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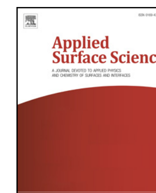

Full Length Article

Observing the evolution of regular nanostructured indium phosphide after gas cluster ion beam etching

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ABSTRACT

Indium phosphide (InP) surfaces develop a pronounced nanostructured texture upon irradiation by energetic ion beams. We have observed the mechanism of nanostructure evolution of InP under irradiation by an Ar gas cluster ion beam (GCIB) using helium ion microscopy (HIM). Initially, metallic indium nanoparticles form on the surface after removal of the top-most oxide layer. These nanoparticles form a mask which shadows the underlying InP. As the ion dose is increased, the masking effect results in substantial nanostructured topography in the form of pillars or nanocones, oriented along the axis of the incident GCIB. The surface sensitivity and high resolution of the HIM facilitates the direct observation of the metallic indium cap at the top of the pillars.

1. Introduction

The impact upon a solid surface by a beam of energetic ions can result in significant topographical and chemical changes along with the ejection of surface atoms and fragments, and implantation effects in the near-surface region. This is put to practical use in surface analysis by secondary ion mass spectrometry (SIMS) where the mass of the ejected fragments is analysed to deduce composition and molecular structure, and in X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES) and SIMS for the removal of unwanted contamination or residues from a surface prior to analysis, or for depth-profiling through a layer or interface by successive etching cycles of surface material during analysis. Prolonged exposure to an ion beam, such as during a sputter depth-profile, can lead to surface structures that have a specific morphological evolution based on an equilibrium between surface roughening (ion erosion) and surface diffusion [1]. This has been demonstrated a number of times on compound semiconductors, and in particular with indium phosphide (InP) [2–5].

Homma et al. [3] observed the preferential sputtering of phosphor from InP under irradiation by monatomic argon ions, coupled with the formation of surface features of the order of 10–100 nm in size depending on beam conditions. The surface morphology that results from such exposure has consequences in analytical depth profiling, where interface depth resolution in a multi-layered stack that includes InP can be degraded [4]. Nanostructured 'cones' were observed by MacLaren et al. and attributed to a surface diffusion effect whereby indium metal is enriched at the surface leading to cone formation due to differential sputter rates of the metallic indium versus InP [5]. This was later supported by Homma who observed a masking effect from particles that exist on the InP surface prior to ion beam etching [6]. Due to the regular and nano-sized structures that could be obtained, these surfaces were subsequently found to be useful for the determination of tip profiles in atomic force microscopy (AFM) [7]. Recently, atom probe tomography has been used to study individual structures on ion-irradiated InP and demonstrated indium enrichment at the surface with very high spatial resolution [8].

Arrays of geometrically optimised InP nanostructures should, in principle, offer highly efficient and cost effective alternatives to planar photovoltaic cells. Employing InP is advantageous as it offers efficient absorption of light in very thin layers, with a favourable match between its bandgap and the peak energy in solar radiation. Indeed Sanatinia et al. demonstrated the applicability of a surface of InP "nanopillars" generated by a nitrogen ion beam [9]. Nanostructured InP surfaces could be a means towards generating efficient nanoparticle-based solar cells. In practice however their large surface area leads to decreased quantum yields due to non-radiative charge recombination pathways via surface defect states [10]. While adequate short circuit currents can be achieved using highly doped nanostructure-array photovoltaics [11],

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achieving high open circuit voltages (V_{OC}) has remained a fundamental issue, with Fermi-level splitting for inorganic semiconductor nanowires typically < 900 meV. Recently we have demonstrated the plasmonic properties of arrays of nanostructured InP, with results showing improvements in the surface enhanced Raman scattering effect from biomolecules, due to the close proximity of the metallic indium nanoparticles. This represents an opportunity to move away from traditional noble-metal SERS substrates to more cost-effective materials [12,13].

The introduction of the gas cluster ion beam (GCIB) into surface analysis represents a step-change in capability, with enhanced sputter yields that are greater for organics versus inorganics enabling selective etch rates [14], and reduced chemical damage that exists in a shallower surface layer than previously [15], much shallower than the information depth of XPS (< 10 nm) for example. Polymer and organic materials can be chemically profiled with high yields and minimal damage [16–18] and the same can be true for inorganics, albeit with markedly lower sputter yields [19–21]. Yet we have observed that for some compound semiconductors preferential sputtering can still occur, and in particular with indium-containing compounds this leads to the formation of an ultra-thin metallic indium layer at the surface [19].

When studying the surface topography of a sputter-etch crater after an XPS or SIMS experiment, AFM is often the first choice. This not only gives a visual representation of the surface, but also metrics on feature size, distribution, height and roughness can be obtained. It is inherently limited, however, when looking at increasingly smaller surface topography by the shape and dimensions of the AFM tip: larger tips simply cannot resolve features much smaller than the tip radius, which might be on the order of 10 nm under ideal conditions. Moreover, high aspect ratio features in the vertical direction, such as those observed on InP, prevent imaging of finer surface details since the tip sidewalls impinge upon neighbouring features. Scanning electron microscopy (SEM) is often another popular choice for studying surface topography on the nano-scale, though it too can be limited in resolution at very high magnification. Helium ion microscopy (HIM) is a relatively new scanning ion microscopy technique that offers a number of advantages over SEM, the most important for the present work being greater resolution at high magnification and increased sensitivity to nanoscale surface topography [22,23].

In this work we investigate the evolution of nanostructures on InP surfaces following argon GCIB depth profiling using HIM as the observation technique. We utilise the high spatial resolution coupled with the surface topographic sensitivity of the HIM to investigate the formation mechanism of these structures, and to extract meaningful metrics about the GCIB etching of the InP.

2. Materials and methods

XPS and ion beam experiments were performed in a Theta Probe XPS instrument (Thermo Scientific, East Grinstead, UK) maintaining a base pressure of 5×10^{-10} mbar. The GCIB was a monomer and gas-cluster ion source (MAGCIS™) capable of delivering monatomic Ar^+ ions at energies of 1–4 keV and Ar_n^+ gas clusters at energies 1–10 keV for n = 75–2000 where n is the centre of the nominal distribution of atoms per cluster. For the present study, Ar_{300} clusters (i.e. 300 atoms

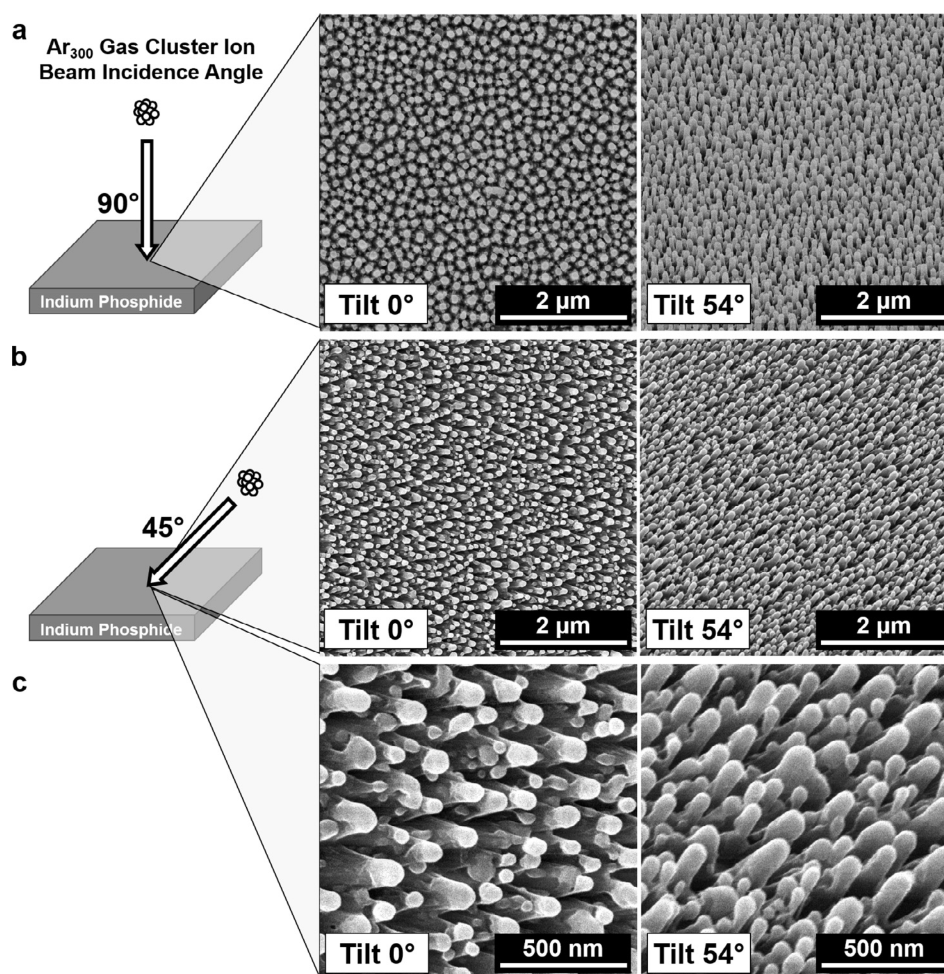

Fig. 1. HIM images of GCIB etched InP surfaces at incidence angles of (a) 90°, (b) and (c) 45°, to the surface plane (indicated by the diagrams to the left of the images). Images were collected at two angles, 0° (top down) and 54°.

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