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Reflection high-energy electron-diffraction and photoemission spectroscopy study of GaAs(001) surface modified by Se adsorption

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Modification of the GaAs surface induced by the adsorption of Se atoms in a vacuum is studied by reflection high-energy electron diffraction (RHEED) and surface-sensitive photoemission spectroscopy. Se-induced variation of the surface structure is examined by RHEED for GaAs(001) surfaces with different surface compositions prepared by molecular-beam epitaxy, and a diagram of the reconstructions for the Se-GaAs(001) system is presented. Se-stabilized surfaces show a (2×1) reconstruction irrespective of the initial As and Ga surface composition. In addition, two intermediate surfaces are also observed for partially selenized surfaces. These intermediate surfaces are characterized in the RHEED patterns by a $\frac{1}{3}$-order streaking in the $[1\bar{1}0]$ direction. Measurements of core-level photoemission peak intensities show considerable As loss at the (2×1) surface. An analysis of observed Ga, As, and Se $3d$ core-level peak intensities for the (2×1) surface is made, assuming the layer attenuation model. It suggests that the surface is terminated with a full atomic layer of Se atoms, which are bonded with Ga atoms of the next layer. It also suggests the occurrence of Se-As exchange near the surface leading to the formation of a selenide layer a few monolayers thick. The Se $3d$ spectrum of the (2×1) surface shows the presence of two chemically shifted components, which are tentatively attributed to the Se atoms terminating the surface and those occupying the As sites below the surface in the proposed layer model. Binding-energy shifts of the As $3d$ core-level peak and valence-band edge suggest that the band is nearly flat for the (2×1) surface, indicative of the Fermi-level unpinning occurring at the surface. Its mechanism is discussed in the proposed structural model.

I. INTRODUCTION

Considerable efforts have been made for many years to control surfaces of III-V semiconductors, such as GaAs, with limited success. Recently, a surface treatment using sulfur has attracted many researchers in the field of GaAs surfaces and device studies since a unique wet-chemical method was reported[1] after an earlier work using H_2S gas.[2] S-treated surfaces exhibit improved properties such as enhanced photoluminescence,[3] increased sensitivity of Schottky-barrier height to the metal work function,[4] and reduced band-gap surface states.[5] The success of the S treatment further stimulated investigation of a treatment by another chalcogen element, selenium, using a wet-chemical method.[6] More recently, we have investigated a treatment using a Se-molecular beam in a vacuum[7] and have demonstrated the elimination of band-gap states on the treated GaAs surface. A method using the H_2Se gas[8] has also been reported.

While the S and/or Se treatments find a variety of device applications, also important from a fundamental point of view is a study of their mechanism, which is closely related to a still-unresolved surface pinning mechanism for compound semiconductors. There are several reports on the characterization of S-treated[9–11] and Se-treated[6–8,12] surfaces. Some of the results, however, are apparently inconsistent concerning the structure and the elements to which S and Se are bonded, probably due to the difference in sample preparation methods and experimental conditions. A more detailed and systematic study characterizing the treated surfaces has to be done to understand the mechanism of the surface modification induced by S and Se. Better controllability and *in situ* characterization capability of the method using a Se-molecular beam are advantageous for such a study. This paper presents the results of reflection high-energy electron diffraction (RHEED) and synchrotron-radiation photoemission spectroscopy studies on GaAs(001) surfaces treated by a Se-molecular beam. The photoemission spectroscopy study is done in more detail than reported previously,[7] and a possible structural model for the treated surface is proposed based on the analysis of core-level peak intensities.

II. EXPERIMENT

The Se treatment was performed in a two-chamber UHV system. A growth of GaAs layers on (001) substrates was done in one chamber using a conventional molecular-beam epitaxy (MBE) method. After the growth, the substrate was cooled down below 300 °C under As flux. The surface shows an As-rich $c(4\times4)$ structure deduced from a RHEED pattern. The sample was then transferred to another connected chamber equipped with a Se effusion cell. In this chamber, the As-rich $c(4\times4)$ surface was heated in a vacuum to prepare surfaces with various As/Ga composition ratios. The surfaces showing various reconstructions were exposed to a Se-molecular beam at substrate temperatures between 250 °C and 600 °C. The Se flux intensity was measured by a nude ionization gauge placed near the substrate. The variation of surface structure induced by the Se exposure was monitored by RHEED at 15 keV. The substrate temperature was measured using the combination of a pyrometer and a thermocouple calibrated with the cleaning temperature of GaAs(001), which is monitored by RHEED and assumed to be 580 °C.

While excess Se atoms are desorbed during treatment at substrate temperatures higher than 200 °C due to the high vapor pressure of Se, deposition of a thick Se film takes place on a substrate held at room temperature. This Se film, which is presumably in an amorphous phase, is found effective in protecting the surface that has been treated by Se. The amorphous (*a*-)Se film can be removed easily by heating above 200 °C, restoring the oxide-free Se-treated surface, even after the sample has been exposed to the atmosphere. This temporary passivation scheme using an *a*-Se film was utilized as follows for preparing samples for synchrotron-radiation photoemission experiments.

The surface exhibiting $c(4\times4)$ surface was prepared as described above on a Si-doped epitaxial GaAs layer grown on an *n*-type (001) substrate. After transfer to the chamber used for Se treatment, the sample was heated up to 400 °C to form the As-stabilized (2×4) surface. A Se flux with the intensity of 1×10^{-6} Torr was applied for 2 min to this surface held at 400 °C. This gives rise to the formation of a (2×1) reconstructed surface as shown in Sec. III. After cooling down to room temperature, the sample was exposed again to the Se flux for deposition of an *a*-Se protection film. The sample, which was taken out to the atmosphere for transfer, was heated in a photoemission chamber in synchrotron-radiation facilities to remove the top *a*-Se film. A clean GaAs(001) surface with no Se atom was obtained by high-temperature heating up to 600 °C. This surface was used as a reference. The photoemission measurements were performed at branch line 8A of the Photon Factory in the National Laboratory for High Energy Physics, Japan. The radiation was monochromatized by a plane-grating x-ray optics[13] and emitted photoelectrons were analyzed using a double-pass cylindrical mirror analyzer. The overall instrumental resolution (Gaussian width) was about 0.4 eV. The Ga, As and Se 3*d* core-level spectra obtained were analyzed by a least-squares fitting using a Lorentzian line shape convoluted with a Gaussian broadening function after subtracting the nearly linear background. For evaluating core-level peak intensities, spectra were normalized to the photon intensity measured as a secondary electron-emission current of a gold mesh placed in front of the sample.

III. RHEED OBSERVATIONS

The RHEED observation reveals reconstructions characteristic of Se-modified GaAs(001) surfaces. The diagram shown in Fig. 1 summarizes the observed variation of the surface structure induced by the adsorption and desorption of Se on several reconstructed GaAs(001) surfaces. Figure 2 shows the typical RHEED patterns of the observed three phases induced by the Se adsorption.

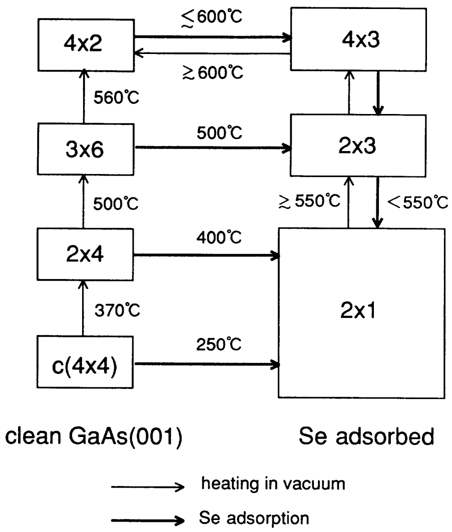

FIG. 1. A diagram of surface reconstructions for Se-GaAs(001) system. Conditions required to go from one phase to another are also indicated. The thin arrow indicates heating in vacuum and the bold arrow indicates adsorption of Se atoms at a specified temperature.

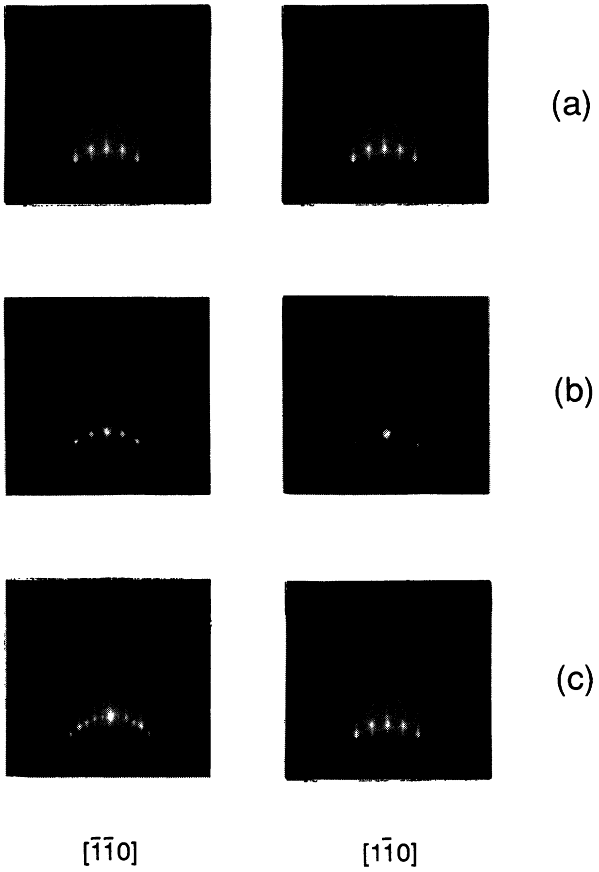

FIG. 2. RHEED patterns of the GaAs(001) surface induced by the adsorption of Se atoms: (a) (2×1) pattern characteristic of a Se-stabilized surface, (b) (2×3) pattern, and (c) (4×3) pattern of partially selenized intermediate phases.

Surfaces with different [As]/[Ga] ratios can be obtained by desorbing excess As atoms from the As-rich $c(4\times4)$ surface by heating in vacuum. With increasing substrate temperature, the RHEED pattern subsequently shows (2×4) reconstruction at 370 °C, (3×6) at 500 °C, and (4×2) at 560 °C, all of which have been observed on clean GaAS(001) surfaces.[14] The (4×2) surface is terminated mostly by Ga.

When these surfaces are exposed to a Se flux with the intensity of 10^{-6} Torr at temperatures ranging from 300 °C to 600 °C, the RHEED pattern changes quickly to one exhibiting a (2×1) reconstruction as shown in Fig. 2(a). This (2×1) reconstruction, which occurs irrespective of the initial surface [As]/[Ga] composition ratio, is characteristic of a Se-stabilized GaAs(001) surface.

Additional intermediate phases are also observed when the intensity of the applied Se flux is reduced to 1×10^{-8} Torr, allowing the transformation to occur gradually. On the Ga-terminated (4×2) surface, relatively broad $\frac{1}{3}$-order streaks appear in the $[1\bar{1}0]$ direction upon exposure at 600 °C, and we get a RHEED pattern exhibiting a (4×3) reconstruction [Fig. 2(c)]. When this surface is cooled down under the Se flux, the $\frac{1}{4}$-order streaks in the $[\bar{1}\bar{1}0]$ direction disappear around 550 °C while the pattern in the other direction is almost invariant [Fig. 2(b)]. Thus a (2×3) reconstructed surface is obtained. Further exposure of this surface to the Se flux leads to the transformation to the (2×1) phase. On the (3×6) surface, the exposure at 500 °C induces the (2×3) reconstruction, which gradually changes to the (2×1) reconstruction at the same temperature. The (2×4) and $c(4\times4)$ reconstructed surfaces transform directly to the (2×1) phase after a prolonged Se exposure at 400 °C and 250 °C, respectively.

This (2×1) structure is preserved after shutting off the Se flux for substrate temperatures below 550 °C. When the (2×1) surface is heated up in vacuum, the surface shows a series of transformations above 550 °C due to the desorption of Se atoms. The RHEED patterns at first show the (2×3) reconstruction, which quickly changes to the (4×3) reconstruction. The RHEED pattern finally changes at 600 °C–640 °C to the one exhibiting (4×2) reconstruction, which is characteristic of the clean Ga-terminated surface. The desorption of Se in this temperature range is also found from the photoemission spectroscopy analysis shown later. The transformations occur in a reversible manner between the Ga-terminated (4×2) structure and the Se-stabilized (2×1) structure through the partially selenized (2×3) and (4×3) structures.

The (4×3) and (2×3) structures often transform into the (2×1) structure when the substrate is cooled down in some residual Se atmosphere. These intermediate structures as well as the (2×1) one, however, can be preserved upon cooling down to room temperature if the ambient Se vapor is carefully removed. This suggests that all these reconstructions are stable also at room temperature.

It is worth mentioning that the (2×1) structure is preserved even when the surface is once exposed to the atmosphere for a few hours. This demonstrates the enhanced chemical stability of the (2×1) surface.

IV. PHOTOEMISSION SPECTROSCOPY RESULTS

We performed a surface-sensitive photoemission spectroscopy analysis to study the nature of the Se-treated GaAs(001) surfaces. The sample was prepared using an *a*-Se protection film as described in the experimental section. A separate RHEED observation shows that heating in vacuum between 250 °C and 550 °C removes the top *a*-Se film and reproduces the (2×1) reconstruction. The effectiveness of the *a*-Se film against contamination is further checked by Auger analysis using nonmonochromatized synchrotron radiation as an excitation source. The reproduced (2×1) surface shows no detectable oxygen or carbon.

Figure 3 shows typical As, Ga 3*d* core-level photoelectron spectra taken after the sample was subsequently heated at 350 °C and 600 °C for 3 min in the photoemission chamber. The top spectra [Fig. 3(a)] show those for the (2×1) surface, and the bottom ones [Fig. 3(b)] for a clean surface obtained after desorbing the Se atoms on the surface. The photon energy used for excitation is 100 eV. The binding energy is referred to the Fermi level as measured from a freshly evaporated gold film. The spectra are normalized to the photon intensity. The smoothed spectra are shown.

As seen in Fig. 3, the As 3*d* peak for the (2×1) surface can be well fitted with a single component presumably of bulk GaAs. The branching ratio of the spin-orbit-split doublet is 0.67 ± 0.03, which is close to the ratio of the number of degeneracy for each level. The energy split is found to be 0.70 ± 0.01 eV, in agreement with the reported value.[15] The Lorentzian width and the Gaussian width obtained from the fit are 0.21 ± 0.05 and 0.53 ± 0.04 eV, respectively. Fitting was also attempted assuming an additional surface component. The intensity of the surface component, if it exists, was found to be less than 3%

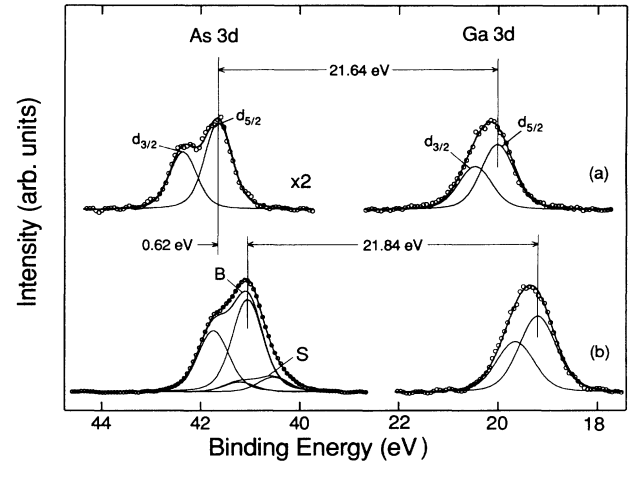

FIG. 3. As and Ga 3*d* photoelectron spectra: (a) a Se-stabilized (2×1) surface, (b) a clean surface obtained after 600 °C heating. The excitation photon energy is 100 eV. The binding energy is referred to the Fermi level. The emission intensity is normalized to the excitation photon intensity. The results of the least-squares fitting are also shown. *B* denotes bulk component, *S* denotes surface component.

of the bulk component. The slightly larger Gaussian width obtained from the fit than the instrumental resolution may be due partly to inhomogeneous band bending across the surface. For the clean surface, a good fit is obtained in the As 3*d* spectra assuming an additional surface component, labeled *S*, shifted 0.51±0.03 eV toward lower binding energy from the bulk component, labeled *B*, as shown in Fig. 3(b). In the fit, the spin-orbit splitting, branching ratio, Lorentzian, and Gaussian widths are assumed to be common for the bulk and surface components. Again, fitting was also attempted assuming two surface components, and the intensity of the last surface component, if it exists, was found to be less than 4% of the bulk component.

The fitting for the Ga 3*d* peaks, on the other hand, is more difficult because chemical shifts for Ga are rather small. To estimate peak positions, fitting was done for the Ga 3*d* spectra in Fig. 3 for both (2×1) and clean surfaces assuming a single spin-orbit-split doublet with a branching ratio of 0.67, a splitting of 0.45 eV (Ref. 15) and the Lorentzian width of 0.21 eV.

The striking feature in Fig. 3 is the large shifts of As, Ga 3*d* peaks for the (2×1) surface toward higher binding energy with respect to those of the clean surface, due mostly to the decrease in upward band bending. The shift of 0.62 eV for the As 3*d* bulk component, in particular, is solely a band-bending shift. The band-bending shift is also seen in the valence-band edge spectra shown in Fig. 4. The valence-band maxima indicated in this figure are determined by linear extrapolation of the edge portion to the background using a least-squares fit. The energy position of the Fermi level is located at 0.74±0.05 eV above the valence-band maximum for the clean surface. This value agrees with the reported one for a clean surface obtained by thermally desorbing the surface oxides.[16] We estimate the Fermi-level position for the (2×1) surface as 1.36±0.06 eV above the valence-band maximum, from the As 3*d* band bending shift of 0.62 eV that is added to the Fermi-level position for the clean surface. This estimate agrees within an experimental uncertainty with the one deduced directly from the valence-band edge position of the (2×1) surface. The estimated Fermi-level position for the (2×1) surface is comparable with the bulk position for the doping density of 1×10^{17} cm^{-3} used here. Thus the band is nearly flat. The flat band is found to be maintained up to 550 °C, above which the surface starts desorbing the Se atoms.

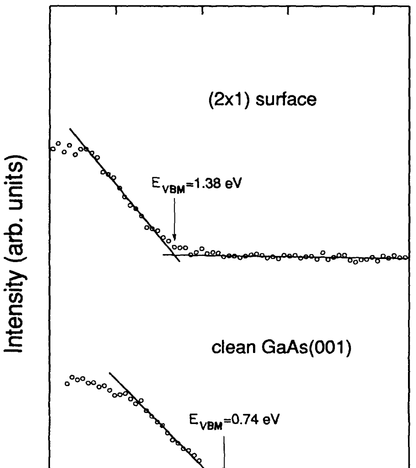

FIG. 4. Valence-band edge spectra of a Se-stabilized (2×1) surface and a clean surface obtained after 600 °C heating. The excitation photon energy is 100 eV. The binding energy is referred to the Fermi level. VBM denotes valence-band maximum.

As seen from Fig. 3, the As 3*d*-to-Ga 3*d* intensity ratio for the (2×1) surface, $I_{\mathrm{As}}/I_{\mathrm{Ga}}$, is considerably smaller than that for the clean surface, $I^c_{\mathrm{As}}/I^c_{\mathrm{Ga}}$. One can also see that the Ga 3*d* intensity for the (2×1) surface, I_{Ga}, is smaller than that for the clean surface, I^c_{Ga}. The intensity ratios are carefully evaluated for a few samples from spectra taken at a lower instrumental resolution to achieve higher counting rates. The ratios thus obtained are $I_{\mathrm{As}}/I_{\mathrm{Ga}}=0.57$, $I^c_{\mathrm{As}}/I^c_{\mathrm{Ga}}=1.23$, and $I_{\mathrm{Ga}}/I^c_{\mathrm{Ga}}=0.79$. The error is less than ±0.05 for all these ratios. The diffraction effect[17] should be small because of the angularly integrated nature of the spectrum taken with a cylindrical mirror analyzer. As discussed further in Sec. V, the fact that $I_{\mathrm{As}}/I_{\mathrm{Ga}}$ is considerably smaller than $I^c_{\mathrm{As}}/I^c_{\mathrm{Ga}}$ indicates that As is deficient even below the surface. This suggests the formation of a thin selenide layer composed mainly of gallium selenide. It should be noted that for the sample examined here the Se treatment to form the (2×1) structure is done on the surface initially exhibiting the As-stabilized (2×4) structure. The exposure to Se flux appears to induce As loss on the surface. Arsenic selenide, which may be formed during the treatment, will be desorbed from the surface due to its high vapor pressure. The same (2×1) reconstructed surface is thus formed irrespective of the initial As and Ga composition. The selenide layer should be epitaxially formed on the substrate since a well-defined reconstruction is observed using RHEED. We believe that this selenide layer is formed as a result of the Se-As exchange reaction in the surface region. The $I_{\mathrm{Ga}}/I^c_{\mathrm{Ga}}$ being significantly less than unity suggests that the surface is terminated with Se atoms, which are bonded with Ga atoms of the next layer. A possible structural model for the (2×1) surface is discussed further in Sec. IV based on the analysis of the measured core-level peak intensity ratios.

The absence of a direct As—Se bond is also suggested from the As 3*d* spectrum for the (2×1) surface in Fig. 3(a), which shows only a bulk component. As shown in Fig. 3, the energy position of the Ga 3*d* peak with respect to the bulk As peak for the (2×1) surface is 21.64 eV, which is 0.2 eV smaller than that for the clean surface. This indicates that the Ga 3*d* peak position for the (2×1) surface is chemically shifted toward higher binding energy than for the clean surface. The presence of chemical shift in the surface Ga has also been shown by comparing spectra taken at surface sensitive and bulk sensitive conditions.[7] Although the value of the shift is not large, its direction is that expected for Ga atoms bonded with Se.

Figure 5 shows a typical Se 3*d* core-level photoelectron spectrum of the (2×1) surface, measured at 125 eV photon energy. One can see the presence of two chemically shifted components, labeled Se1 and Se2. The inset shows the Se 3*d* spectrum for a thick *a*-Se film, consisting of a single component. A least-squares fit showed the spin-orbit split of 0.86 ± 0.01 eV, the branching ratio of 0.65 ± 0.01, and the Lorentzian width of 0.18 ± 0.03 eV for Se 3*d*. The spectrum for the (2×1) surface was fitted assuming two components having the same spin-orbit split, branching ratio and Lorentzian width as those extracted from the spectrum for the thick *a*-Se. The Gaussian width was assumed to be common for the two components. The fitting showed the energy separation E_{Se1}-E_{Se2} of 1.00 ± 0.02 eV and the intensity ratio $I_{\mathrm{Se2}}/I_{\mathrm{Se1}}$ of 0.70 ± 0.02. The Se1 peak was found to be shifted 0.25 ± 0.05 eV toward lower binding energy from the bulk-Se peak position measured from a thin (10-Å) *a*-Se film deposited on the (2×1) surface.

Desorption of Se atoms is observed above 550 °C through photoemission measurements in agreement with the RHEED results. Variation of the Se 3*d* spectrum during desorption is shown in Fig. 6. The binding energy in this figure is referred to the valence-band maximum. The excitation photon energy is 125 eV. The spectra are normalized to the photon intensity. A fitting is done again using two components. After 560 °C heating, the intensities of both Se1 and Se2 peaks are decreased, and the intensity ratio $I_{\mathrm{Se2}}/I_{\mathrm{Se1}}$ is increased from those for the (2×1) surface. The Se1 and Se2 peaks in the spectrum after 560 °C heating shows additional shifts of 0.2 and 0.4 eV, respectively, toward higher binding energies. Although one-to-one correspondence is not established between photoelectron spectra and surface reconstructions for the intermediate phases, we believe that the Se 3*d* spectrum (b) in Fig. 6 shows either the (2×3) or (4×3) surface. Spectrum (c) in Fig. 6, taken after 580 °C heating, shows only the Se1 peak, which is eliminated at 600 °C.

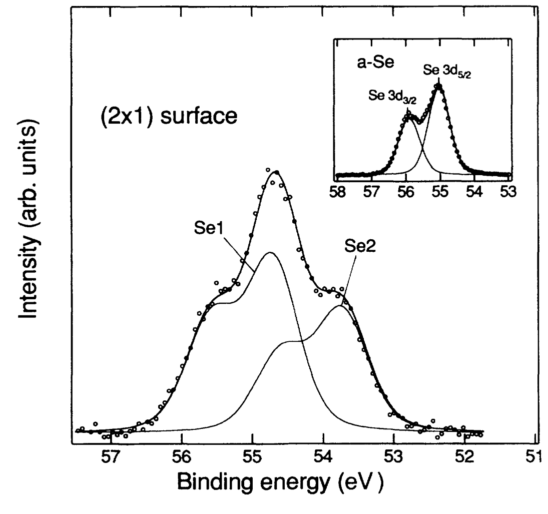

FIG. 5. Se 3*d* photoelectron spectrum for a Se-stabilized (2×1) surface measured with 125-eV photon for excitation. The inset shows the Se 3*d* spectrum for a thick amorphous (*a*-)Se film. The binding energy is referred to the Fermi level. The results of the least-squares fit are also shown. The spectrum for the (2×1) surface is fitted assuming two components, labeled Se1 and Se2 (see text for more detail).

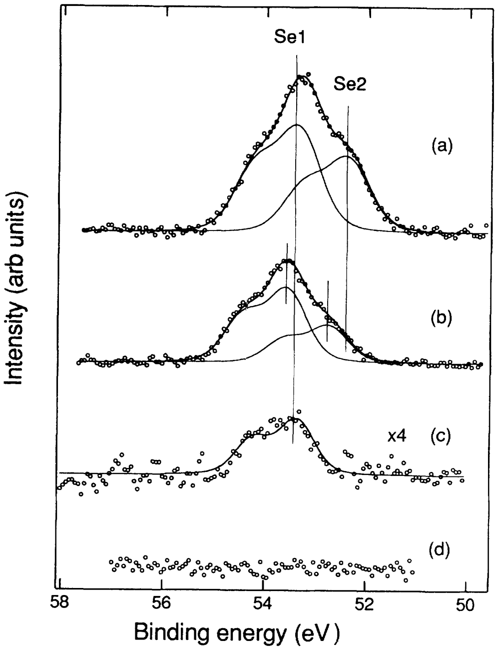

FIG. 6. Variation of the Se 3*d* photoelectron spectrum upon desorption: (a) (2×1) surface, after (b) 560 °C, (c) 580 °C, and (d) 600 °C heating for 3 min. The horizontal axis shows the binding energy measured from the valence-band maximum. The spectra are normalized to the photon intensity.

V. DISCUSSION

In order to derive a possible structural model for the Se-stabilized (2×1) surface, the measured core-level photoemission peak-intensity ratios are analyzed in the standard layer-attenuation model. In the analysis, the Se atoms are assumed to be adsorbed on the Ga atoms and terminate the surface, and also exchanged with As atoms below the surface. We first estimate the fractional coverage x_1 of the Se atoms terminating the surface from the observed attenuation of the Ga 3*d* peak of the (2×1) surface from that of the clean surface. The intensity ratio of the Ga 3*d* peaks for the (2×1) surface and the clean surface can be expressed in the layer attenuation model as

$$\frac{I_{\mathrm{Ga}}}{I_{\mathrm{Ga}}^{c}}=\frac{(1-x_1+x_1A)}{(1-x_{\mathrm{As}}+x_{\mathrm{As}}A)}\ , \tag{1}$$

where $A=\exp(-d/l)$ is the attenuation of photoelectrons passing through a monolayer, and is expressed with the interlayer spacing $d=1.413$ Å along [001] direction and an electron escape depth l. The attenuation factor A is assumed to be common for Ga, As, and Se monolayers. The parameter x_{As} is the fractional coverage of As atoms on the clean surface. The Se coverage x_1 can be found from the measured $I_{\text{Ga}}/I^c_{\text{Ga}}$ using Eq. (1) if the value for x_{As} and the escape depth l are assumed. As mentioned before, the clean surface obtained by desorbing the Se atoms in the photoemission experiment is presumably the Ga-terminated (4×2) surface. An Auger analysis[18] has estimated the fractional As coverage of the (4×2) $[c(8\times2)]$ surface as $x_{\text{As}}=0.22$. The structural model proposed in a recent scanning tunneling microscope (STM) study[19] suggests $x_{\text{As}}=0.14$. Varying the value of x_{As} from 0.14 to 0.22, taking the escape depth $l=5.5\pm0.5$ Å, and using the observed value of $I_{\text{Ga}}/I^c_{\text{Ga}}=0.79$, we obtain $x_1=0.96-1.18$. Thus, the number of Se atoms terminating the surface is about a full (001) atomic layer. The (2×1) reconstruction observed by RHEED may be attributed to dimerization of this top Se monolayer.

We next examine the $I_{\text{As}}/I_{\text{Ga}}$ intensity ratio to estimate the extent to which the Se-As exchange reaction occurs below the surface. Assuming that the As atoms in the layers below the surface are replaced with Se atoms with fractional Se occupancies of x_2, x_3, x_4, and so on, we get the expression for the intensity ratio $I_{\text{As}}/I_{\text{Ga}}$ for the (2×1) surface as

$$\frac{I_{\text{As}}}{I_{\text{Ga}}}=\frac{I^0_{\text{As}}}{I^0_{\text{Ga}}}(1-A^2)[(1-x_2)A+(1-x_3)A^3+(1-x_4)A^5+\cdots] . \qquad (2)$$

The attenuation factor is assumed to be the same for Ga and As $3d$ photoelectrons. I^0_{As} and I^0_{Ga} are emission intensities of the As and Ga monolayers, respectively, and their ratio can be determined from the observed intensity ratio for the clean surface $I^c_{\text{As}}/I^c_{\text{Ga}}$ through the equation

$$\frac{I^0_{\text{As}}}{I^0_{\text{Ga}}}=\frac{I^c_{\text{As}}}{I^c_{\text{Ga}}}\,\frac{1-x_{\text{As}}+x_{\text{As}}A}{(1-x_{\text{As}})A+x_{\text{As}}} , \qquad (3)$$

if the values for x_{As} and l are given. If available As atoms are replaced with Se atoms from the surface, an agreement with the observed intensity ratio $I_{\text{As}}/I_{\text{Ga}}$ is reached at which $x_2=1$ and $0<x_3<1$, i.e., the entire As layer just below the surface and a part of the next As layer are replaced with Se.

We further point out that a consistency with the observed intensity ratio of the two Se components, $I_{\text{Se2}}/I_{\text{Se1}}$, can be obtained in the present structural model if we attribute the Se1 atoms to those adsorbed on the surface and Se2 atoms to those occupying As sites below the surface. The intensity ratio $I_{\text{Se2}}/I_{\text{Se1}}$ is then given by

$$\frac{I_{\text{Se2}}}{I_{\text{Se1}}}=\frac{(1-x_1+x_1A)(x_2A+x_3A^3+x_4A^5+\cdots)}{x_1} . \qquad (4)$$

If we assume $x_1=1$, i.e., full atomic layer of Se atoms terminating the surface, and also $x_2=1$, $x_4=x_5=\cdots=0$, we can determine the values of x_3, x_{As}, and the escape depth l in a self-consistent manner from Eqs. (1)–(4). Using the observed value of $I_{\text{Ga}}/I^c_{\text{Ga}}=0.79$, $I_{\text{As}}/I_{\text{Ga}}=0.57$, $I^c_{\text{As}}/I^c_{\text{Ga}}=1.23$, and $I_{\text{Se2}}/I_{\text{Se1}}=0.70$, we obtain $x_3=0.34$ at $x_{\text{As}}=0.14$ and $l=5.2$ Å. The value of x_{As} agrees with that suggested from the STM study cited before for the Ga-stabilized $c(8\times2)$ surface. The value of l, which is assumed to be common for Ga, As, and Se $3d$ photoelectrons, is also reasonable for the kinetic energies of 80 eV (Ga $3d$), 70 eV (Se $3d$), and 58 eV (As $3d$). The structural model is schematically shown in Fig. 7 indicating the Se occupancy deduced from the present analysis.

The assumptions $x_2=1$ and $x_4=x_5=\cdots=0$ made in the above analysis do not have any additional support. Although the assumptions seem to be reasonable, the Se atoms may occupy only a part of the As layer just below the surface, and their occupation may extend to deeper layers. The total number of Se atoms, estimated as about two monolayers in the present analysis,.is thus considered as the lower limit.

The present analysis shows that the (2×1) surface is terminated with one atomic layer of Se atoms, which totally eliminate Ga dangling bonds. The transformation from the (2×1) surface to the clean Ga-terminated surface occurs in a reversible manner as shown by the RHEED observation. Thus, the reduced band bending for the (2×1) surface with respect to the clean Ga-terminated surface shown by the photoemission measurement can be attributed most naturally to elimination of Ga dangling-bond states, which are assumed here to be responsible for the Fermi-level pinning at the Ga-terminated surface. Although an explanation using the defect model[20] may also be possible, As_{Ga} antisites, which are claimed to be responsible for the midgap pinning in this model, are less likely to be present on surfaces richer in Ga, such as the Ga-terminated surface. Electron-energy-loss measurements have shown the presence of empty gap states associated with Ga dangling bonds at a Ga-terminated $c(8\times2)$ surface.[21] A tight-binding calculation on an ideal Ga-terminated GaAs(001) surface has also shown Ga dangling-bond states in the gap.[22] For the surface covered by monolayer Se atoms, these dangling-bond states should be raised toward the conduction band and converted to antibonding states through interaction

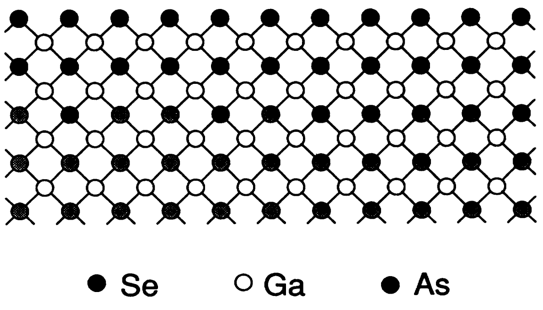

FIG. 7. A structural model for a Se-stabilized (2×1) surface consistent with the observed photoelectron intensity ratios in the layer attenuation model (see text for more detail).

with the Se valence orbital derived from the 4*s* and 4*p* orbitals, the energy levels of which are well below the band gap. The states can be removed from the gap if the interaction is strong enough. The recent band calculation for a GaAs(001) surface has indeed shown elimination of surface-gap states by terminating the surface Ga atoms with one monolayer of sulfur, and a similar effect is expected for a surface terminated with a Se monolayer.[23]

For clean As-rich surfaces, other sources for the Fermi-level pinning than Ga dangling bonds should also be considered, such as excess As,[24] $\mathrm{As_{Ga}}$ antisites,[20] and As dangling bonds.[25] The present study suggests that the Se treatment can also remove gap states associated with As, since the treatment makes surfaces As-deficient even when the surfaces are initially As-rich.

In the present structural model, a part of the adsorbed Se atoms are assumed to occupy As sites below the surface in the zinc-blende lattice as a result of anion exchange. This is supported by the fact that there exists a zinc-blende gallium selenide compound, Ga_2Se_3, which has a lattice parameter of 5.43 Å, comparable with that of GaAs.[26] The present analysis shows that this anion exchange takes place over a few atomic layers. Occurrence of anion exchange reaction has also been shown for a GaAs(001) surface treated by H_2Se gas.[8] One may anticipate that the Se-treatment induces an *n*-type layer near the surface since Se acts as a shallow donor impurity in GaAs. However, the flat-band shift of the *a*-Se/GaAs diode capacitance-voltage curve in Ref. 7 is small, suggesting that *n*-type doping at the interface is not significant.[27] It is thus suggested that the adsorbed Se atoms mostly form a compound which is related to Ga_2Se_3. The interface between this selenide layer and the substrate should be free of dangling bonds if the layer is coherent with the substrate. This thin selenide layer can be expected to enhance the stability of the surface, as has also been suggested for the surface treated by H_2Se gas.[8]

In the rest of this section, we discuss other RHEED and photoemission observations concerning adsorption behavior of Se atoms on GaAs(001). The Se 3*d* spectra in Fig. 6 indicate that while the intensities I_{Se1} and I_{Se2} are decreased, their ratio $I_{\mathrm{Se2}}/I_{\mathrm{Se1}}$ is increased for the partially selenized surface from those of the (2×1) surface. This can be interpreted in terms of the present attribution for the Se1 and Se2 components as an increase in the relative number of surface-to-subsurface Se atoms for the partially desorbed surface. As seen in Fig. 6(c), the Se1 is the only persistent component at low coverage upon desorption. Adsorption and desorption occur in reverse as found from the RHEED observation. The present attribution for the Se1 component thus suggests that Se atoms prefer to occupy the on-surface sites in the initial adsorption step.

The adsorption behavior of Se atoms on GaAs(001) surfaces is closely related to that observed for Te atoms on GaAs(001).[28] A (2×1) reconstruction is observed at the highest Te coverage and the photoelectron spectrum of this surface shows the presence of two peaks with their energy separation and intensity ratio comparable to those found in this study for the Se-induced (2×1) surface. In addition, the intermediate phase having a $\times3$ reconstruction is also observed in the Te-GaAs(001) system. The Te 3*d* photoelectron spectrum of this surface[28] resembles spectrum (b) in Fig. 6. The Se2 peak in Fig. 6(b) is apparently shifted by 0.4 eV toward higher binding energy. For the Te-induced $\times3$ reconstructed surface, the Te 3*d* spectrum is interpreted as showing a component shifted from the lower binding energy component that is eliminated. Such agreement in the adsorption behavior can be attributed to the similar chemical properties of Se and Te. It should, however, be mentioned that the attribution of the two Te components in Ref. 28 is not in parallel with the present attribution of the two Se components. The present attribution is partly based on the observation of Ga and As photoelectron spectra, which is not done in the Te adsorption study.

The relatively higher-order reconstructions and the additional shifts in the Se1 and Se2 peaks for the intermediate phases indicate the involvement of complicated processes in the formation of these phases. A more detailed description of the structure of these surfaces is left for future study.

Reconstructions relevant to the intermediate phases have been observed by other people in different contexts and experimental conditions. Surfaces with the characteristic $\times3$ reconstructions $[(2\times3)$ and $(4\times3)]$ have been observed for the GaAs(001) surface heated in an MBE chamber used for growing zinc selenide.[29] The present results strongly suggest that these surfaces are obtained as a result of partial selenization by ambient Se in the chamber. The surfaces treated by a Se-containing solution[12] and H_2Se gas[8] have shown a (4×1) reconstruction. These surfaces may be related to the (4×3) surface observed in this study, since the $\frac{1}{3}$-order streaks the RHEED pattern are rather broad as shown in Fig. 2(c) and in some cases hardly recognized.

VI. CONCLUSIONS

GaAs(001) surfaces modified by the adsorption of Se atoms in a vacuum are characterized using RHEED and photoemission spectroscopy. Se-stabilized surfaces show a characteristic (2×1) reconstruction irrespective of the initial surface composition. Intermediate phases having $\times3$ reconstruction are also observed for partially selenized surfaces. Measurements of core-level peak-intensity ratios for the (2×1) surface show considerable As loss at the (2×1) surface. The analysis of the intensity ratios using the layer-attenuation model suggests that one atomic layer Se atoms are adsorbed on Ga atoms and terminate the surface for the (2×1) surface. It also suggests the occurrence of Se-As exchange near the surface leading to the formation of a selenide layer a few monolayers thick. The Se 3*d* spectrum shows the presence of two chemically shifted components, which are tentatively attributed to the Se atoms terminating the surface and those occupying As sites below the surface. The (2×1) surface formed on an *n*-type substrate exhibits a nearly flat band, indicative of the Fermi-level unpinning at the surface. According to the present structural model, the reduced gap states and the improved chemical stability of the Se-modified (2×1) surface are attributed to the termination of the Ga dangling bond by one monolayer Se on the surface and the formation of the thin epitaxial selenide near the surface.

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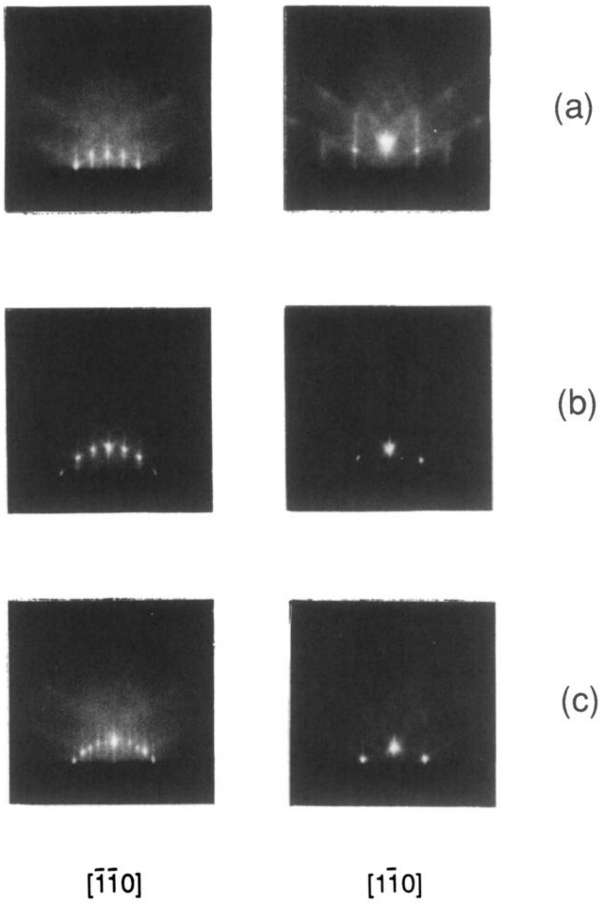

FIG. 2. RHEED patterns of the GaAs(001) surface induced by the adsorption of Se atoms: (a) (2×1) pattern characteristic of a Se-stabilized surface, (b) (2×3) pattern, and (c) (4×3) pattern of partially selenized intermediate phases.

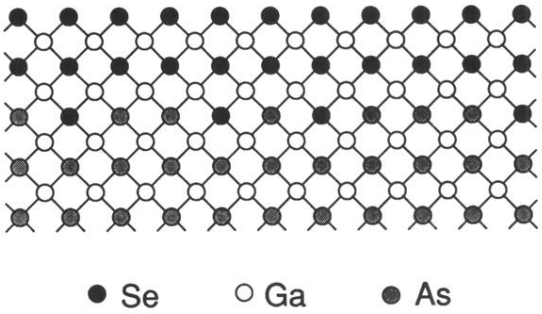

FIG. 7. A structural model for a Se-stabilized (2×1) surface consistent with the observed photoelectron intensity ratios in the layer attenuation model (see text for more detail).