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In-situ probing of near and below sputter-threshold ion-induced nanopatterning on GaSb(1 0 0)

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This work presents in-situ near and below sputter-threshold studies for GaSb(1 0 0) at energies 50, 100 and 200 eV and current densities near 50 μA/cm². Variation of incident particle energy probes the energy deposition distribution and its relation to surface composition. In-situ analysis is conducted over irradiation modification using Ar singly-charged ions at normal incidence of the surface using complementary techniques including: X-ray photoelectron spectroscopy (XPS) and ion-scattering spectroscopy (LEISS). The former probes 1–3 nm and the latter technique probes the first 1–2 ML or 0.3–0.6 nm. Ex-situ analysis includes HR–SEM to correlated surface morphology with surface composition studied in-situ during irradiation. Results indicate ordering of nanodot formation at fluence threshold of about 10¹⁷ cm². Both XPS and LEISS identify Ga₂O₃ islands formation due to GaSb chemical affinity for oxygen followed by an initial enhancement of Ga/Sb = 1.20 ratio and then a sharp drop in Ga relative concentration with LEISS reaching a Sb-dominated terminating 1–2 nm region corresponding to the implantation depth between 50 and 200 eV. XPS shows a slight enrichment of Ga in sub-surface layers that levels to a 1:1 stoichiometry of the crystalline GaSb(1 0 0) surface.

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1. Introduction

Bottom-up, parallel processing techniques are beginning to rival other nanolithography approaches to nanopatterning [1]. However, much work remains in understanding scaling from short-range to long-range ordering as device features continue to decrease beyond sub-20 nm size. Device feature size introduces limits on ion-beam sputtering (IBS) nanopatterning conditions such as incident particle energy given the penetration range 1–4 nm for energies between 0.05 and 2 keV Ar⁺ irradiation. Therefore as device functionality require dimensions approaching 1–5 nm, understanding nanopatterning at these scales become more important. Applications of quantum dot confinement also introduce scaling limits and motivate systematic study of dot characteristic size against IBS parameters (e.g. ion energy, angle, ion-target interaction, etc.). Correlating in-situ surface composition and sputter erosion evolution to nanostructure synthesis could elucidate on self-organization mechanisms such as the balance between physical sputtering and surface diffusion.

In this work we present a systematic study of near and below sputter-threshold energies between 50 and 200 eV Ar⁺ irradiation at normal incidence of GaSb to examine in-situ the role of surface concentration on nanopatterning. In particular, we conduct in-situ surface characterization of ion-irradiated surfaces during early stage growth (e.g. 10¹⁵–10¹⁷ cm⁻²) of ion-induced nanostructures. XPS and LEISS studies of GaSb irradiated by energetic ions are sparse. W. Yu et al. studied GaSb, InSb and CdSe surfaces with LEISS and XPS; however these were irradiated with Ar⁺ at energies above 3 keV [2]. Another study of GaSb by Möller et al. [3] assessed the role of surface oxides, which for this particular paper it is relevant since the incident particle energy is below 0.2 keV and the implantation is ultra-shallow (<1.0 nm) where oxide coverage needs to be assessed when investigating early stage (low fluence) growth of ion-induced nanostructures on GaSb. The work by LeRoy et al. indicated two possible mechanisms for growth of ion-induced nanostructured pillar features from flat surfaces of Ga–Sb. In particular for GaSb, the segregation of Ga during sputtering as a shield in Ga–Sb erosion. However, Ga and Sb erode near identically due to similar heats of sublimation. In fact for an energy of about 1 keV Ar⁺ on GaSb, the corresponding sputter yields are about: YGa = 1.28 and YSb = 1.25 according to SRIM. Our work elucidates on the important early stages of growth with the strong segregation of Ga to the surface primarily due to the reduction of...
surface oxide followed by a sharp decrease in Ga at the ion-induced amorphous layer with a steady-state Sb-dominant region.

2. Experimental setup

All in-situ modification and characterization was performed at the Particle and Radiation Interaction with Hard and Soft Matter (PRIHSM) facility at Purdue University. PRIHSM is an ultra-high vacuum (UHV) surface science facility with in-situ ion-beam modification and characterization capabilities. Modification is carried out with a gridded broad-beam non-reactive ion source with current densities of up to 40 μA/cm² and energies from 10 to 200 eV. In-situ characterization techniques are carried out using a VG Scienta R3000 charged particle analyzer allowing ultraviolet photoelectron spectroscopy (UPS), angle resolved photoelectron spectroscopy (ARPES), X-ray photoelectron spectroscopy (XPS), and low energy ion-scattering spectroscopy (LEISS). The sample temperature is controllable via a combination of electron-beam heating and liquid nitrogen cooling to achieve sample temperature control up to a maximum of 1150 °C. Surface morphology can be investigated ex-situ using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

Undoped (1 0 0) GaSb samples were cleaned in chemical baths of methanol, distilled water, methanol followed by nitrogen gas drying. Due to high chemical reactivity of GaSb surfaces a thin oxide layer (~4–5 nm) is found with in-situ diagnosis using XPS and LEISS. Surface modification was driven by a normal incidence broad-beam Ar⁺ source from 50 to 200 eV at current densities from 10 to 40 μA/cm². Total fluencies range from $1 \times 10^{15}$ to $1 \times 10^{18}$ cm⁻². Surface composition was measured in-situ pre- and post-irradiation with XPS. For select samples LEISS and XPS were performed at intermediate fluences throughout the irradiation.

XPS was performed at normal emission of photoelectrons with a source-analyzer angle of 54.7°. A non-monochromatic Mg Kα (1245.3 eV) X-ray source was used with an anode voltage of 13.0 kV and an emission current of 15.0 mA. LEISS employing a 1500 eV He⁺ beam was performed at a backscattering angle of 145°. The total probing beam current was 150 nA with a maximum beam flux of $1.4 \times 10^{13}$ cm⁻² s⁻¹. For both XPS and LEISS an analyzer pass energy of 100 eV was used with a 3.0 mm wide straight slit. All samples were cooled to ensure a temperature from 0 to 25 °C throughout the irradiation in order to guard against varying thermal diffusion effects as a function of current density and beam energy. All in-situ work was carried out at base pressures of less than 5 x 10⁻⁸ Torr.

Surface morphology was probed post-irradiation using an ex-situ H4700 Field-Emission SEM. Quantification of XPS spectra into relative surface concentrations was performed using CasaXPS and IGOR Pro v. 6. For LEISS data IGOR Pro software, the background was subtracted from each peak of Ga and Sb and an integral was taken of each resultant, background-subtracted peak. The area from these integrals was used to compare the relative concentration of Ga to Sb as a function of fluence using the formula:

$$y = \frac{A_{Ga}}{A_{Ga} + A_{Sb}}$$

Fig. 1. (a) LEISS spectra shown for 50 eV as a function of Ar⁺ fluence and (b) 100 eV compared to (c) XPS spectra of Ga 2p₃/₂ and (d) Sb 3d₅/₂ and Sb 3d₃/₂ spectra with 100 eV Ar⁺ irradiation as a function of fluence.
where \( A_{Ga} \) and \( A_{Sb} \) are the areas under the curves of Ga and Sb, respectively, and \( \sigma_{Ga} \) and \( \sigma_{Sb} \) are the laboratory cross-sections of Ga and Sb, respectively.

The XPS photoelectron spectra ranged from 350 to 1400 eV. Chemical analysis and elemental concentration was conducted for Ga and Sb along with C and O, the primary impurities present within the system. For quantification at species concentrations, high resolution scans of Ga 3d and Sb 4d peaks were used. The Ga 2p\(_{3/2}\) corresponding to the Ga oxide and Ga–Sb bond was identified as a function of fluence. Similarly, the Sb 3d\(_{5/2}\) peak was used having both the Sb oxide bond and Sb–Ga bond. Bond identification was made based on recent literature on GaSb [3].

3. Results and discussion

Fig. 1 shows the low-energy ion-scattering spectroscopy (LEISS) data for the case of 50 and 100 eV irradiation of GaSb (1 0 0) at normal incidence over the course of irradiation to a cumulative fluence of about \( 10^{18} \) cm\(^{-2}\). Both spectra show a strong backscattering ion signal at pre-irradiation and early stage nanopatterning growth up to about \( 10^{16} \) cm\(^{-2}\) indicative of surface oxide. This is consistent with XPS core level data of Ga 2p\(_{3/2}\) and Sb 3d\(_{5/2}\) for similar fluence level. In Fig. 1c and d the shift from Ga–O bonding and Sb–O bonding is correlated with the LEISS spectra in Fig. 1a and b, where the LEISS peak corresponding to oxygen surface atoms at 600 eV disappears. Ex-situ SEM data showed no distinct dot nanopatterns until a threshold of about \( 10^{17} \) cm\(^{-2}\). The difference in LEISS and XPS spectra is also evidenced by plotting the Ga relative concentration (with respect to Sb) as a function of Ar\(^+\) fluence. Dotted line indicates 1:1 stoichiometry of GaSb. The characteristic size of the ion-induced nanopattern is plotted as a function of energy and compared to Facsko et al. data and (c–e) shows the corresponding SEM nanopatterns for 200, 100 and 50 eV energies, respectively for a fluence of \( 10^{18} \) cm\(^{-2}\). Data in (b) adapted from Facsko et al. 2001 [4].

Fig. 2. (a) LEISS and XPS data are shown for the Ga relative concentration (with respect to Sb) as a function of Ar\(^+\) fluence. Dotted line indicates 1:1 stoichiometry of GaSb. (b) The characteristic size of the ion-induced nanopattern is plotted as a function of energy and compared to Facsko et al. data and (c–e) shows the corresponding SEM nanopatterns for 200, 100 and 50 eV energies, respectively for a fluence of \( 10^{18} \) cm\(^{-2}\). Data in (b) adapted from Facsko et al. 2001 [4].

where \( \sigma_{Ga} \) and \( \sigma_{Sb} \) are the areas under the curves of Ga and Sb, respectively.
conjecture subject to further investigation. Enrichment of Sb on the first monolayer is consistent with high-energy (∼3 keV) irradiation data on GaSb(1 0 0) by Yu et al. Similar behavior is found for InSb. The mechanism described by Yu et al. is primarily linked with Gibbsian surface segregation driving Sb from sub-surface regions (probed by XPS) to the first monolayer due to the lower surface energy of Sb to Ga atoms as Sb is preferentially sputtered during irradiation. Another possible mechanism involves ion-induced surface flows leading to redistribution of Sb eroded over the surface of evolving nanostructures as recently described by Bradley and Shipman [5]. At fluencies between $2–7 \times 10^{17}$ cm$^{-2}$ slight enrichment of Sb is evidenced by XPS. LEISS shows that once nanostructures are stabilized in GaSb, about 60% of the top 1–2 ML is covered with Sb atoms. This is indirect evidence of possible redistribution of Sb atoms likely responsible for the nanopattering instability. It is known that once protruding regions are created in early stage growth, steeper angles of ion implantation could lead to ion-induced shock fronts having propagative mechanisms that stabilize surface morphology [6–8]. Although these studies focused on the “metastability” of flat surfaces, at normal incidence these propagative mechanisms could play a key role over erosion-dominated mechanism given the threshold energies in our work. Early stage growth at threshold and sub-threshold sputtering energies and correlation of nanotopography with ion-modified surface stoichiometry is the subject of continued investigation by our group.

4. Conclusions

Nanopatterning of GaSb(1 0 0) has been studied with in-situ surface characterization during irradiation with Ar$^+$ at energies near and below sputter threshold energy regimes between 50 and 200 eV at normal incidence. Early stage growth examined with the combination of monolayer-sensitive LEISS data and sub-surface XPS data elucidates on the composition-dependent evolution during irradiation and consequent pattern formation. Enrichment of Sb at the first monolayer is driven by ion-induced preferential sputtering, surface energy-driven segregation from sub-surface regions and possibly ion-induced shock fronts leading to redistribution of Sb eroded over the surface of evolving nanostructures.

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