O.; Nardi, A.; Kärtner, F. X.; Berggren, K. K.; Keathley, P. D. Light phase detection with on-chip petahertz electronic networks. *Nature Communications* **2020**, *11*, 3407.
- (50) McPeak, K. M.; Jayanti, S. V.; Kress, S. J. P.; Meyer, S.; Iotti, S.; Rossinelli, A.; Norris, D. J. Plasmonic Films Can Easily Be Better: Rules and Recipes. *ACS Photonics* **2015**, *2*, 326–333.
- (51) Johnson, P. B.; Christy, R.-W. Optical constants of the noble metals. *Physical Review B* **1972**, *6*, 4370.
- (52) Palik, E. D. *Handbook of optical constants of solids*; Academic press, 1998; Vol. 3.

- (53) Philipp, H. R. Optical properties of silicon nitride. *Journal of the Electrochemical Society* **1973**, *120*, 295.
- (54) Konig, T. A.; Ledin, P. A.; Kerszulis, J.; Mahmoud, M. A.; El-Sayed, M. A.; Reynolds, J. R.; Tsukruk, V. V. Electrically tunable plasmonic behavior of nanocube–polymer nanomaterials induced by a redox-active electrochromic polymer. *ACS Nano* **2014**, *8*, 6182–6192.
- (55) Wagner, R. S.; Ellis, W. C. Vapor-liquid-solid mechanism of single crystal growth. *Applied Physics Letters* **1964**, *4*, 89–90.
- (56) Barth, S.; Hernandez-Ramirez, F.; Holmes, J. D.; Romano-Rodriguez, A. Synthesis and applications of one-dimensional semiconductors. *Progress in Materials Science* **2010**, *55*, 563–627.
- (57) Hobbs, R. G.; Petkov, N.; Holmes, J. D. Semiconductor Nanowire Fabrication by Bottom-Up and Top-Down Paradigms. *Chemistry of Materials* **2012**, *24*, 1975–1991.
- (58) Putnam, W. P.; Hobbs, R. G.; Keathley, P. D.; Berggren, K. K.; Kärtner, F. X. Optical-field-controlled photoemission from plasmonic nanoparticles. *Nature Physics* **2017**, *13*, 335–339.
- (59) Hobbs, R. G.; Yang, Y.; Fallahi, A.; Keathley, P. D.; De Leo, E.; Kärtner, F. X.; Graves, W. S.; Berggren, K. K. High-Yield, Ultrafast, Surface Plasmon-Enhanced, Au Nanorod Optical Field Electron Emitter Arrays. *ACS Nano* **2014**, *8*, 11474–11482.
- (60) Sugiyama, T.; Mishiba, N.; Kamiko, M.; Kyuno, K. Fabrication of crystalline Ge thin films by co-deposition of Au and Ge at low substrate temperatures (<200 °C) without post annealing. *Applied Physics Express* **2016**, *9*, 095501.
- (61) Chockla, A. M.; Korgel, B. A. Seeded germanium nanowire synthesis in solution. *Journal of Materials Chemistry* **2009**, *19*, 996–1001.

- (62) Yang, H.-J.; Tuan, H.-Y. High-yield, high-throughput synthesis of germanium nanowires by metal–organic chemical vapor deposition and their functionalization and applications. *Journal of Materials Chemistry* **2012**, *22*, 2215–2225.
- (63) Lu, X.; Fanfair, D. D.; Johnston, K. P.; Korgel, B. A. High Yield Solution-Liquid-Solid Synthesis of Germanium Nanowires. *Journal of the American Chemical Society* **2005**, *127*, 15718–15719.
- (64) Geaney, H.; Mullane, E.; Ryan, K. M. Solution phase synthesis of silicon and germanium nanowires. *Journal of Materials Chemistry C* **2013**, *1*, 4996–5007.
- (65) Wang, F.; Dong, A.; Buhro, W. E. Solution–Liquid–Solid Synthesis, Properties, and Applications of One-Dimensional Colloidal Semiconductor Nanorods and Nanowires. *Chemical Reviews* **2016**, *116*, 10888–10933.
- (66) Okamoto, H.; Massalski, T. B. The Au-Ge (Gold-Germanium) system. *Bulletin of Alloy Phase Diagrams* **1984**, *5*, 601–610.
- (67) Adhikari, H.; Marshall, A. F.; Goldthorpe, I. A.; Chidsey, C. E. D.; McIntyre, P. C. Metastability of Au-Ge Liquid Nanocatalysts: Ge Vapor-Liquid-Solid Nanowire Growth Far below the Bulk Eutectic Temperature. *ACS Nano* **2007**, *1*, 415–422.
- (68) Braun, J. L. et al. Hydrogen effects on the thermal conductivity of delocalized vibrational modes in amorphous silicon nitride ($a\text{-SiN}_x$: H). *Phys. Rev. Mater.* **2021**, *5*, 035604.
- (69) Scott, E. A.; Lee, H.; Nogan, J. N.; Bethke, D.; Sharma, P. A.; Hopkins, P. E.; Lu, T.-M.; Thomas Harris, C. Suspended Silicon Nitride Platforms for Thermal Sensing Applications in the Limit of Minimized Membrane Thickness. *Journal of Microelectromechanical Systems* **2024**, *33*, 419–426.

- (70) Baffou, G.; Polleux, J.; Rigneault, H.; Monneret, S. Super-heating and micro-bubble generation around plasmonic nanoparticles under cw illumination. *The Journal of Physical Chemistry C* **2014**, *118*, 4890–4898.
- (71) Singh, S.; Rath, D. K.; Kumar, S.; Ahlawat, N.; Sharma, S.; Singh, A.; Pandey, S. C.; Rout, P. S.; Bansal, L.; Sahu, B.; Srivastava, S.; Chondath, S. K.; Chattopadhyay, M. K.; Kumar, R. Abrupt Raman Line-Shape Evolution and Quantifying Short-Range Order Parameter: Laser-Driven Nanocrystallization in Amorphous Germanium. *The Journal of Physical Chemistry C* **2025**, *129*, 13329–13336.
- (72) Jalilian, R.; Sumanasekera, G. U.; Chandrasekharan, H.; Sunkara, M. K. Phonon confinement and laser heating effects in Germanium nanowires. *Phys. Rev. B* **2006**, *74*, 155421.
- (73) Zhang, Y. F.; Tang, Y. H.; Wang, N.; Lee, C. S.; Bello, I.; Lee, S. T. Germanium nanowires sheathed with an oxide layer. *Phys. Rev. B* **2000**, *61*, 4518–4521.
- (74) Biswas, S.; Singha, A.; Morris, M. A.; Holmes, J. D. Inherent control of growth, morphology, and defect formation in germanium nanowires. *Nano Letters* **2012**, *12*, 5654–5663.

TOC Graphic

