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High-resolution photoemission study of hydrogen interaction with polar and nonpolar GaAs surfaces

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We have used synchrotron-based high-resolution core-level photoemission and valence-band emission measurements to characterize hydrogen chemisorption on nonpolar GaAs(110) and polar GaAs(100) and GaAs(001) surfaces. Chemisorbed atomic hydrogen forms both Ga-H and As-H bonds on all three surfaces, causing chemical shifts of core-level binding energies and changing the valence-band emission. For low hydrogen exposures arsenic desorbs from all surfaces. However, at higher exposures, the (110) surface transforms into a Ga-rich structure with traces of metallic Ga, while the (100) surface transforms into an As-rich structure. We have also observed some additional changes in the binding energy of bulk components of Ga and As core levels as a function of hydrogen exposure, which may be explained by hydrogen-induced changes in band bending.

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I. INTRODUCTION

The interaction of hydrogen with semiconductor surfaces has been attracting considerable interest over the past 20 years for both technological and fundamental reasons. For example, the incorporation of hydrogen into crystalline semiconductors can deactivate electrical activity of both shallow acceptor and donor impurities,[1] while a hydrogen plasma can be used to etch and to clean surfaces and to remove their oxides.[2] On the other hand, information about physical and chemical properties of adsorbed hydrogen is needed for the development of some fundamental mechanistic concepts in the field of surface science addressing, for example, adsorption and desorption processes, epitaxial growth, or rearrangement of surface atoms.

The hydrogenated GaAs surface has been recognized as an ideal system for studying chemisorption processes and rearrangements of surface atoms. Many surface-sensitive techniques, ranging from high-resolution electron-energy-loss spectroscopy[3] (HREELS), low-energy electron diffraction[4] (LEED), and scanning tunneling microscopy[5] (STM) to temperature programmed desorption[6] (TPD) and photon-stimulated desorption[7] (PSD), have been employed to study the interaction of atomic hydrogen with GaAs surfaces.

Synchrotron radiation photoemission spectroscopies have also been used for characterizing the chemisorption of hydrogen on GaAs surfaces.[8] For example, from high-resolution core-level photoemission measurements one can separate the surface contribution from the bulk contribution to the line shape of core-level emission and determine the chemical shift in core-level binding energy as a function of hydrogen coverage. In addition, the integrated ratio of Ga and As core-level lines may provide information about changes in surface stoichiometry as a function of hydrogen exposure. On the other hand, the valence-band emission is a very sensitive probe for hydrogen chemisorption on semiconductor surfaces as it reveals some characteristic, hydrogen-induced modifications of valence states.

The majority of experimental results has suggested that hydrogen chemisorbs on both Ga and As atoms even at low hydrogen coverages of GaAs surfaces, while As loss from the surface (most likely in the form of AsH_3) at higher exposures causes surface roughening and dramatic changes in surface stoichiometry towards a Ga-rich composition.[3,5,9]

However, several reports have provided quite different pictures of hydrogen-induced changes in surface composition. For example, in an early synchrotron-based core-level photoemission study of hydrogen chemisorption on polar GaAs(100) and GaAs(111) surfaces, Bringans and Bachrach[10] reported preferential bonding of atomic hydrogen to As atoms and formation of an As-rich structure for surfaces saturated with hydrogen, even for the initially Ga-rich reconstructions. An overall As enrichment of the GaAs(100) surface (initially Ga-rich) has also been reported by Stietz *et al.*[11] However, while a constant increase of the As/Ga intensity ratio as a function of H dose has been reported in Ref. 11, the same intensity ratio in Ref. 10 exhibits a pronounced maximum at lower exposures, followed by a steady increase at higher exposures.

The apparent discrepancy between these reports may be related to some extent to different surface preparation (cleaved surfaces versus *in situ* or *ex situ* grown molecular beam epitaxy (MBE) structures versus commercial wafers cleaned *in situ*) and different orientation and reconstruction of GaAs samples used in different studies. In addition, one of the problems one may encounter when comparing results from different studies is the estimation of the hydrogen coverage of the surface. Usually, hydrogenation is done by exposing the clean GaAs surface to atomic hydrogen produced from molecular hydrogen by dissociation at a hot filament (~2000 °C). The filament is placed a few centimeters from the sample surface. The hydrogen exposure is given in langmuirs (L), representing the product of the uncorrected ion gauge reading and the time of filament heating ($1\ \mathrm{L} = 10^{-6}$ Torr s of H_2). Different hydrogenation geometries (regarding the distance and the orientation of the filament in relation to the sample surface), filament temperature, and base pressure during hydrogenation (pressures ranging from 10^{-7} to 10^{-4} Torr have been reported in the literature) may lead to the quite different hydrogen coverages of the surface for the same nominal exposure in langmuirs.

Surprisingly, there are few reports in the literature on comparative hydrogenation studies of different GaAs surfaces undertaken by the same technique and under the same hydrogenation conditions (Ref. 10 is one of the few exceptions). In this paper we report on photoemission studies on polar and nonpolar GaAs surfaces, hydrogenated under identical conditions and analyzed in the same way. We employed both core-level and valence-band photoemission measurements, using synchrotron radiation, to characterize hydrogen interactions with the surface.

II. EXPERIMENT

The GaAs samples used in this study were grown by MBE using semi-insulating GaAs (110), (001), and (100) substrates. Following thermal oxide removal, a Si-doped ($5 \times 10^{18}\ \mathrm{cm}^{-3}$) GaAs buffer layer approximately 0.25 μm thick was grown on each substrate, having either the nonpolar (110) surface with an equal number of Ga and As atoms or the polar As-terminated (100) or (001) surface. The samples were then allowed to cool under an As_2 flux while a liquid-nitrogen-cooled finger contacted the substrate mounting block. Over a period of some hours an amorphous arsenic layer capped the surface, thus protecting it against degradation. The samples were stored under an Ar atmosphere in a vacuum vessel and transported to the synchrotron-radiation facility.

All measurements were performed at room temperature in an ultrahigh vacuum (UHV) chamber connected to beam line 2B1 of the Pohang Light Source, which delivers photons in the 12–1200-eV range. The main chamber is equipped with a hemispherical electron analyzer (Gammadata SES 100) for photoemission studies and a LEED system for monitoring surface reconstructions, while the heated sample holder and a manifold with a hot filament for hydrogenation purposes is placed in the prechamber.

The protective arsenic cap on GaAs samples was removed in the prechamber by heating the sample to ~350 °C, followed by annealing at ~440 °C for several minutes. This procedure is known to produce surfaces of quality similar to as-grown MBE surfaces.[12]

Following the cap removal, the clean surface was exposed to atomic hydrogen, produced by dissociation of H_2 at a hot tungsten filament (~2000 °C) placed about 6 cm and out of the line of sight to the sample surface. All hydrogenation was done at similar pressures in the 10^{-5}-Torr range and up to a maximum dose of 5×10^5 L.

The valence-band spectra were obtained using photons of $h\nu = 50$ eV and a mixed *s* and *p* polarization, filtered by an Al filter to remove the contributions of higher-order light to the spectrum. The core-level photoemission was measured around Ga 3*d* and As 3*d* levels, using 70- and 90-eV photons, respectively.

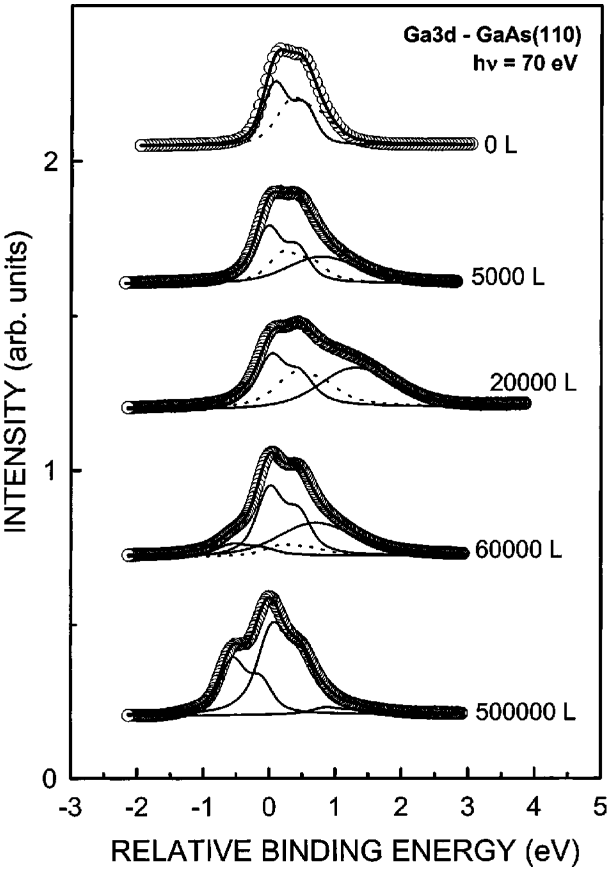

FIG. 1. Photoemission spectra for Ga 3*d* levels in GaAs(110) as a function of hydrogen exposure. The solid line is a numerical fit of experimental curves (open circles), representing superposition of two doublets (clean surface) or three doublets (hydrogenated surface).

III. RESULTS AND DISCUSSION

A. Core-level photoemission

The majority of synchrotron-based photoemission measurements on the effects of hydrogen chemisorption on GaAs surfaces has been done previously on the GaAs(110) surface (which can be easily prepared *in situ* by cleavage), which has confirmed that atomic hydrogen bonds to both Ga and As atoms and that, at higher hydrogen exposures, a Ga-rich surface develops as a consequence of preferential etching of As atoms from the surface.[8,9,13] Following the same arguments, one may expect that, at even higher exposures, some metallic Ga droplets may form on the surface,[11] leading eventually to surface metallization. However, to the best of our knowledge, no photoemission studies from GaAs surfaces have shown this full range of possible transformations induced by hydrogen chemisorption.

If metallic Ga builds up on the GaAs surface, one should be able to measure the chemical shift in the Ga 3*d* photoemission signal originating from the metallic layer. In Fig. 1 we show a set of representative Ga 3*d* emission curves from the GaAs(110) surface (open circles) as a function of H dose up to 5×10^5 L, taken by 70-eV photons and normalized to the photoemission current measured at the Au mesh. Clearly, the Ga 3*d* emission changes dramatically with H exposure and represents a superposition of several emission lines. To analyze these curves in more detail, we simulated them with several sets of characteristic Lorentzian doublets convoluted with Gaussian functions.[14]

The Ga 3*d* peak from the clean surface was deconvoluted into two doublets (solid and broken lines), shifted from each other by 0.26 eV and with a spin-orbit (SO) splitting of 0.44 eV and branching ratio of 0.63. These parameters were held fixed for all fittings, while the zero position of the binding energy scale were taken at the Ga $3d_{5/2}$ position of the bulk component. The two doublets and the fitting parameters we used are characteristic for the bulk- and surface-related contributions to the core emission, with the surface part shifted to the higher binding energy E_b.[13,15]

The emission from the hydrogenated samples cannot be simply fitted by only two doublets. However, the introduction of a third doublet, shifted towards higher E_b by 0.6 eV, gives an excellent fit to experimental curves in the lower-coverage regime (up to 2×10^4 L) (see Fig. 1). The intensity of the third doublet increases dramatically with hydrogen exposure, while at the same time the intensity of the surface-related doublet drops. We associate this new doublet with the formation of Ga–H bonds on the surface. The binding energy of this component increases with hydrogen dose and reaches the maximum value of 1.1 eV below the bulk emission at 2×10^4 L, while the Ga 3*d* surface component remains at the same binding energy for all exposures. At the same time, the Lorentzian width of the H-related doublet increases from 0.5 eV (at 5×10^3 L) to 0.65 eV (at 2×10^4 L), while the Gaussian component remains constant at 0.8 eV.

The same trend in chemical shift of Ga 3*d* emission and the asymmetric broadening of the H-related Ga 3*d* doublet with hydrogen dose has also been reported in Ref. 13 (although the H-induced effects reported there seems to be on a smaller scale) and explained in terms of some unresolved high-binding-energy components related to the disorder on a rough, Ga-rich surface.[13]

For even higher exposures (6×10^4 L), the hydrogen-induced component decreases, while, at the same time, an additional structure emerges at the lower E_b edge, shifted by 0.55 eV from the main bulk emission line. To reproduce this structure, we have introduced an additional doublet with the same SO splitting and branching ratio as the bulk component. The intensity of this additional component increases even more for the highest H exposure used in this experiment (5×10^5 L). The shift in binding energy of this new component corresponds to the chemical shift from elemental Ga (Ref. 16) and we associate it with the emission from metallic Ga formed on the GaAs surface.[11]

The As 3*d* emission, taken using 90-eV photons and displayed in Fig. 2, shows much less pronounced changes with hydrogen exposure. We analyzed the emission curves in the same way as the Ga 3*d* curves. Again, the spectrum from a clean surface was decomposed in terms of bulk and surface doublets. We found the surface shift to be 0.38 eV towards the lower binding energy, a SO splitting of each doublet of 0.69 eV, and a branching ratio of 0.66, in excellent agreement with the published data.[13,15]

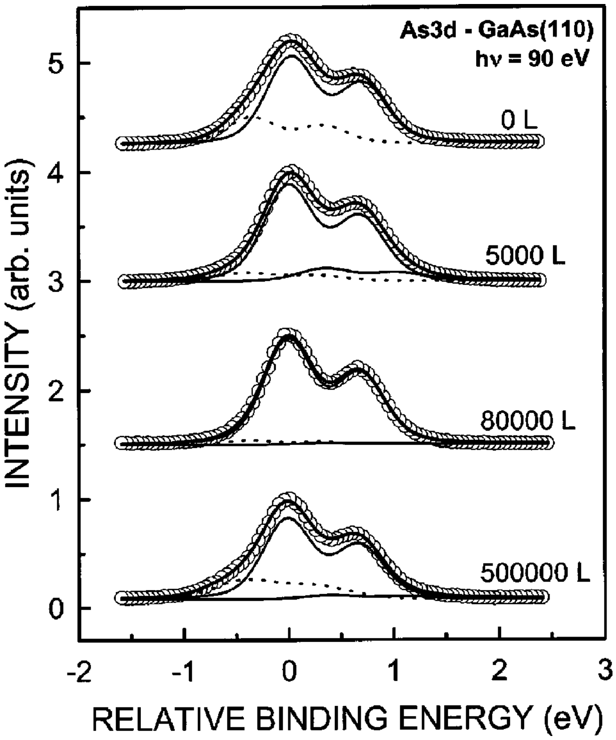

FIG. 2. Photoemission spectra for As 3*d* levels in GaAs(110) as a function of hydrogen exposure. Experimental curves (open circles) are simulated by two or three doublets, as in Fig. 1.

The As 3*d* emission from the hydrogenated samples requires an additional doublet to achieve the best fit with the experimental curves (see Fig. 2). Again, we associate the new doublet component with the reaction of atomic hydrogen with surface As atoms and the formation of As–H bonds. This hydrogen-related component has the same SO splitting and branching ratio as the bulk component and is shifted by 0.35 eV towards higher E_b. In contrast to the Ga 3*d* emission, the binding energy and the width of the hydrogen-related doublet in the As 3*d* emission curves remain constant for all hydrogen exposures. However, the intensity of this doublet decreases at higher exposures corresponding to the formation of a Ga-rich surface as in Fig. 1. This result confirms some previous reports on hydrogen-induced preferential etching of As from GaAs(110) surfaces.[13]

Turning now to the photoemission data from polar (100) and (001) surfaces, we first notice that the Ga 3*d* photoemission exhibits much fewer changes as a function of hydrogen exposure than the corresponding emission from the nonpolar GaAs(110) surface. In addition, our measurements on polar surfaces did not show the pronounced "metallic" Ga contribution, not even at the highest exposure used in our experiments [see Fig. 3(b)]. This is in agreement with some previous reports from polar surfaces showing only very small changes in line broadening of the Ga 3*d* core-level[11] or no changes at all.[10]

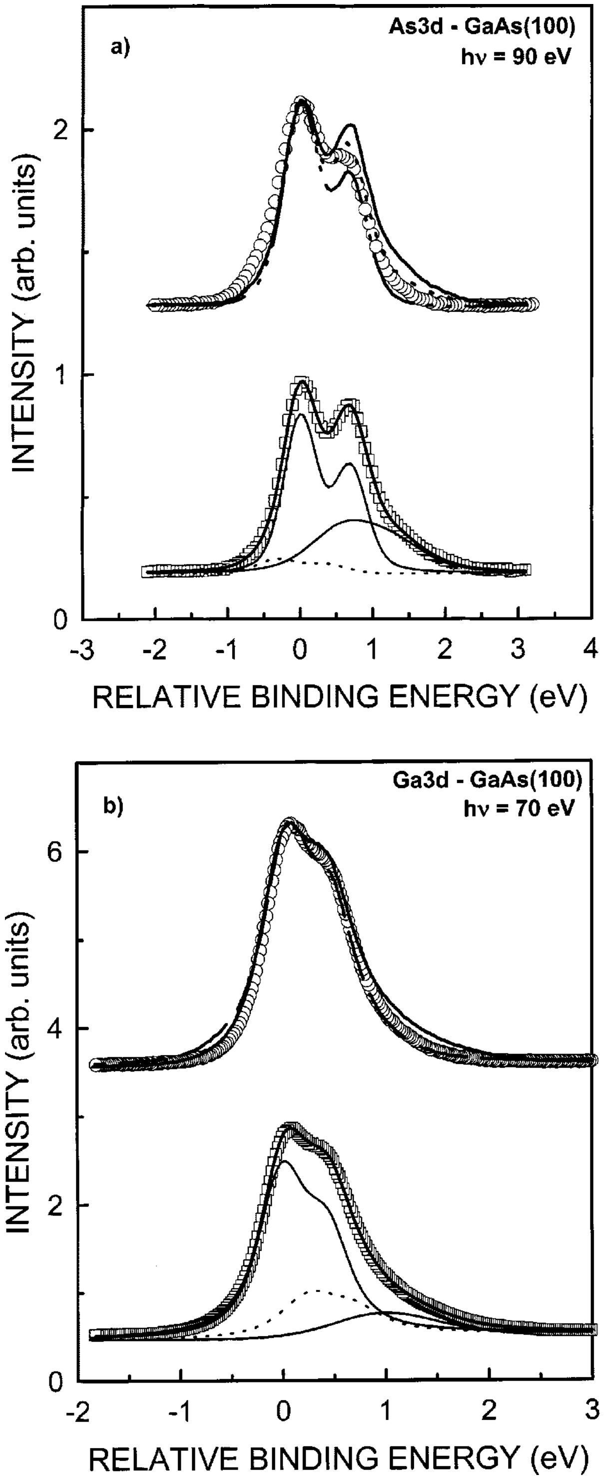

FIG. 3. (a) Photoemission spectra for As 3d levels in GaAs(100) for three different hydrogen doses: 10^3 L (solid line), 5×10^3 L (dotted line), and 5×10^5 L (dashed-dotted line). The clean surface is represented by open circles. Superposition of three doublets gives an excellent fit to the experimental lines of hydrogenated samples, as shown in the lower part for hydrogen exposure of 10^3 L. (b) Selected photoemission curves for Ga 3d core levels in GaAs(100) at different hydrogen exposures (open circles for clean surface; solid line for 2×10^4 L; dashed line for 5×10^5 L). Simulation, given for hydrogen exposures of 6×10^4 L, is shown in the lower part.

The emission taken around As 3d core levels is slightly different. While the GaAs(001) surface shows only small changes in As 3d emission with hydrogen exposure (not shown), the GaAs(100) surface exhibits several pronounced features [see Fig. 3(a)].

In Fig. 3, as an example, we show some representative Ga 3d and As 3d emission curves taken from hydrogenated GaAs(100). The fitting parameters for clean surfaces (SO splitting, branching ratio, and shifts) were fixed to the same values as in the case of the GaAs(110) surface. Again, the broadening of experimental curves at the higher E_b edge upon hydrogen exposure required an additional, hydrogen-related doublet for the best fit.

In Fig. 3(a) we show the As 3d emission from the (100) surface for three different hydrogen exposures [shown in the upper part of Fig. 3(a)]. The emission from the clean surface, as in the case of the (110) surface, shows the surface and the bulk contribution, and also the small contribution from elemental As, originating from either arsenic dimers on the top of the As-rich surface or some remaining As from the cap.[7] At 10^3 L, the emission curve develops a pronounced, hydrogen-induced shoulder at the higher E_b edge, which indicates the formation of As–H bonds. It has been simulated with an additional doublet as shown in the lower part of Fig. 3(a). At higher hydrogen exposures (5×10^3 L) the emission curve approaches the original shape and finally becomes slightly sharper for 1.4×10^5 L. This behavior is consistent with a reduction in the number of As–H bonds at the surface and desorption of As, most likely in the form of AsH_3 at higher hydrogen exposures.

The line shape of Ga 3d emission, shown in Fig. 3(b), also exhibits similar changes. The pronounced hydrogen-induced component, shown by the solid line for 6×10^4 L, has been simulated by the third doublet in the lower part of Fig. 3(b). At the highest hydrogen exposure used in our experiments (5×10^5 L), the hydrogen-related contribution almost disappears, possibly indicating the loss of Ga from the surface in the form of Ga hydrides.[11]

The minimum changes in core-level emission were found on the GaAs(001) surface (not shown). To confirm the hydrogen bonding on this surface, we turn to the valence-band emission.

B. Photoemission from the valence states

Hydrogen chemisorption is known to affect significantly the valence-band spectra of GaAs. For example, on the GaAs(110) surface hydrogen removes states from near the top of the valence band and introduces several new structures in the valence band and the heteropolar gap.[17] The new emission peak around −5.5 eV (with respect to the valence-band maximum) is believed to be dominated by bonding states formed by Ga s orbitals and H adsorbed on Ga atoms.[9] It has been shown that this emission increases with H dose on the nonpolar GaAs(110) surface.[17] The emission at −8.5 eV comes from states localized in the heteropolar gap of GaAs. It also increases with H dose and is believed to reflect the etching action of hydrogen and removal of As from the

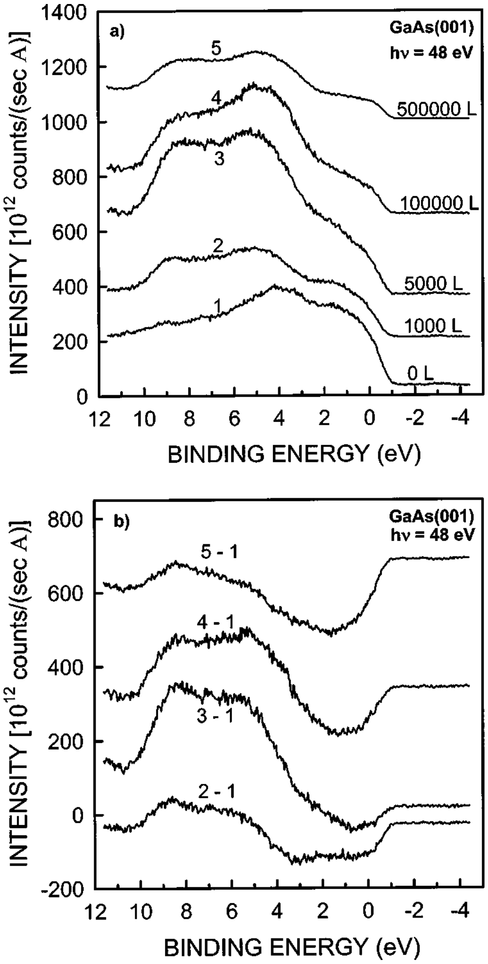

FIG. 4. (a) Valence-band emission and (b) difference curves for the hydrogenated GaAs(001) surface.

surface.[17] Finally, the emission at around −11 eV arises from As *s* orbitals and hydrogen adsorbed on As atoms.[9]

However, there are no detailed studies available in the literature on the valence-band spectra of polar GaAs surfaces as a function of H exposure. In Fig. 4 we show a set of representative curves taken from the GaAs(001) surface as a function of H exposure.

The curves in Fig. 4(a) are plotted after subtraction of the secondary background and normalization to the beam current. The clean surface exhibits a pronounced peak close to the valence-band maximum ($E_{\mathrm{VBM}}=0$), which probably represents a mixture of emission from the surface states and some As *p*–like dangling bonds.[9] Hydrogen chemisorption removes these states from near the top of the valence band and introduced new bands around −5.5 and −8.5 eV, as shown by the difference curves in Fig. 4(b).

In agreement with the previous work on nonpolar GaAs(110) surfaces,[9,13,17] we assign the −5.5-eV emission to the Ga–H bonds. It increases with H exposure, indicating an increasing number of Ga–H bonds. The hydrogen-induced emission at −8.5 eV is believed to reflect the etching action of hydrogen and depletion of As from the surface, following the formation of volatile AsH_3.[17] On the other hand, the relative drop in the −5.5-eV emission at the highest hydrogen exposure of 5×10^5 L may indicate the buildup of metallic Ga droplets on the surface.[11] We have also observed the reduction in emission around −11 eV upon hydrogen adsorption, which may reflect the removal of As *s*–like surface states.[13]

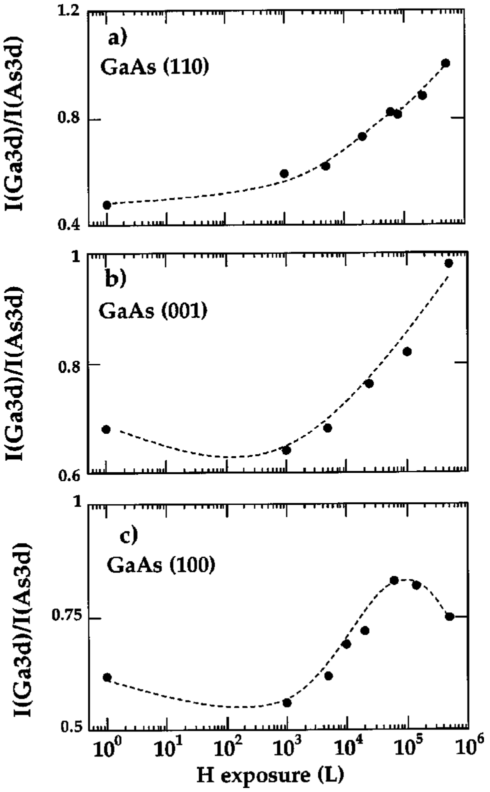

FIG. 5. Integrated intensity ratio of the Ga 3*d* and As 3*d* core-level photoemission for (a) GaAs(110) surface, (b) GaAs(001) surface, and (c) GaAs(100) surface.

The results from Fig. 4 confirm that hydrogen bonds to both Ga and As atoms on GaAs(001) and that hydrogen adsorption introduces qualitatively the same features to the valence-band emission from both polar and nonpolar GaAs surfaces.

C. Surface composition

The interaction of hydrogen with GaAs surfaces may dramatically change the surface stoichiometry and reconstructions. For example, hydrogen adsorption has been reported to preferentially remove arsenic from nonpolar GaAs surfaces, causing roughening of the surface and leading to Ga-rich structures.[8,13] On the other hand, both As-rich and Ga-rich polar surfaces can be transformed into As-rich composition after chemisorption of atomic hydrogen.[10,11]

Photoemission measurements around Ga and As core levels have often been employed to study the variation of surface stoichiometry with H exposure. In general, the Ga to As ratio has been calculated from integrated emission intensities of Ga 3*d* and As 3*d* core levels. Sorba *et al.* have shown a linear increase of the Ga 3*d*/As 3*d* ratio as a function of H exposure for the GaAs(110) surface.[13] Such behavior clearly reflects the preferential removal of As and formation of a

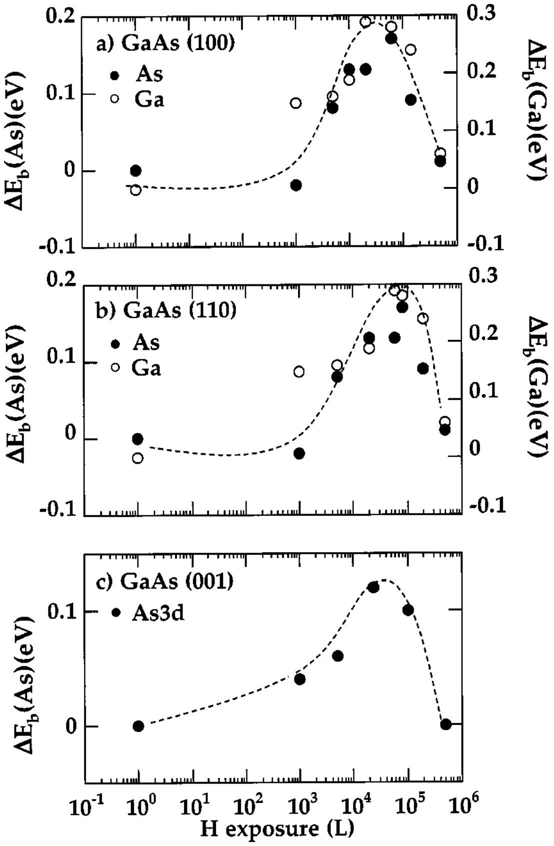

FIG. 6. Change in binding energy (ΔE_b) for As $3d$ and Ga $3d$ levels as measured on (a) GaAs(100), (b) GaAs(110), and (c) GaAs(001) surfaces.

Ga-rich surface. On the other hand, data from Ref. 11 show a nonlinear decrease of Ga $3d$/As $3d$ ratio with H exposure, indicating an overall As enrichment of the GaAs(100) surface, in agreement with the work from Ref. 10. However, results presented in Ref. 10 clearly show three different regions: initial decrease of the Ga/As ratio for low H exposures, followed by a rapid increase of the Ga/As ratio after a minimum obtained at intermediate exposures, and, finally, a slow but steady decrease for higher exposures.

In Fig. 5 we plot the normalized ratio of the integrated intensities of Ga $3d$ and As $3d$ emission curves as a function of hydrogen dose for all three surfaces used in our study. In contrast to the results from Ref. 13 (showing a linear increase of the Ga/As intensity ratio with hydrogen exposure of (110) surfaces), our measurements on the (110) surface show more likely an exponential dependence of the Ga/As ratio as a function of hydrogen exposure. The (001) surface exhibits behavior similar to the (110) surface, except for an initial drop in the Ga/As intensity ratio [Fig. 5(b)].

The intensity ratio from the (100) surface shows some more structure [Fig. 5(c)]. It decreases initially from the clean-surface value, then increases almost exponentially with hydrogen exposure in the $10^3 - 5\times10^4$ L range, and finally starts to decrease for higher exposures. This result, qualitatively quite similar to that from Ref. 10, indicates an overall change towards the As-rich stoichiometry upon exposure of the GaAs(100) surface to a high dose of hydrogen. The enrichment of the (100) surface with As also has been reported in Ref. 11.

However, our core-level photoemission data around the As $3d$ level [see Fig. 3(a)] indicates removal of As–H bonds from the surface and As desorption at high hydrogen exposure. Therefore, an overall As enrichment of the surface should be caused by either some additional Ga desorption, probably in the form of Ga hydrides,[10,11] or by an enhanced diffusion of As to the surface.[10] The Ga $3d$ emission data [see Fig. 3(b)] would favor the former proposition as the hydrogen-related component disappears from the Ga $3d$ emission curve at higher hydrogen exposures.

D. Binding energy shifts

Turning now to hydrogen-induced shifts in binding energy, we note that some small changes of both Ga and As $3d$ core levels has been reported in Ref. 11 for the hydrogenated GaAs(100) surface. An increase of Ga $3d$ binding energy from 19.8 to 20.4 eV was measured even at very low hydrogen coverage, while, at the same time, the As $3d$ binding energy increased from 41.85 to 42.45 eV. However, at H exposures above 10^5 L, the binding energy of both Ga and As $3d$ levels returns to the clean-surface value.

Our measurements on three different GaAs surfaces, summarized in Fig. 6, show a similar trend. In Fig. 6(a) we show the normalized shift in binding energy, ΔE_b, for the bulk component of the As $3d$ level (full circles) from the (100) surface. After $\sim 10^3$ L the binding energy starts to increase and reaches a maximum, or a plateau, between 10^4 and 10^5 L. For higher exposures, ΔE_b decreases towards the clean-surface value. However, the overall variation in binding energy is about a factor of 2 smaller than has been reported previously,[11] while the nominal hydrogen exposures are shifted towards higher values. The corresponding changes in As $3d$ binding energy as a function of H exposure for GaAs(110) and GaAs(001) surfaces [Figs. 6(b) and 6(c)] exhibit the same general behavior.

In Figs. 6(a) and 6(b) we have also plotted changes of the Ga $3d$ binding energy as a function of hydrogen exposure (open circles) for GaAs(100) and GaAs(110) surfaces, respectively. The overall variation in the Ga $3d$ shift is slightly higher than the As $3d$ shift, but otherwise follows the same trend. The values of ΔE_b for the Ga $3d$ level from the hydrogenated GaAs(001) surface were scattered around the clean-surface value and are not shown in Fig. 6(c).

The variation in binding energy can be understood to some extent in terms of hydrogen-induced band bending. In general, the band bending results from the additional charge in the surface layer, which is compensated by an opposite space charge inside the semiconductor. The formation of this space-charge layer is responsible for the band bending with a maximum value at the surface. The numerical estimation of band bending on the GaAs(100) surface as a function of H exposure has been determined previously from fitting the HREELS measurements to a simple theoretical expression for the energy-loss probability in the dipole scattering theory.[18] At low exposures, up to a few hundred langmuirs, the band bending decreases from 350 to around 250 meV (and shows some zigzag-type variation), while at higher exposures it increases dramatically to ~700 meV at the highest exposure of 10^5 L used in Ref. 18. Our hydrogenation experiments also show two distinctive regions in band-bending variation, although the nominal hydrogen exposures used in our experiments differ from those in Ref. 18.

Looking now at Fig. 6, we first notice that ΔE_b for the (100) surface [Fig. 6(a)] closely follows the variation of surface stoichiometry, given in Fig. 5(c) by the integrated ratio of Ga and As core-level emission curves. The initial increase of ΔE_b for hydrogen exposures up to $\sim 5 \times 10^4$ L implies the reduction in band banding. For these exposures, as demonstrated in Figs. 3 and 5, As desorbs from the surface and the surface stoichiometry changes towards a Ga-rich composition. The missing As atoms are related to the localized electronic defect states, which act as acceptors and can be occupied by electrons. Therefore, the hydrogen-induced changes in surface stoichiometry affect the net surface charge and may change (reduce or increase) the width of the depletion layer in our *n*-type samples which will, in turn, change the band bending. Indeed, some angle-resolved ultraviolet photoelectron spectroscopy experiments on the GaAs(001) surface[19] have shown that a change in surface As concentration changes the band bending. In addition to hydrogen-induced changes in surface stoichiometry, the atomic hydrogen itself can also affect the band bending. The diffusion of H into the bulk of GaAs may passivate the electrically active dopants and affect the band bending, again by changing the width of the depletion layer.[18]

The same reasoning can be applied to band bending on the GaAs(110) surface [Fig. 6(b)] for hydrogen exposures up to $\sim 5 \times 10^4$ L. However, at higher exposures, the final stoichiometry of (100) and (110) surfaces differs significantly [see Figs. 5(a) and 5(c)], while the binding energy changes in almost the same way. To explain this discrepancy we point out once again that at lower hydrogen exposures both surfaces lose As through preferential etching, thus developing similar changes in the net surface charge and, consequently, similar changes in band bending.

At higher hydrogen exposures, the (100) surface becomes enriched in As, while, at the same time, some metallic Ga builds up on the (110) surface. A metal/semiconductor contact is known to introduce a depletion layer in an *n*-type semiconductor, followed by band bending.[20] In the case of metals on the GaAs(110) surface, a very small initial change in thickness of the metallic overlayer drastically increases the band bending,[21,22] which, in turn, reduces the binding energy.

IV. CONCLUSION

Atomic hydrogen bonds to both Ga and As on polar and nonpolar GaAs surfaces, causing a dose-dependent chemical shift of 0.8–1.1 eV for Ga 3*d* core levels and 0.35 eV for As 3*d* levels. Hydrogen removes states from near the top of the valence band and introduces some new similar structures in the valence band and the heteropolar gap on both polar and nonpolar GaAs surfaces. In addition, chemisorbed hydrogen induces preferential etching of As at room temperature on the nonpolar GaAs(110) surface, leading to a Ga-rich composition and metallization of the surface at high hydrogen exposures. Preferential removal of As has also been observed on polar surfaces in the low exposure limit (below 10^4 L of H_2). However, at higher exposures (above 10^5 L of H_2), an As-rich composition develops on the GaAs(100) surface. The change in binding energy of the bulk component of both Ga and As core levels closely follows the change in surface stoichiometry and composition with hydrogen exposure and can be understood in terms of band bending. The band bending decreases for low hydrogen exposure but increases again at higher exposures.

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