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The plasmonic properties of argon cluster-bombarded InP surfaces

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Gas cluster ion beam sputtering has been used to study the self-organising behaviour of In metallic nanoparticles produced by preferential sputtering of phosphorus atoms in InP. Discrete plasmonic In nanoparticles are observed at the earliest stages of surface modification. The surfaces have been investigated *in situ* by reflection electron energy loss spectroscopy, Auger electron spectroscopy, and photoluminescence spectroscopy. By altering the excitation intensity, we observe alterations of the photoluminescence spectrum that are attributed to photoconductive-coupling between In nanoparticles. The devices presented are suitable for visible wavelength surface enhanced Raman spectroscopy and, potentially, offer a route to active all-optical switches. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4993535>]

Ion irradiation of semiconductors for the production of optoelectronic devices continues to receive much attention due to the low cost, high reproducibility, and high throughput achievable.^{1–6} InP, in particular, has been extensively studied, with its use in the mask-less lithographic production of quantum dots,⁷ photovoltaic cells,⁸ and surface-enhanced Raman scattering (SERS) substrates⁹ being reported. Each of these applications utilises the optical properties of self-organising nano-sized surface structures that form post-ion irradiation. However, debate about the composition and properties of these nanostructures is ongoing.

Self organising structures have been previously observed for InP under noble gas ion bombardment by several research groups and is generally attributed to the preferential sputtering of P atoms from the InP surface.^{10–12} Frost *et al.* reported on the roughness evolution of InP within the context of the Bradley-Harper model, which is described as a formation of surface ripples due to competing curvature-dependent sputtering and surface diffusion properties. It was concluded that this could only partially account for the formation of InP mounds and that the preferential sputtering of P atoms could not be ignored.¹³ The enhanced diffusion of In atoms under ion bombardment resulted in the formation of In nanoparticles (NPs) which increases the surface roughness. The production of In NPs by ion irradiation has been subsequently proven by transmission electron microscopy in some cases.⁸ However, it has also been reported that ordered arrays of InP nanodots can result from ion-beam irradiation, which was rationalised by the presence of a broad photoluminescence (PL) peak (~550–700 nm) that is significantly blue-shifted from the near band-edge emission region.⁷ Radny and Gnaser also reported only minimal In enrichment in nanodots prepared by low energy Ar⁺ bombardment when analysed by atom probe tomography.¹⁴

Gas cluster ion beam (GCIB) technology has recently achieved widespread application in surface analysis due to the very low energy per atom interaction achieved. While GCIB

bombardment has been reported to reduce preferential sputtering in some inorganic compound semiconductors when compared to monatomic ion beams,¹⁵ observations of surface chemical damage have still been reported for In-containing compound semiconductors.¹⁶ Additionally, we recently demonstrated visible wavelength SERS using In nanostructures formed by argon GCIB etching of InP substrates.⁹ SERS utilises the resonant excitation of localised surface plasmons to boost the scattering efficiency from samples, suggesting that these materials may possess some interesting plasmonic properties. However, the optical properties of GCIB sputtered InP have yet to be fully explored or understood.

In this letter, we investigate the optical properties of In/InP nanostructures produced by GCIB sputtering. The evolution of the nanostructures as a function of etch time is characterised by helium ion microscopy (HIM), X-ray-induced Auger electron spectroscopy (AES), and reflection electron energy loss spectroscopy (REELS). Excitation intensity-dependent photoluminescence and excitation wavelength-dependent Raman spectroscopy of the resulting nanostructures are also presented in order to elucidate the mechanisms for the aforementioned visible wavelength optical properties.

Samples were prepared by irradiating undoped InP (100) with Ar₃₀₀ clusters (i.e., 300 atoms per cluster) at 8 keV (~27 eV/atom) using a monomer and gas-cluster ion source (MAGCISTM) (mounted inside a Thermo Scientific Theta Probe X-Ray Photoelectron Spectrometer) at an angle of 45°. A total beam current of 5 nA was measured for this particular mode of the ion gun, and the beam was rastered across an area of 1 × 2 mm². The chamber was also equipped with a Thermo iXR Raman spectrophotometer with a 532 nm laser, allowing *in situ* PL analysis, and electron flood gun, which was used to collect REELS.

Figure 1 shows HIM images, obtained using a Zeiss Orion NanoFab, of the InP wafer surfaces after GCIB bombardment. Clearly resolvable features appear after just 10 s of etching. As the etching continues, rounded particles corresponding to In metal nanoparticles are observed that increase in size and decrease in population, though the particle size

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FIG. 1. HIM images of InP surfaces after GCIB bombardment with 8 keV Ar_{300} at 5 nA.

distribution appears narrow after each etch phase. The particles also appear fairly evenly distributed around the substrate.

The GCIB-sputtered InP was studied by AES to observe changes in the surface chemistry as a function of etch time. Figure 2 shows the In MNN edge, which evolves under GCIB bombardment. The spectra consist of a series of well-resolved doublets separated by ~ 7 eV, with the most prominent doublets occurring at 401 eV and 408 eV, which are attributed to InP. Before sputtering, a low kinetic energy shoulder at 397 eV and a corresponding feature at 404 eV are observed but disappear after sputtering. The peak shape and 4 eV shift is consistent with a surface oxide layer.¹⁷ The doublet features at 403 eV and 410 eV are attributed to metallic In. The metallic In appears after sputtering and increases proportionally to the InP until 900 s of sputtering.

FIG. 2. In MNN Auger electron spectra for InP wafer after different durations of GCIB sputtering. Peaks corresponding to metallic indium are observed to increase in intensity relative to InP as the sputtering time is increased.

This correlates well with the HIM images (Fig. 1), which show that the size and distribution of NPs on the InP surface remain largely unchanged after 900 s of GCIB sputtering.

REELS was used to investigate the plasmonic properties of the In-InP structures as a function of GCIB etching time (Fig. 3). Only a broad, high energy emission corresponding to the bulk InP plasmon can be observed before etching. After an etch time of 5 s, a peak appears at 6 eV corresponding to the dipolar (DP) In metal plasmon. The origin of the peak at 6 eV was confirmed by calculating the electron energy loss spectrum for 5 nm In nanoparticles using the boundary element model (BEM) (also shown Fig. 3). Electron energy loss probability calculations were computed using the EELS classes in the MNPBEM toolbox.¹⁸ As the REELS experiments are performed with a broad beam, the width of the electron beam was set to greater than the nanoparticle radius with the impact parameter in the centre of the nanoparticle. The validity of this approach was confirmed by varying the electron beam width greater and smaller than the nanoparticle radius. The spectra remain constant at beam widths greater than the nanoparticle radius. The beam energy was set to 300 eV.

FIG. 3. REELS spectra collected using a 300 eV electron beam for the In nanoparticles *in situ* as a function of etch time. The calculated energy loss probability for 5 nm In nanoparticles in vacuum shows the energy of the dipolar surface plasmon.

In the experimental data, this peak becomes sharper and grows in intensity until etch times >100 s, after which higher order (HO) and bulk modes appear for metallic In as the nanoparticles increase in size. The DP mode appears slightly red-shifted in comparison to the calculated spectrum, which is attributable to the shift induced by the high refractive index InP substrate. However, no shift in the DP mode is observed as a function of etch time. The REELS, in conjunction with the HIM images, confirm the formation of discrete, sub-5 nm, plasmonic indium nanoparticles during the earliest stages of surface roughening.

Figure 4(a) shows the PL spectra of the In/InP nanostructures after 1500 s of GCIB etching. Excitation intensity-dependent PL spectra were recorded *in situ* to prevent oxidation of the In/InP nanostructures and to minimise contamination. The bandgap energy of zincblende InP is 1.34 eV, while for wurzite InP it is 1.42 eV.¹⁹ The wavelength range recorded (Fig. 4) is sufficiently high enough in energy so as to prevent observation of features related to the near-band edge emission. At a maximum irradiance of 14 W/mm², a broad emission is observed from ~ 560 to 650 nm with a peak at 590 nm. This is in agreement with PL previously recorded from ion-beam irradiated InP.⁷ However, as the irradiance is reduced through 2 orders of magnitude to 0.14 W/mm², the intensity of the PL is significantly reduced, and several features become resolvable. First, Raman peaks corresponding to the D and G bands of adventitious carbon are identified [see Fig. 4(b)]. This is attributed to carbon contamination condensing on the sample surface from inside the vacuum chamber. Second, the PL emission undergoes a red-shift to 610 nm.

To probe the near-field enhancement properties of the structures, SERS measurements were made after immersing 1500 s GCIB-etched substrates in 2.5×10^{-4} M solutions of R6G in methanol. An excitation wavelength of 532 nm was

used with an irradiance of 14 W/mm². The results are compared to those obtained from R6G on a bare InP wafer [Fig. 4(c)]. The Raman spectra collected from In/InP structures are the characteristic of R6G. No Raman signal was detected from the bare InP substrate. The Raman-shifted wavelength region under these excitation conditions overlaps with the region of PL emission. The authors argue that these near-field enhancement characteristics in the presence of metallic In nanoparticles suggests that the PL emission is due to surface plasmon-related phenomena.

Although the PL has previously been attributed to the formation of InP quantum dots, our results contradict this conclusion in several qualitative ways. First, the REELS and AES measurements confirm that the nanostructures are indeed metallic In. Second, the near-field enhancement properties observed in the SERS measurements are most commonly attributed to surface plasmons. Additionally, quantum size effects have been found to occur only in sub-5 nm InP nanoparticles, excluding those effects from being observed from ion-beam etched InP nanodots.²⁰

In light of these observations, the authors argue that the photoemission is from photoconductively coupled plasmons. Many reports have assigned the emission to the radiative decay of the surface plasmon^{21,22} and noted a resemblance between the PL and dark-field scattering spectra.²³ It has also been demonstrated that PL emission is sensitive to the coupling of plasmonic structures.²⁴ The PL wavelength modulation observed in Fig. 4(a) can be understood in terms of the photo-excited carrier concentration. Two types of charge carrier-modulated resonances have been proposed for plasmonic nanoparticles bridged by a semiconductor, both resulting in blue-shifts as the carrier concentration increases.²⁵ In capacitively coupled plasmonic systems, a reduction in the Coulomb interaction in the gap due to increasing charge carriers results in a blue-shift of bonding dipolar plasmons

FIG. 4. (a) and (b) Excitation intensity-dependent PL spectra of 1500 s GCIB sputtered InP. (c) SERS of R6G deposited onto GCIB sputtered InP surfaces compared to the InP wafer.

FIG. 5. (a) Excitation wavelength-dependent Raman spectra of 1500 s GCIB sputtered InP. (b) Lorentzian fitting of the LO phonon modes revealing the wavelength-dependence of the Fröhlich mode.

(BDP) due to the reduction in capacitive coupling. In the conducting limit, where the current flow is too great to sustain capacitive-coupling, the BDP resonance will be damped. However, in the conductively coupled regime, an increase in the carrier concentration results in a buildup of charge carriers at the poles of the nanoparticles and hence, an increase in the intensity of charge-transfer plasmons. In Fig. 4(a), the intensity of the peak increases simultaneously with the excitation intensity and peak energy, suggesting that this peak arises due to photoconductive-coupling. Photoconductively coupled plasmonic nanoantennas comprising metallic nanoparticles bridged by a semiconductor have been proposed that could potentially offer a route to ultrafast, compact, and active all-optical switches,²⁵ though this has never been proven experimentally. The observed shifts in the PL emission as a function of excitation intensity suggest that these structures could be suitable for use as optical switches.

As a final test for the presence of size effects in the nanostructured InP, excitation wavelength-dependent Raman spectra of 1500 s GCIB-sputtered InP was performed using a Horiba Jobin Yvon HR800 UV (Fig. 5). The transverse optical phonon (TO) is observed due to symmetry breaking of the crystal at the surface due to the increase in roughness. The second order peaks recorded with both 457 nm and 514 nm excitation wavelengths are similar in appearance. However, the first order longitudinal optical phonon (LO) is significantly asymmetrically broadened in the spectra collected with a 514 nm excitation wavelength when compared to those collected with a 457 nm excitation wavelength. A low frequency shoulder is clearly resolvable with the shorter excitation wavelength that is attributed to a Fröhlich mode. In fact, the asymmetry in the LO peak of both spectra can be well described by fitting pairs of Lorentzian peaks corresponding to the LO and Fröhlich modes [Figs. 5(b) and 5(c)]. Fröhlich modes are observed in porous, heterogeneous materials and considered the dominant electron-phonon coupling mechanism for polar crystals such as InP.²⁶ They also exhibit coupling that is inversely proportional to the difference between the excitation energy and bandgap energy. This is generally quantifiable by calculating the Huang-Rhys parameter S ,²⁷ which in the case of InP is linearly proportional to $2LO/LO$. For excitation wavelengths of 457 nm and 514 nm, S was determined to be 14.5 and 6.4, respectively.

In contrast, the phonon confinement model of Richter *et al.* does not predict the lineshape of LO to alter with the excitation wavelength.²⁸ The authors, therefore, find that the Fröhlich model better accounts for the asymmetry in the LO peak.

In summary, GCIB sputtered InP surfaces have been investigated by HIM, Raman spectroscopy and *in situ* by AES, REELS, and PL. It has been observed that even during the earliest stages of surface modification, discrete plasmonic indium nanoparticles are formed. No evidence for the production of InP nanocrystals has been observed. The photoemission related to these self-organising structures has been shown to promote SERS effects and to be sensitive to the excitation intensity. Consequently, the phenomena are attributed to plasmonic coupling effects promoted by photo-excited carriers in the InP substrate. The devices presented here could find a range of applications including SERS substrates, quantum information devices, or easily be incorporated into InP-based integrated photonic circuits as active all-optical switches. Additionally, the demonstration of tunable, visible wavelength plasmonic properties from materials thought only to produce resonances deep into the UV may open up new horizons for non-noble metal plasmonic materials.

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