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Hydrogen interaction with Sb-terminated GaAs and InP (110) surfaces

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The interaction of atomic hydrogen with InP(110) and GaAs(110) surfaces terminated with a well-ordered antimony monolayer was investigated using spectroscopic ellipsometry and Raman spectroscopy. The characteristic features of the surface dielectric function associated with the Sb monolayer and the Raman lines from the excitation of surface vibrational modes disappear with increasing hydrogen exposure, indicating the etching of the Sb monolayer. No additional structure in the surface dielectric function and no shift in the phonon frequencies were detected during the etching process. By comparing the experimental results with *ab initio* calculations we conclude that the etching of the Sb monolayer starts at defect sites of the Sb monolayers and then propagates through the Sb surface chains.

I. INTRODUCTION

Antimony forms well-ordered pseudomorphic (1×1) monolayers on the (110) surfaces of InP and GaAs (hereafter denoted as InP:Sb and GaAs:Sb, respectively).[1] The ease of preparation and the relative simplicity of these Sb-terminated surfaces make them an ideal system for the investigation of the electronic structure of monolayer adsorbates. The Sb monolayer introduces surface states and resonances near the band edges of the (110) III-V semiconductor surfaces. An extensive description of the surface band structure is found in Refs. 2, 3, and 4. The near-gap surface states are very similar for all Sb-monolayer terminated III-V substrates and arise from the bond between the Sb chains and the first substrate layer.[2–7] In recent years, pure optical techniques such as spectroscopic ellipsometry[5] (SE), reflectance difference spectroscopy,[6–9] and Raman scattering[10–12] have been used to probe the optical and vibrational properties of these III-V (110):Sb surfaces. The vibrations of surface Sb atoms have been the subject of several theoretical[13–15] and experimental investigations.[10–12]

Hydrogen chemisorption constitutes the simplest system for studying the effects of gas-phase adsorbates on the surface atomic and electronic structure. In addition, a strong technological motivation arises from the fact that hydrogen is used in different technological processing steps of III-V semiconductors such as etching and chemical vapor deposition.[16] The hydrogen interaction with GaAs(110) and InP(110) surfaces has been studied by different methods such as Auger electron spectroscopy,[17] photoemission spectroscopy,[18–20] high-resolution electron energy-loss spectroscopy (HREELS),[21–23] and by temperature-programmed desorption.[24–26] The influence of hydrogen on the optical properties of these surfaces has been investigated by spectroscopic ellipsometry and by differential reflection spectroscopy.[27,28]

In this contribution we have used SE and Raman spectroscopy to investigate the preparation of InP:Sb and GaAs:Sb (110) surfaces and their interaction with atomic hydrogen. To our knowledge, this is the first report on the interaction of atomic hydrogen with Sb-terminated surfaces. The features of the surface dielectric function associated with the Sb monolayer and the Raman lines from surface phonons reduce in intensity and eventually disappear with increasing exposure to atomic hydrogen. This effect is attributed to the etching of the Sb monolayer. No energy shift of the phonon lines or of the features of the surface dielectric function was observed during etching. The experimental results are compared with *ab initio* calculations of the surface electronic structure and vibrational modes for a hydrogen-terminated GaAs:Sb surface. On the basis of this comparison we conclude that the Sb monolayer is removed before a hydrogen-terminated surface is formed on the III-V:Sb surface.

II. EXPERIMENTAL DETAILS

The studies reported here were performed in a UHV chamber (base pressure $< 10^{-9}$ mbar) equipped with special windows for the optical measurements.[29] The preparation and the subsequent hydrogen-induced modifications of the Sb monolayers were monitored by recording the ellipsometric pseudodielectric function, $\langle \varepsilon \rangle$, and the Raman spectrum of surface phonon modes. The ellipsometric measurements were performed using a rotating analyzer ellipsometer with a 22-cm focal length monochromator (Spex 1680) and photomultiplier detection. The plane of incidence of the incoming light was

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aligned halfway between the $x = [001]$ and $y = [0\bar{1}1]$ principal axes of the surface. This configuration yields, to a good approximation, the average of the dielectric tensor components along these two directions.[30] The wavelength resolution of the ellipsometric measurements, determined by the monochromator slit widths, and angle of incidence, were set to 2.25 nm and 67.5°, respectively. The Raman spectra were recorded in the backscattering geometry using the $\lambda = 514.5$ nm line from an Ar^+ laser as the excitation source. In order to reduce surface heating due to light absorption, the laser beam (~ 100 mW) was focused on the sample using a cylindrical lens. The scattered light was analyzed by a 1-m double spectrometer (Jarrel-Ash 25-100) with photon counting detection.

III. RESULTS

Typical SE and Raman spectra during the different preparation stages of (110) InP:Sb are illustrated on the left and right panels of Fig. 1, respectively. Similar qualitative behavior was also observed for GaAs:Sb(110) surfaces and will not be discussed in detail here. The undoped InP substrates were initially cleaved in UHV in order to expose a clean (110) surface. The imaginary part of the dielectric function ($\langle\varepsilon_2\rangle$) of the pristine cleaved surface is indicated by the thin lines on the left panel of Fig. 1. The ellipsometric spectra display maxima near the critical point energies $E_1 = 3.15$ eV, $E_1 + \Delta_1 = 3.30$ eV, and $E_0' = 4.7$ eV (with a high-energy shoulder assigned to the $E_2 = 4.96$ eV and $E_0' + \Delta_0' = 5.17$ eV transitions[31]) of the InP substrates, indicated by the vertical dot-dashed lines in Fig. 1 (left panel).[32] The Raman spectrum of the clean surface (not shown in Fig. 1) reveals a single line at 305 cm^{-1} related to the excitation of zone-center TO phonons. The subsequent evaporation of a 10–15-Å-thick Sb layer leads to drastic modifications in $\langle\varepsilon_2\rangle$, as indicated by the thick line in Fig. 1 (left panel). The increase in $\langle\varepsilon_2\rangle$ in the low-energy range (<4 eV) is consistent with the metallic character of the Sb layer. The Raman spectrum [Fig. 1(a), right panel] reveals a broad structure centered at 150 cm^{-1} associated with amorphous Sb.[33] Note that the thin Sb film is partially transparent and the characteristic features of the substrate dominate the ellipsometric spectra in Fig. 1(a).

The samples were then annealed at 120 °C for a few minutes in order to crystallize the amorphous Sb layer. The crystallization is evidenced by the appearance of additional lines in the Raman spectrum of Fig. 1(b) (right panel), which was recorded with incident and scattered polarizations halfway between the [001] and

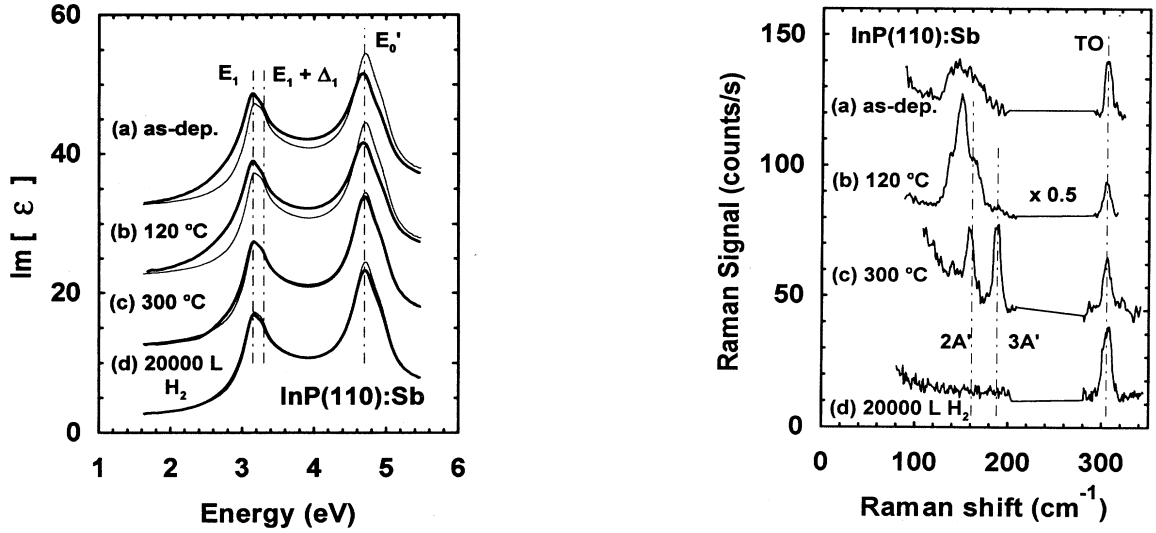

FIG. 1. Imaginary part of the dielectric function, $\mathrm{Im}[\langle\varepsilon\rangle]$ (thick lines on the left panel; the thin lines represent the results for the pristine cleaved surface) and Raman spectra (right panel) of (110) InP:Sb surfaces (a) after evaporation of a 15-Å-thick Sb monolayer and after subsequent thermal annealing at (b) 120 °C and (c) 300 °C, leading to the formation of a well-defined surface monolayer. (d) displays the corresponding spectra after a 20 000-L exposure of the Sb-terminated surface to atomic hydrogen. The vertical dot-dashed lines on the left panel indicate the position of the critical points E_1, $E_1 + \Delta_1$, and E_0' of bulk InP. The spectra on the left (right) panel are shifted vertically with respect to each other by 10 units (40 counts/s). The structures indicated in the right panel by $2A'$ and $3A'$ correspond to the excitation of surface phonons associated with the Sb monolayer. The Raman spectra in (a) and (b) were recorded for incoming and outgoing polarization halfway between the $x = [001]$ and $y = [1\bar{1}0]$ surface axes $[z(x+y, x+y)\bar{z}$ configuration]. In (c) and (d) the incoming and outgoing polarization lie along the $y = [1\bar{1}0]$ axis $[(y, y)$ configuration].

[1$\bar{1}$0] surface axes. This configuration, hereafter denoted $z(x+y, x+y)\bar{z}$, allows the observation of modes with both diagonal and nondiagonal Raman tensor components. The line at 148 cm^{-1} with shoulders at 134 and 161 cm^{-1} has been previously assigned to the vibrational modes of a substrate-stabilized crystalline phase of Sb.[8] Interestingly, the pseudodielectric function is almost insensitive to the structural modification with $\langle \varepsilon_2 \rangle$ remaining essentially unchanged after this low-temperature annealing step.

In order to expose the first Sb monolayer grown on the substrate the samples were further annealed to 300 °C for approximately 10 min to desorb the excess Sb.[7] The desorption of the Sb film was detected by monitoring the pressure changes in the UHV recipient and the modifications in the Raman and ellipsometric spectra as the temperature was increased to 300 °C. The Raman spectrum recorded in the $z(y,y)\bar{z}$ configuration [Fig. 1(c) (right panel)] displays additional lines (indicated by $2A'$, and $3A'$) associated with the vibrational modes of an epitaxial Sb surface monolayer on the InP substrate[10] (the notation used here to describe the surface modes is the same as in Refs. 9, 10, and 13). We also observed an additional mode (A'') at 161 cm^{-1} in spectra recorded in crossed polarization, i.e., $z(x,y)\bar{z}$ configuration (not shown here). The scattering intensity of these surface modes is comparable to that of the TO substrate phonon.[10] The dielectric function [Fig. 1(c) (left panel)] resembles that of the cleaved surface except for modifications near the critical point energies and in the energy range between 2 and 3 eV, which are attributed to electronic transitions associated with the Sb-covered surface (see discussion below).[3,9]

To access the surface electronic properties we calculated the surface excess function, SEF [see Eq. (11) in Ref. 34] from the ellipsometric data displayed in Fig. 1(a). The SEF (in units of length) corresponds to the difference between the dielectric function of the Sb-covered surface and that of the clean surface, multiplied by the effective thickness of the surface layer. Since in this manner the substrate contribution is eliminated, the SEF directly reflects the changes in the surface optical properties. The imaginary part of the SEF of (110) InP:Sb is displayed in Fig. 2(a) (left panel). The structures S_A (2.05 eV) and S_B (2.63 eV) are associated with the Sb monolayer. They have been previously identified in the reflectance difference spectra and assigned to transitions involving surface states and surface resonances.[7] The minima in Im(SEF) near the InP critical points E_1, $E_1+\Delta_1$, and E_0' evidence the reduction of oscillator strength of these substrate-specific transitions, when the surface is covered by the Sb monolayer.

The interaction of the InP:Sb and GaAs:Sb surfaces with hydrogen radicals was investigated by monitoring the changes in the ellipsometric and Raman spectra induced by hydrogen exposure. Pure molecular hydrogen was introduced in the UHV chamber and the formation of active radicals was achieved by decomposition of the molecular species in a hot tungsten filament located ~ 5 cm away from the Sb-terminated surfaces. The exposure doses will be expressed in Langmuirs, L, of molecular hydrogen (1 L=10^{-6} Torr sec). The changes induced in the dielectric function and in the Raman spectra after a high hydrogen exposure (20 000 L) are illustrated in Fig. 1(d). The main effect of hydrogen exposure is to remove the Sb-related contribution to the dielectric function be-

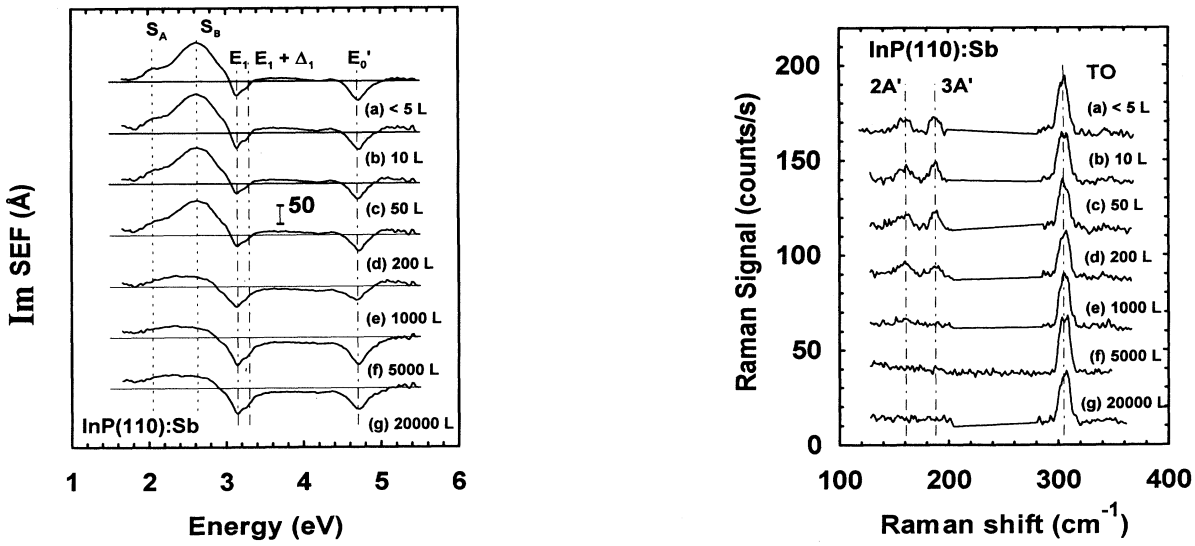

FIG. 2. Imaginary part of the surface excess function, Im[SEF] (left panel) and Raman spectra (right panel) of an Sb-terminated InP(110) surface after different exposures to atomic hydrogen. The exposure dose is indicated in each case. On the left panel the spectra were shifted vertically and horizontal thin lines indicate the origin of the vertical scale. The vertical dot-dashed lines on the left panel indicate the position of the critical points E_1, $E_1+\Delta_1$, and E_0' of bulk InP. The Raman spectra ($\lambda = 514.5$ nm) were recorded with crossed incoming and outgoing polarizations oriented halfway between the [1$\bar{1}$0] and the [001] main surface axes [$z(x+y, x-y)\bar{z}$ configuration].

tween 2 and 3 eV and to decrease the amplitude of Im[ε] at the substrate critical points E_1, $E_1+\Delta_1$, and E_0'. As we shall see in detail below, this effect is associated with a hydrogen-induced etching of the Sb monolayer and disordering of the top substrate layers.

The evolution of the SEF and of the Raman spectra with increasing hydrogen exposure is displayed in Fig. 2. Because of the small amplitude of the changes in the dielectric function, care was taken not to move the sample during hydrogen exposure, thereby assuring reproducibility of the experimental results. The Raman spectra in Fig. 2 (right panel) were recorded in the $z(x+y,x-y)\bar{z}$ configuration:[35] according to the selection rules for Raman scattering from surfaces phonons,[10] only modes with A' symmetry are allowed for this scattering geometry. The width of the surface phonon lines in Figs. 1 and 2 is limited by the experimental resolution of the Raman setup [full width at half maximum (FWHM) of 12 cm^{-1}].

The SEF and Raman spectra remain essentially unchanged for H exposures up to 200 L [Figs. 2(a)–2(d)]. For higher exposures both the S_A and S_B SEF features and the surface phonon lines reduce in intensity and disappear for exposures above 1000 L [Figs. 2(e)–2(g)]. This effect is attributed to etching of the Sb monolayer by the hydrogen radicals. It is interesting to note that within the experimental resolution (less than FWHM/2–6 cm^{-1}) no frequency shift of the surface phonon lines could be detected during hydrogen exposure. Also, the reduction in intensity of the S_A and S_B structures in Im(SEF) was not accompanied by changes in the line shape nor by the appearance of additional structures in the surface dielectric function.

Exposures above 1000 L induce a negative background in the imaginary part of the surface excess function between 3 and 5 eV, and an increase in the dips at the critical points of the InP substrate. Similar changes were observed in hydrogen-exposed GaAs(110) surfaces and attributed to hydrogen-induced etching and disordering of the substrate surface.[28]

GaAs:Sb(110) surfaces behave upon hydrogen exposure in a similar way to the InP:Sb(110) surfaces. The evolution of the Raman spectra of an Sb-terminated GaAs sample is illustrated in Fig. 3. The Raman spectra were recorded in the crossed [i.e., $z(x,y)\bar{z}$ configuration]. They show in addition to the substrate TO line (269 cm^{-1}) the excitation of the nondiagonal A'' mode at 168 cm^{-1}.[10] Due to resonance effects, the scattering intensity for this mode at the excitation wavelength of 5145 Å is considerably larger than for the A' modes.[7] The atomic displacements for the A'' mode are entirely localized at the Sb monolayer[9,13–15] and it should, therefore, be very sensitive to changes in the surface structure. The phonon line and the structures of the surface excess function associated with the Sb monolayer reduce in intensity for exposures above 1000 L. As in the case of InP:Sb, no energy shift of the phonon lines was observed.

The experimental results of this section are summarized in Fig. 4, which displays for the two surfaces the intensity of the S_B SEF feature (squares) and of the different surface phonon lines (normalized to the TO intensity and represented by the dashed lines) as a function of hydrogen exposure. For each surface, the intensity of the phonon lines follows closely the changes in the surface excess function, indicating a common mechanism for the two effects. Note, however, that the exposure dose necessary to etch the GaAs:Sb(110) surface is a factor

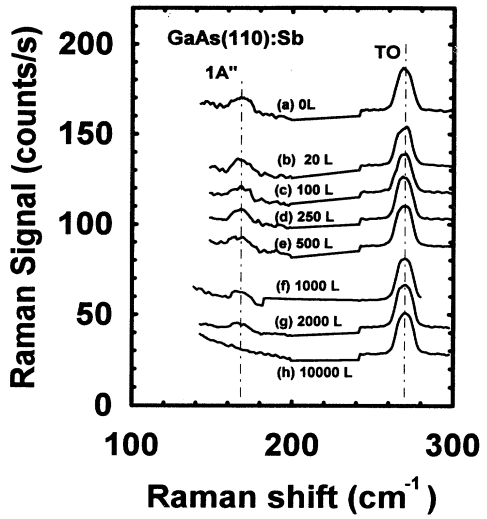

FIG. 3. Raman spectra of an Sb-terminated GaAs(110) surface after different exposures to atomic hydrogen. The exposure dose is indicated in each case. The spectra were shifted vertically and horizontal thin lines indicate the origin of the vertical scale. The vertical dot-dashed lines indicate the position of the bulk GaAs TO phonon and of the A'' surface phonon (168 cm^{-1}). The Raman spectra ($\lambda = 514.5$ nm) were recorded with crossed incoming and outgoing polarizations oriented along the [1$\bar{1}$0] and the [001] main surface axes, respectively [$z(x,y)\bar{z}$ configuration].

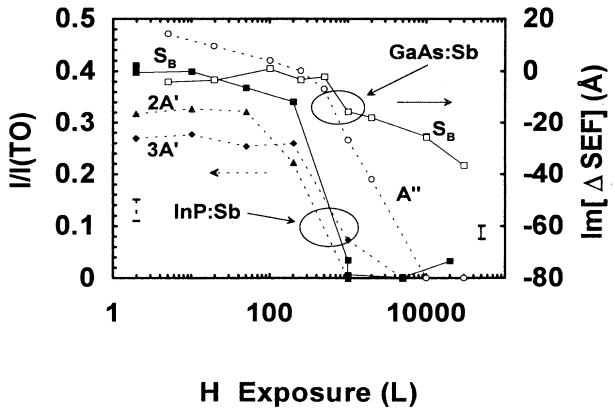

FIG. 4. Solid lines and squares: intensity of the S_B feature of the surface excess function on the hydrogen exposure. Dashed lines: dependence of the intensity ratio between different surface phonon lines and the bulk TO line on hydrogen exposure. The filled and empty symbols correspond to Sb-terminated InP and GaAs (110) surfaces, respectively.

$\sim$ 2–4 larger than for InP:Sb, thus pointing to a higher stability of the former surface against hydrogen radicals. A higher stability of the GaAs:Sb in comparison with the InP:Sb(110) surface was also verified in thermal desorption experiments.[37]

IV. DISCUSSIONS AND CONCLUSIONS

Different processes have been identified in the literature for the interaction of hydrogen atoms with clean GaAs(110) surfaces. For low hydrogen exposures, HREELS reveals the characteristic signatures of the Ga-H and As-H vibrations, indicating that hydrogen binds to both the anion and cation substrate atoms.[21–23,25] The hydrogen chemisorption reduces the relaxation of the clean substrate surface, leading to a reduction of the optical anisotropy present in the clean surface.[28] High hydrogen exposures induce the breaking of surface bonds and the preferential desorption of AsH_x hydrides, leaving behind a roughened, Ga-rich surface.[17,19] Though less experimental data about the interaction of hydrogen with (110) InP surfaces are available,[22,25] a behavior similar to that of the GaAs surface is expected.

In this work we investigated the interaction of the Sb-terminated InP and GaAs (110) surfaces with atomic hydrogen by following the changes in the surface excess function and in the Raman spectrum induced by hydrogen exposure. The imaginary part of the surface dielectric function of the Sb-terminated InP surface is dominated by the structures S_A and S_B [see Fig. 2(a), left panel] associated with transitions involving surface states and surface resonances.[7] The Raman cross section is strongly enhanced for excitation energies near these transitions and the Raman spectrum displays sharp lines [see Fig. 2(b)] corresponding to the excitation of surface phonons of the Sb-terminated surfaces.

We find that the hydrogen exposures necessary to induce changes in the optical properties of Sb-terminated InP and GaAs (110) surfaces are considerably larger (by approximately an order of magnitude[36]) than for the clean (110) GaAs (Ref. 28) surface and for different reconstructions of the GaAs(100) surface.[38,39] This result clearly evidences the higher chemical stability of the Sb-terminated surfaces. One of the most interesting aspects of the results presented here is that within the experimental accuracy neither the phonon lines nor the S_A and S_B SEF features shift in energy during hydrogen exposure. The implications of this result to the interaction mechanism between hydrogen and the Sb-terminated surfaces are discussed below.

In order to check the possibility of the formation of a H-saturated surface during hydrogen exposure we performed *ab initio* calculations for such a GaAs:Sb:H system. Hydrogen atoms were placed in front of the Sb dangling bonds and the hydrogen, antimony, and six uppermost substrate atoms were allowed to relax until the total energy was minimized. The computational details were the same as those in Refs. 15 and 40. As a result of the total-energy minimization according to the Hellmann-Feynman forces we find an equilibrium geometry that is characterized by considerably weakened Sb-substrate bonds. The Sb-As (Sb-Ga) bonds are 24% (8%) longer due to the Sb-H bonding. Interestingly, we find a small contraction of the Sb-Sb bonds within the antimony zigzag chain (by about 1%). Proceeding from this relaxed geometry we calculated the zone-center surface phonons. Thereby we employed an *ab initio* frozen-phonon approach that has proven to yield reliable results for clean[40] and 1-ML antimony-covered III-V(110) surfaces.[15] The eigenvalues and eigenvectors ($\mathbf{u}$) were obtained by diagonalizing the matrix equation,

$$\mathbf{M} \cdot \ddot{\mathbf{u}} = \mathbf{K} \cdot \mathbf{u}, \tag{1}$$

where $\mathbf{M}$ represents the vector of the atomic masses. The elements $k^{ij}_{\alpha\beta}$ of the dynamical matrix $\mathbf{K}$, which describes the interatomic forces, were obtained by displacing atom i from its equilibrium position in the direction α and calculating the force acting on atom j in the direction β. Here, $\alpha, \beta = (x, y, z)$ and $i, j = 1, N$, where N is the number of atoms in the uppermost four (hydrogen + antimony + two substrate) layers. By comparison of the eigenvectors with those of an earlier calculation for GaAs:Sb in the absence of hydrogen[15] we are able to determine the frequency shifts due to the hydrogen adsorption. In particular we obtain shifts of -20, -19, 17, and 11 cm^{-1} for the $1A'$, $2A'$, $3A'$, and A'' modes, respectively. These shifts can be explained by the weakened Sb-substrate and strengthened Sb-Sb bonding induced by hydrogen. Note that the energy shifts are larger than the experimental resolution of the Raman experiments and should, therefore, be detectable in the Raman spectra. The absence of any shifts in the experimental data for the surface phonon energies suggests that the Sb-terminated surface as a whole does not evolve through an intermediate, hydrogen-covered stage before Sb removal.

Apart from the shifted phonon frequencies the calculations reveal strong changes in the band structure of the antimony-covered GaAs(110) surface due to the hydrogen adsorption. Both the energetical position and the dispersion of the surface states are strongly modified. For example, we find the transition energies between the highest unoccupied and lowest occupied bands at the high symmetry points of the surface Brillouin zone to be enlarged by 0.09 (Γ point), 0.49 (X'), -0.55 (M), and -0.52 eV (X) upon hydrogen adsorption. Changes in the surface band structure of such magnitude should certainly be observable in the surface excess function. However, as for the phonon frequencies no such changes in the surface excess function were found in the experiments, thus corroborating our hypothesis that the Sb-terminated surface does not evolve through such an intermediate, hydrogen-saturated stage before Sb removal. This is, however, not too astonishing. In contrast to the clean III-V(110) surface, the dangling bonds of the Sb-terminated III-V surfaces are completely filled,[2–4] so that hydrogen bonding is expected to be less favorable compared to the clean surfaces. The Sb termination leads thus to surface passivation.

Based on the arguments presented above the formation of a H-saturated surface during hydrogen exposure can be excluded since the accompanying modifications of the Raman and SEF spectra have not been observed experimentally. Instead, we propose that surface etching takes place locally through hydrogen-induced breaking of Sb-Sb bonds, most probably at defect sites of the Sb monolayer. Adsorption of additional H atoms at the same site may then induce surface etching and further weaken the neighboring bonds. As a result, only a small fraction of the bonds between the Sb monolayer and the substrate atoms are affected by hydrogen adsorption during most of the etching process. These modified bonds thus remain undetectable by Raman and SE. At the regions of ideal Sb monolayer termination the reactivity is much lower, thus inhibiting a chemical reaction between Sb and H.

In conclusion, we have used spectroscopic ellipsometry and Raman scattering from surface phonons to study the formation of Sb monolayers on InP and GaAs (110) surfaces and their interaction with hydrogen radicals. The results have been compared with *ab initio* calculations of the structure and vibrational modes in the case of the GaAs:Sb:H system. Based on this comparison we conclude that the Sb monolayer is etched before a hydrogen-terminated surface forms on the III-V:Sb(110) surface.

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[35] In the $z(x+y,x-y)\bar{z}$ configuration, only modes with A'-like symmetry are observed. Their intensities, however, are a factor of 4 smaller than for the $z(y,y)\bar{z}$ configuration used in Fig. 1(b), explaining the different intensities of the surface phonon modes in Figs. 1 and 2.

[36] Although we did not measure the actual concentration of atomic hydrogen (the exposure levels are given in Langmuirs of molecular hydrogen) the experimental conditions in Refs. 28, 38, and 39 were very similar and the atomic hydrogen exposures comparable in the three cases.

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