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Toward making layered films using selective ionization in InSb and GaSb laser ablation plumes

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The 308 nm laser ablation of InSb and GaSb has been investigated with the goal being to exert macroscopic control over the ablation plume. By taking advantage of the lower ionization potential of the group III element, In or Ga can be selectively ionized within the ablation plume by a 193 nm (6.4 eV) photon. The ionized species are removed from the plume with an electric field. As shown by x-ray photoelectron spectra, films subsequently deposited are diminished in In or Ga. A three-cycle deposition study demonstrates that a depleted layer of InSb can be deposited between two nondepleted layers of InSb. © *2004 American Institute of Physics.*
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I. INTRODUCTION

Pulsed laser deposition (PLD) has become an increasingly useful method for making thin films.[1–3] Since an ablation laser can generate large powers over small areas, even hard materials such as carbides can be readily introduced into the gas phase with subsequent movement of material to a deposition substrate. However, as PLD processes become more sophisticated, a greater degree of influence over both the ablation and deposition parts of the process is being sought. Such advances will lead to improvements in film morphology as well as one's ability to control dopants.

Historically, experimental parameters such as laser power and wavelength have been utilized as a means of affecting the deposition process.[4] More recently, picosecond and femotosecond lasers have gained success as vehicles for dramatically altering peak laser powers and essentially eliminating all laser/plume interactions,[5–7] such interactions being a feature that nanosecond laser pulses cannot avoid. Additionally, external influences have been implemented via magnetic[8,9] and electric fields.[10,11] In these cases, the external fields can steer and consequently separate small ions from neutrals and large particulates contained within an ablation plume, thereby changing the nature of the plume that ultimately impinges on the deposition surface. Such approaches deepen our appreciation of how PLD processes can be both understood and influenced.

In addition to exerting coarse control over PLD events through the use of electric fields,[10,11] our group has explored how selective ionization can be used to alter the chemical composition of not only an ablation plume[12,13] but a deposited film as well.[14] Specifically, I-III-V targets such as $K_4In_4Sb_6$ were ablated with 308 nm radiation, while 248 nm (5.0 eV) light was used to irradiate the resulting plume.[12] Since K has a 4.34 eV ionization potential (IP),[15] which is much lower than the IP for either In or Sb, the K atoms are selectively ionized. If the selective ionization is done in an electric field, not only is the ablation plume depleted in potassium,[12] but the resulting thin film deposit is significantly depleted in K also.[14]

In the current work, the goal is to make a layered film using selective ionization. The example used is the binary precursor InSb. Procedurally, PLD is used to deposit a thin film. Next, a film is deposited in the same spot during which time selective ionization and removal of In using a 193 nm ionization laser is incorporated. Finally, PLD is employed to deposit a film of InSb in the same spot once again. Characterization with x-ray photoelectron spectroscopy (XPS) demonstrates that a layered film can indeed be constructed.

II. EXPERIMENTAL SECTION

The experimental apparatus shown in Fig. 1 has been described in greater detail elsewhere.[11] Briefly, an ablation laser beam, either the second harmonic (532 nm) of a neodymium-doped yttrium aluminum garnet (Nd:YAG) laser or the output of a XeCl excimer laser (308 nm), impinges on the target substrate. Here, the target is a pressed pellet of InSb or GaSb that is continually rotated to refresh the ablation surface. The ablation laser is either slightly focused or unfocused producing a fluence on the order of 1 J/cm^2 at the ablation surface. A second laser serving as an ionization source (193 nm; ArF excimer laser) is cylindrically focused to a line perpendicular to the target and aimed ~5 mm from the target surface. The ionization laser pulse intersects the ablation plume following a suitable delay from the firing of the ablation laser pulse. Ionized species are then diverted by electric fields (plates biased typically at 500 V), and depending on what is rotated into place, the remaining neutral species propagate toward either a deposition stub or a hole to a quadrupole mass spectrometer (QMS) for detection. Ionization within the QMS is achieved by electron impact.

The III-V compounds used in these experiments were acquired from Aldrich in powdered form and pressed into pellets. The pellets were glued with silver paint to aluminum mounting stubs for use as ablation targets. Blank aluminum stubs served as the deposition substrates. The stubs were filed smooth and cleaned with methanol before being in-

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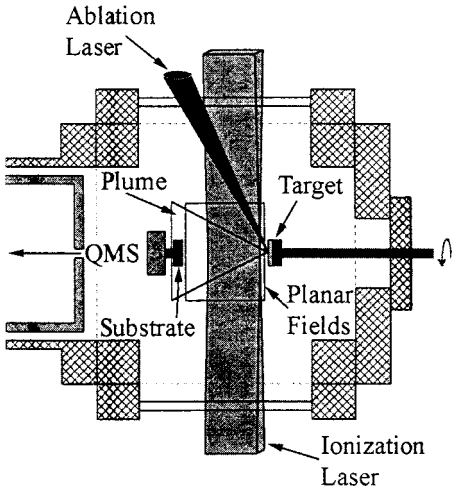

FIG. 1. Drawing depicting the laser ablation and selective ionization region of the experimental system.

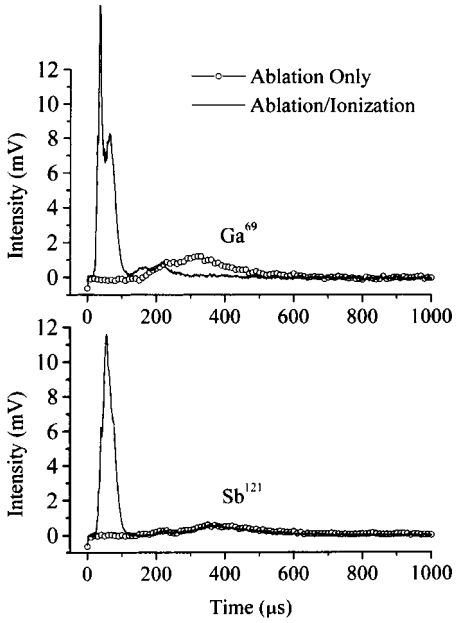

FIG. 2. Time-of-flight spectra for ^{69}Ga and ^{121}Sb as measured by the QMS.

serted into the experimental chamber. After deposition, the deposited samples were transferred to a surface analysis chamber via a vacuum suitcase[11] so that no direct exposure to atmosphere was involved. Note, however, that the vacuum suitcase is only a high vacuum device, not an ultrahigh vacuum device. Consequently, the substrates do not remain perfectly clean during transport.

X-ray photoelectron spectroscopy was used to characterize the ablation targets and thin film deposits. This technique is sensitive to the outermost layers of the surface (roughly 1 nm), but when coupled with argon ion etching, it can provide an approximate depth profile throughout the entire film. All XPS spectra were taken with a VG ESCALab MK II surface analysis instrument equipped with an Al/Mg twin anode x-ray source and an AG21 argon ion gun. The XPS spectra were taken using Al $K\alpha$ radiation (1486.6 eV) in a constant analyzer energy mode. Samples were introduced into the chamber and spectra taken without any further purification. The samples were then etched with the argon ion gun for 10 s and another XPS spectrum was taken immediately. This process was repeated until the ratio of the peaks remained relatively constant from scan to scan or, as in the case of the films, a spectrum began to show signs of the underlying aluminum substrate. It was in this way that a depth profile of a sample was obtained.

III. RESULTS

Figure 2 presents time-of-flight traces of ^{69}Ga and ^{121}Sb resulting from the 308 nm ablation of GaSb under conditions of (1) ablation only and (2) ablation followed by 193 nm laser ionization. Note that the ionization laser produces a very large signal in the early part of the spectrum for both the ^{69}Ga and ^{121}Sb features. Since this peak is generated even in the absence of the laser ablation pulse (not shown), we attribute the peak to some type of photoscattering event producing a direct impingement on the detector in the QMS. More significantly in Fig. 2, the later features in the spectra are due to neutral species being ionized in the detection region of the QMS, and the ^{69}Ga spectrum clearly shows a significant decrease in the neutral atom signal when the ionization laser is introduced. The ionization laser is definitely affecting the ablation plume by clearly reducing the Ga signal, and this effect occurs well before the plume reaches the QMS. On the other hand, the ^{121}Sb neutral atom signal shows little effect due to the 193 nm light. Since the ionization potentials for Ga and Sb atoms are 6.00 and 8.64 eV, respectively,[15] it is not surprising that the 193 nm (6.4 eV) light induces the observed behavior. In Fig. 3, experimental results analogous to those depicted in Fig. 2 are shown, except in Fig. 3 the target is InSb instead of GaSb. Once again, the lower IP for the group III atom (In, IP=5.79 eV) (Ref. 15) manifests itself as a significant reduction in the In neutral signal when the 193 nm ionization laser is used.

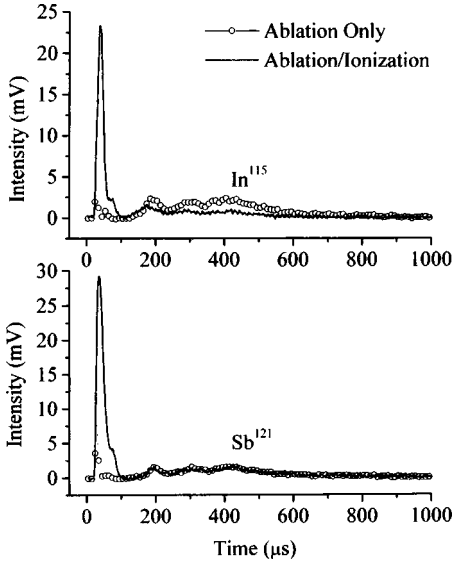

FIG. 3. Time-of-flight spectra for ^{115}In and ^{121}Sb as measured by the QMS.

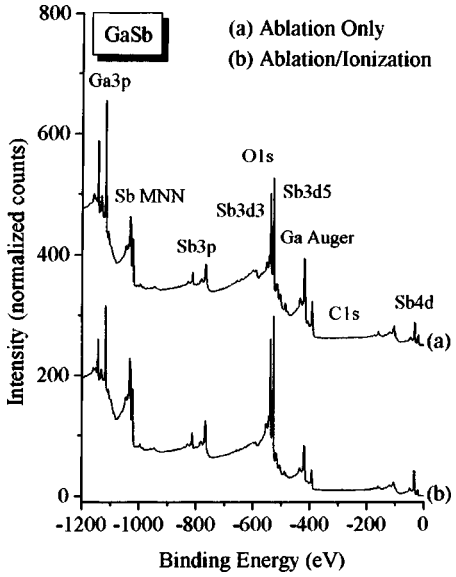

FIG. 4. XPS of GaSb films generated by (a) ablation only and (b) ablation followed by the selective ionization of Ga. Note that *p*, *d*, *d*3, and *d*5 denote $P_{1/2}$, $D_{1/2}$, $D_{3/2}$, $D_{5/2}$, respectively.

While Figs. 2 and 3 clearly demonstrate that one can use an ionization laser to selectively alter the intensity of the neutral In or Ga present in the ablation plume, it is another matter to macroscopically deplete the relative amount of In or Ga that deposits on a substrate. Figure 4 shows XPS spectra for GaSb ablation and subsequent thin film deposition in two distinct situations. In case (a) no ionization laser was used, while in case (b) the ionization laser was used to reduce the Ga/Sb ratio in the ablation plume. The resulting XPS spectra show that the deposited film has a Ga/Sb ratio clearly diminished when the ionization laser is used. For example, the Ga($3P_{1/2}$) feature is significantly reduced, while the signal due to an Sb($3P_{1/2}$) electron remains virtually unchanged when the ionization laser is used. In Fig. 5, an analogous situation has occurred in the case of InSb deposition. When the ionization laser is used, the In($3P_{1/2}$) feature is diminished while the Sb($3P_{1/2}$) signal remains unchanged. Note that typical growth rates with the lasers operating at 20 Hz were ~10 nm/h; thus a 2 h run produced a film ~20 nm thick.

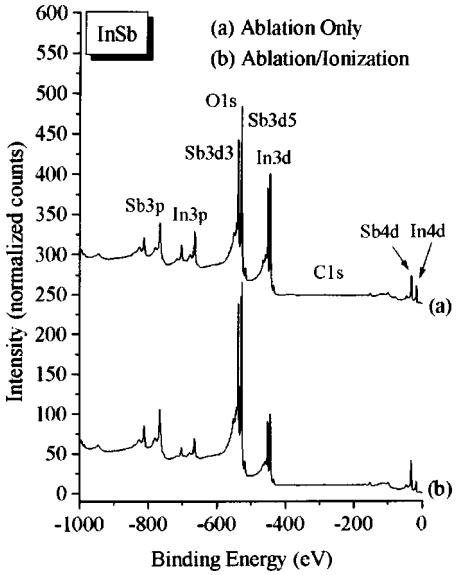

FIG. 5. XPS of InSb films generated by (a) ablation only and (b) ablation followed by the selective ionization of In. Note that *p*, *d*, *d*3, and *d*5 denote $P_{1/2}$, $D_{1/2}$, $D_{3/2}$, $D_{5/2}$, respectively.

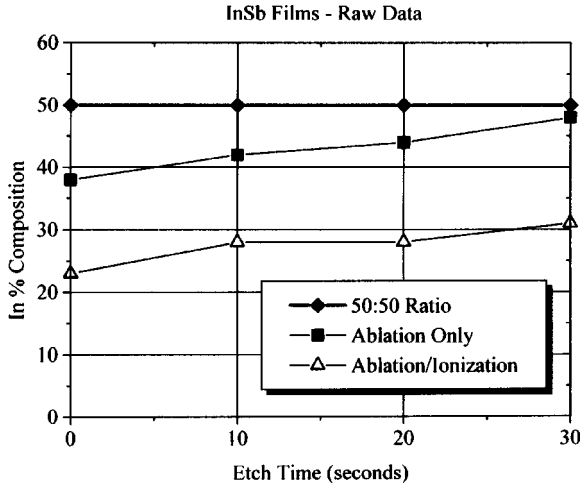

FIG. 6. Graph of XPS data used to provide systematic corrections for argon ion etching effects.

For both GaSb and InSb, the effect of the laser ionization beam in a typical experiment is to change the stoichiometry from 50/50 to ~30/70 in terms of Ga or In reduction. Note, however, that care had to be taken when interpreting both In/Sb and Ga/Sb ratios via XPS when a sample had not been initially cleaned (i.e., etched) by the argon ion gun. Even the starting pellets (not shown) with known 50/50 ratios displayed changing ratios until the third cycle of cleaning (~30 s of total etching). Beyond this time period, all subsequent ratios were constant. The root of this effect is unclear to us, but the net result was to produce anomalously high Sb values in unetched samples, be they bulk pellet or deposited film. Fortunately, since our main concern is looking at relative changes in the In/Sb or Ga/Sb ratios, we could normalize the data over the first few etching cycles. For instance, to calculate the normalization factors for the InSb pellet films, the In($3D_{5/2}$) and the Sb($3D_{5/2}$) peaks were used. We assumed that when no ionization laser was used a 50/50 stoichiometry was transferred from pellet to film. Consequently, we could correct the observed In/Sb ratio (after taking into account sensitivity factors) to a 50/50 stoichiometry after each etching cycle. When the ionization laser was actually used, the correction factors as a function of etching time had already been established.

Results for a typical InSb film are shown in Figs. 6 and 7. By normalizing the raw data, one can see that the removal rate when the ionization laser is used is, in fact, fairly constant. From the raw data in Fig. 6, one can see that a 50/50 ratio is observed after the third etching cycle in the ablation only film. Beyond 30 s, additional adjustments were not needed.

In order to test our ability to effect layering in a film, InSb was chosen as the target and the following experiment

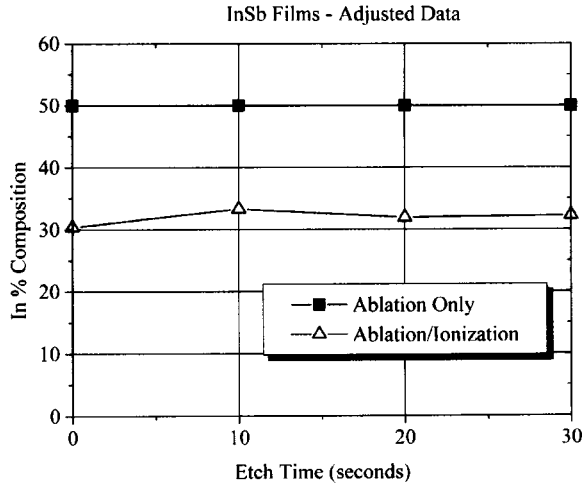

FIG. 7. Graph of In/Sb ratio as a function of depth after accounting for argon ion etching effects.

performed. First, a film was deposited under ablation only conditions. After the ionization laser was turned on, a second layer was deposited using the ablation/ionization process. Finally, a third layer was deposited using the ablation laser only. Each of the three layers was deposited for approximately 3 h at an estimated deposition rate of ~3 nm/h, thereby yielding a film with a ~30 nm thickness. The results of the depth profile are shown in Fig. 8, where one can clearly infer a 50/50 In/Sb ratio in the upper layers, a significant drop in the middle to a ratio of ~40/60, and a return to 50/50 in the bottom layers. Note that the profile has a slight asymmetric appearance. We attribute this asymmetry, in part, to experimental uncertainty brought about by the normalization procedure described above. This procedure is necessary for the first three etching cycles (30 s of etch time), so it is not too surprising that the first half of the depth profile in Fig. 8 is more uneven than the latter half.

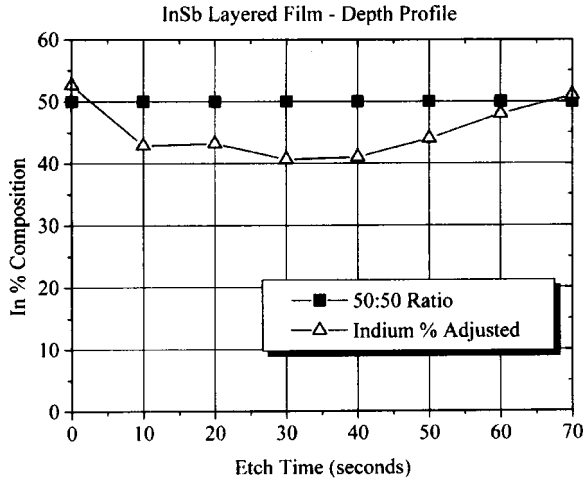

FIG. 8. Graph of In/Sb ratio as a function of depth after accounting for argon ion etching effects. Three film layers have been deposited. The first and last used no ionization laser. The middle layer used an ionization laser to selectively ionize and remove In.

IV. DISCUSSION

Figures 2 and 3 are important because they demonstrate that 193 nm (6.4 eV) radiation can selectively ionize and remove Ga (IP=6.00 eV) and In (IP=5.79 eV) from ablation plumes of GaSb and InSb, respectively, with the Sb (IP=8.64 eV) neutral component remaining virtually unchanged. In principle, such ''filtering'' capabilities based on photon energy versus IP seem straightforward. In practice, having an IP below the laser photon energy does not always mean that a species will avoid being removed by the ionization laser. For example, 248 nm (5.0 eV) laser radiation can ionize K (IP=4.34 eV) in an ablation plume of $K_3Ga_3As_4$, but it will also ionize and remove a comparable amount of As (IP=9.81 eV) (Ref. 15) in the form of As_2 through a strong electronic resonance at 248 nm.[13,16] In contrast, 266 nm (4.6 eV) radiation misses the As_2 resonance but still is above the IP of K and indeed will selectively ionize and remove K atoms.[13] As shown in Figs. 2 and 3, the neutral Sb signal seems relatively unaffected by the 193 nm ionization laser. In other words, no unexpected spectroscopic resonances for Sb or Sb_2 are occurring.

Establishing that selective ionization will deplete an ablation plume is one thing; showing that such depletion will manifest itself macroscopically in a thin film is another. Figures 4 and 5 demonstrate that films significantly depleted in In or Ga can be generated. The reduction value of ~30/70 for the In/Sb ratio of Fig. 7 (in contrast to the 50/50 starting stoichiometry) is not necessarily optimized, meaning that lower values are quite possibly obtainable. Both the ionization and ablation laser beam characteristics are important here including energy, wavelength, pulse duration, etc. If the ablation pulse is too intense and creates a preponderance of ions, most of the ablated material will be diverted by the electric fields. On the other hand, a weak ablation pulse will simply move too little material, making thin film growth times intolerably long. More work is needed in order to find optimal conditions for selective removal of the In species.

Being able to generate a depleted film is the starting point for making layered films, but characterizing these layered films through depth profiling is a significant task. Our choice of using the argon ion gun to essentially dig through the film is an admittedly coarse one. However, since the samples had to be cleaned anyway (see Fig. 6), and XPS data could be obtained immediately in the adjacent chamber of the ESCALab, it seemed to be a reasonable method for determining whether or not layered films could be made in the fashion that we had planned.

Figure 8 demonstrates that a crude layered structure can indeed be generated using selective ionization, i.e., the film goes from 50/50 to 40/60 then back to 50/50 with regard to its In/Sb ratio as a function of film depth. Note, however, that the middle region ''dip'' goes to an In/Sb ratio of only 40/60, not 30/70 as shown in Fig. 7. We attribute this result to the argon ion beam acting in somewhat of a ''churning'' fashion, as opposed to a more ideal ''slicing'' fashion, as it interrogates the film stoichiometry as a function of film depth. The sharpness of the actual layering is unclear for now.

Nonetheless, what is clear is that one can alter ablation plumes in an understandable way during film growth with these binary systems.

Finally, one can envision the overall approach having application in different ways. For example, decreasing the intensity of the ionization laser would generate a smaller dip in the In/Sb ratio. If the intensity of the laser were slowly increased, one could see a In/Sb gradient across the depth of the film ranging from 50/50 at one end to 40/60 at the other end. On the other hand, one could start at 40/60 and slowly decrease the laser intensity to achieve a 50/50 ratio at the opposite end. Also, it should be noted that the method is not restricted to InSb and GaSb systems. By taking advantage of differential ionization potentials and the correct choice of laser wavelengths, a variety of systems should be amenable to influence by this approach. Consequently, our ability to exert control over ablation plumes and their associated films should continue to improve.

ACKNOWLEDGMENTS

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