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Sb-induced reconstruction on Sb-terminated GaAs(001)

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The surface structural changes occurring on Sb-rich Sb-terminated GaAs(001) was investigated by using reflection high-energy electron diffraction and core-level photoelectron spectroscopy. Another surface reconstruction of 2×8 superstructure was found, and the analysis of the core-level photoelectron spectra revealed that more of the Sb atoms on this surface are bonded to Sb atoms than to Ga atoms. This indicates the presence of a local structure of stacking double (or triple) Sb layers in which the Sb atoms in the lowest-layer bond with the underlying Ga atoms and in which the number of Sb atoms in the lowest layer is smaller than the number in the other layer(s). [S0163-1829(99)12635-3]

To control the initial stage of heteroepitaxial growth for heterostructure fabrication based on a III-V compound semiconductor, the adsorption control of group-V elements is important because heteroepitaxial growth often begins with the alternation of the group-V element flux supply. Therefore, several studies have been done on some combinations of group-V elements and III-V compound substrates. The study of Sb-terminated GaAs(001),[1] whose reconstruction is 2×4, is currently one of the very attractive issues in surface science and many theoretical[2,3] and experimental[4–7] studies have been reported since the Sb termination was found.

While investigations of the 2×4 Sb-terminated GaAs(001) surface itself are of course important, investigations of other reconstructed surfaces that can change to or from the Sb-terminated surface can also help us for understand the properties of that surface. For this reason, we reported the 1×4 and 1×3 surface reconstructions observed before Sb termination[1] when Sb was deposited on an As-terminated GaAs(001) and also reported the 4×2 reconstruction that appeared after Sb desorption.[1] The order of Sb coverage on these reconstructions can be summarized as follows: 1×4, 1×3, 2×4, and 4×2 (largest coverage on the 1×4 surface and no Sb on the 4×2 surface). The 1×4 and 1×3 surfaces are more Sb rich than the Sb-terminated surface but As-Sb bonding remains in the reconstructed regions of these surfaces. While Sb-rich As-terminated surfaces have thus already been reported, the surface changes that occur under Sb-rich conditions on Sb-terminated surfaces have not to our knowledge. Such changes are important because several competing models have been proposed and theoretical calculations are based on Sb coverage. We therefore, used reflection high-energy electron diffraction (RHEED) and photoelectron measurements to investigate the surface changes occurring on Sb-rich Sb-terminated GaAs(001).

The substrates were *n*-type GaAs(001) doped with Si to a carrier density of $3.0\times10^{18}\,\mathrm{cm}^{-3}$. After chemical etching the substrates, we attached them with In solder to Mo holders and placed them in a molecular-beam-epitaxy (MBE) growth chamber. After a substrate was annealed at 600 °C in an As-molecular flux to remove surface oxides and a buffer layer about 200-Å thick was homoepitaxially grown on it at 570 °C, a sharp streaky 2×4 RHEED pattern was observed under the As flux. The substrate was then cooled to 470 °C and an Sb flux (1×10^{-6} Torr) was supplied for 5 min. The 2×4 RHEED pattern that was then observed confirmed that an Sb-terminated surface had been obtained. After the substrate was cooled to room temperature (RT), about two monolayers (ML) of Sb were deposited on it and it was transferred under ultrahigh vacuum to an analysis chamber[8] connected to the beamline of ABL-3B at the normal-conducting accelerating ring.[9]

In the experiment, a sample was heated for 10 min at several substrate temperatures between 220 °C and 520 °C and cooled to less than 200 °C before a RHEED observation was made and a photoelectron spectrum was measured. In the photoelectron measurements, the photon energy was set at 90 eV and the takeoff angle (from the sample surface) was set at 25°. The photon energy was calibrated by measuring the Au Fermi edge, and the total energy resolution was determined to have been 0.17 eV.

As the substrate temperature increased, the RHEED patterns changed and two kinds of surface reconstruction were observed. First, on the initial surface on which 2 ML of Sb had been deposited at RT, an 1×1 RHEED pattern with weak fundamental streaks and a bright background was observed. At a substrate temperature of 220 °C, almost the same pattern was observed. When the substrate temperature was increased to 400 °C or 460 °C however, a clear 2×8 RHEED pattern was evident. This 2×8 surface superstructure has not been reported before. At substrate temperatures below 400 °C, such as 340 °C and 280 °C, some broad streaks were observed. But because the background was very bright, however, it is not clear whether these streaks were real fractional streaks or shade produced by the nonuniformity of the RHEED screen. The exact 2×8-ordering temperature therefore remains unknown, but it is somewhere between 220 °C and 400 °C. On further heating, a 2×4 clear pattern was observed at 520 °C. This RHEED pattern is the same as that obtained from a 2×4 Sb-terminated surface when a thin Sb film is initially formed on an As-terminated surface.[1]

We investigated the chemical bonding structure of the surface by measuring core-level photoelectron spectra at various substrate temperatures. With increased temperature, the shape of the Sb 4*d* spectrum changed drastically, but that

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TABLE I. Fitting parameters for As $3d$, Sb $4d$, and Ga $3d$ core-level spectra obtained from Sb/GaAs(001). The range of the each full width at half maximum (FWHM) and branching ratio is due to the fitting of the spectra of various annealing temperatures.

	As $3d$	Sb $4d$	Ga $3d$
FWHM (eV)	0.615±0.015	0.58±0.01	0.55±0.01
Spin orbit splitting (eV)	0.68	1.243	0.45
Branching ratio	0.64±0.01	0.71±0.01	0.66±0.01

of the As $3d$ spectrum did not. A very small change in the shape of the Ga $3d$ spectrum was observed below 460 °C, but a remarkable change was observed when the temperature was increased to 520 °C.

To get more information about surface reactions, we deconvoluted the core-level spectra and examined the intensity of each deconvoluted component. The fitting parameters for each component are summarized in Table I. This fitting was based on the procedure described in Ref. 1. Figure 1 shows the deconvolution results for the spectra under typical surface conditions corresponding to surface reconstruction events. In the case of As $3d$, the double peaks caused by spin-orbit splitting show that only one component was resolved from the initial Sb-deposited surface to the 2×4 reconstructed surface. This indicates that the observed component can be assigned as a bulk (GaAs substrate) component and is denoted ''B'' in the figure. Furthermore, the binding energy of the As $3d$ peak position shifted slightly as the annealing temperature increased. The average value of the binding energy and shift were -41.1 and ±0.08 eV for the As $3d$ bulk component. Since the As $3d$ spectrum is composed of a single component, this shift directly reflects surface band bending and was taken into consideration when the Ga $3d$ and Sb $4d$ spectra were deconvoluted and assigned.

In the Ga $3d$ spectra, the most prominent component in the every surfaces was assigned as bulk component. This component is also denoted ''B''. The binding energy of this bulk component was -19.2 ± 0.15 eV. Because only one bulk component exists in GaAs, the ''$S1$,'' ''$S2$,'' and ''$S2$*'' components are assigned as surface components with binding energy shifts (from that of the bulk component) of -0.38 ± 0.015, 0.415 ± 0.015, and 0.3 eV, respectively. Although the components designated ''$S2$'' and ''$S2$*'' have similar binding energies these components are assigned as two different components because they have different binding energy differences from the binding energy of the bulk component. For Sb $4d$ spectra, several surface components were resolved by considering band bending: ''$S1$,'' ''$S2$,'' ''$S3$,'' and ''$S3$*.'' The binding energy of the ''$S2$'' component was -32.1 ± 0.07 eV, and the binding energies of the ''$S1$'' and ''$S3$'' components differed from that of this component by -0.48 ± 0.05 and 0.45 ± 0.05 eV. By taking account of the band bending, the difference of ''$S3$*'' is 0.1 eV from the standard binding energy where ''$S2$'' should be located if this component remained. This is much smaller the value for ''$S3$.'' Furthermore, the composition of photoelectron components of the spectrum obtained at 520 °C when 2×4 RHEED pattern was observed is the same as that of the photoelectron components in the spectrum of the Sb-terminated surface. Therefore, ''$S3$*'' can be assigned to the surface component of Ga-Sb bonding,[1] which is related to $S1$(Ga) and differ from ''$S2$,'' which is assigned to Sb-bulk component as described below. For this reason, we distinguished ''$S3$*'' from ''$S2$'' and ''$S3$''.

The component intensities and the corresponding substrate annealing temperatures are summarized in Fig. 2. Because photoelectron intensity is proportional to the intensity of the incident monochromatized light, the component photoelectron intensities were normalized by using the photocurrent of a monochromatized beam monitor. In this figure only the intensity of the $S2$(Sb) component is shown to decrease continuously as the annealing temperature increases. Because Sb atoms desorb during this annealing process, this continuous decrease indicates that the $S2$(Sb) component can be assigned as the chemical state of the bulklike Sb atoms, which are composed only of Sb-Sb bonding. On the other hand, the intensity of $S1(Sb)$ component decreases when the annealing temperature is between 280 °C and 460 °C, but increases when the temperature is below 280 °C. A continuous increase in the intensities of the other component can be recognized after allowing for statistical error.

To analyze the bonding-structure changes that occurred between substrate temperatures of 280 °C and 460 °C, we normalized the component intensities by using the As bulk component intensity at each temperature. The normalized

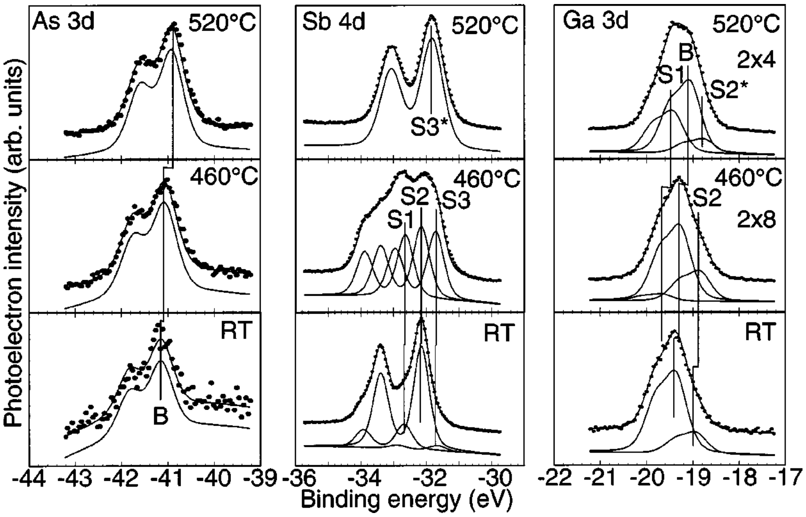

FIG. 1. Deconvolution results for As $3d$, Sb $4d$, and Ga $3d$ core-level photoelectron spectra of Sb/GaAs(001). The 520 °C and 460 °C temperatures are typical annealing temperatures used to obtain 2×4 and 2×8 RHEED patterns.

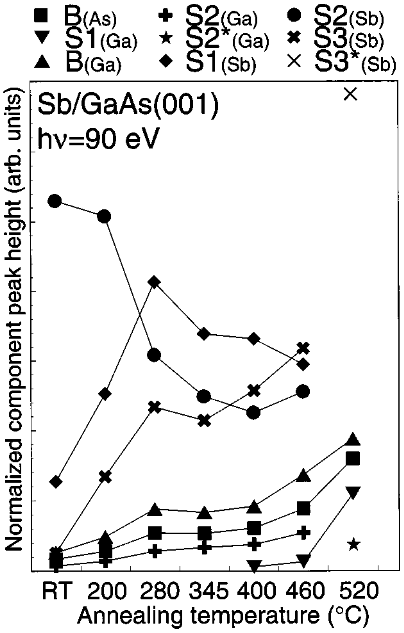

FIG. 2. Deconvoluted component intensity changes corresponding to the substrate annealing temperatures.

component intensities are summarized in Fig. 3, where the intensity at 280 °C is unity. For reference, the normalized intensities at 520 °C are also shown, as are the normalized intensities of the components $S2^*$(Ga) and $S3^*$(Sb). These values were normalized by using the intensities of the $S2$(Ga) and $S3$(Sb) components at 280 °C.

Figure 3 shows that the components can clearly be divided into two types. One type is indicated by the line showing the intensity of the bulklike Sb component, $S2$(Sb), which reveals that the Sb atoms have been desorbed from the surface. The other is indicated by the line showing the intensity of the substrate bulk component, B(Ga), which indicates that these atoms remain at the surface. As for the $S2$(Ga) component, although the intensity at 345 °C was greater than that at 280 °C, it was almost constant between 345 °C and 460 °C. Therefore, this component has a correlation with the intensity change of the bulk component and the Ga atoms remain at the surface. In the B(Ga) type, the intensities slightly decrease although we can consider that they are almost constant compared to other components. This is probably due to differences in the electron attenuation length between As $3d$, Sb $4d$, and Ga $3d$. However, the other effects, such as photoelectron diffraction and interlayer width relaxation, are also probabilities for the influence of this change. The reason for this slight decrease is thus not clear at present. On the other hand, the decrease of the $S2$(Sb) intensity shows that several Sb coverages exist on the 2×8 surface and each coverage is in accordance with the quantity of the remaining Sb atoms that correspond to the $S1$ and $S2$ components.

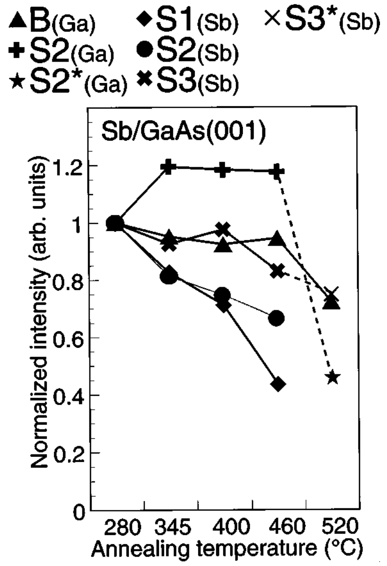

FIG. 3. Normalized component intensities of annealing temperatures between 280 °C and 520 °C. The normalized intensities are calculated by dividing the component intensity by the As $3d$ peak intensity at each annealing temperature. Unity is taken to be the intensity at 280 °C.

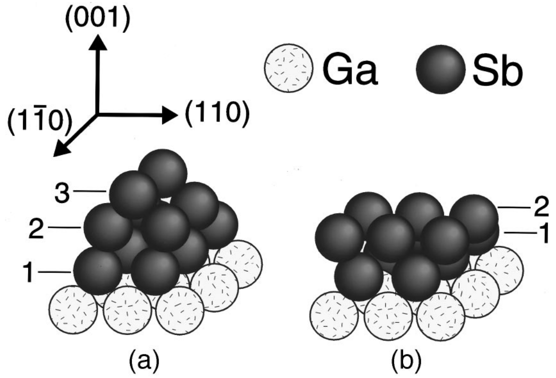

FIG. 4. Examples of local atomic bonding structures for the 2×8 surface that explain our experimental results if 0.5 ML-Sb atomic arrangement models are assumed for 2×4 Sb-terminated GaAs(001). The numbers shown next to the Sb atoms are the stacking-layer numbers.

We now discuss the 2×8 surface structure discovered through this study. We think that the assignment of the core-level spectra of the 2×8 surface in Fig. 3 is important for this discussion. The normalized intensities of the components $S3$(Sb), B(Ga), and $S2$(Ga) are nearly constant while those of the component $S1$(Sb) and $S2$(Sb) decrease. From this result, the presence of $S3$(Sb) can be considered to be due to Ga-Sb bonding. Furthermore, because the normalized intensities of the $S1$(Sb) and $S2$(Sb) components are not related to those of the Ga component, these components can be assigned to Sb atoms that have not bonded to Ga atoms; their presence is due to Sb-Sb bonding. The sum of the $S1$(Sb) and $S2$(Sb) component intensities, however, is twice the intensity of the $S3$(Sb) component, even after annealing at 460 °C.

At the spectrum of 400 °C, the sum of the two component intensities divided by the $S3$(Sb) intensity equals 2.3. When an electron mean free path of 5.5 Å (Ref. 10) and a takeoff angle of 25° are used, the photoelectron intensity calculated on the basis of a layer attenuation model attenuates with the ratio of 0.48 per atomic layer. In this calculation, we assumed an interlayer spacing of 1.7 Å, which is the spacing between the Sb layer and Ga layer of a 2×4 Sb-terminated surface.[7] If we assume there are only simple two layers of Sb atoms and that the top layer is the source of the $S1$ and $S2$ components and the second layer is the source of the $S3$ component, the number of Sb atoms in the top layer is 10% larger than that in the second layer. In this case the Sb coverage of the atomic layer is assumed to be unity. Therefore, when the Sb coverage is smaller than unity similar to 2×4 Sb-terminated surface model, the photoelectron attenuation should be smaller and the number of Sb atoms in the top layer should be larger than this estimation. But, because the surface model has not been determined, we cannot estimate the coverage more precisely at present.

In any case, more Sb atoms contribute to the $S1$ and $S2$ components than to the $S3$ component indicating that more Sb atoms do not bond with Ga atoms than do. This can be explained by the number of Sb atoms that have bonded with only Sb atoms being larger than the number of underlying Sb atoms that have bonded with Ga atoms. This situation is not observed in other group-V element rich III-V compound (001) surfaces without GaSb (001)-2×5,[11–13] whose atomic arrangement model has not been determined. If we assume that the 0.5-ML Sb models[2,7] are correct, the double layer of Sb atoms stacked on the terminating Sb atoms that is shown in Fig. 4(a) and that is similar to the atomic arrangement model of GaSb (001) 2×5 (Ref. 13) is one possibility for the atomic local bonding structure. Another is a model where there are a larger number of Sb atoms than terminating Sb atoms which are spread laterally [Fig. 4(b)].

In summary, this investigation of surface changes occurring on Sb-rich Sb-terminated GaAs(001) revealed a 2×8 surface reconstruction that appears before an Sb film forms. By analyzing the chemical bonding and the component intensity of the core-level photoelectron spectra of this surface, we found that more Sb atoms are bonded to other Sb atoms than are bonded to Ga atoms. This means that a local structure of stacking double or triple-Sb layers whose Sb atoms at the lowest Sb layer bond with the underlying Ga atoms exist and that the number of Sb atoms at the lowest layer is smaller than that of the top layer (when double-Sb layer model) or top and second layers (when triple-Sb layer model). Because a 2×4 Sb-terminated surface appears as a result of the disappearance of Sb atoms bonded to other Sb atoms, the 2×8 surface structure may be a key to determining the atomic structure of an Sb-terminated GaAs surface.

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