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X-ray standing-wave study of an Sb-terminated GaAs(001)-(2$\times$4) surface

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The Sb-Sb dimer structure of a 2$\times$4 reconstructed Sb/GaAs(001) surface was investigated by core-level photoelectron collection mode of back reflection soft x-ray standing-wave technique. Sb atoms occupy the bridge site forming bonds with two underlying Ga atoms and form symmetric Sb-Sb dimers lining up in the $[1\overline{1}0]$ direction. The first-layer Sb atomic plane is estimated to be 1.81 ± 0.02 Å above the second-layer Ga lattice plane. The bond length of the Sb-Sb dimer on a GaAs(001) surface is estimated to be 2.95 ± 0.06 Å, which is longer than the reported Sb-Sb bond length for Sb/GaAs(110) surface.

The behavior of group-V elements on III-V compound semiconductor surfaces is technologically important and also quite interesting in surface science. Although there have been many chemical and structural studies of various reconstructed GaAs(001) surfaces, there have been few investigations of other group-V element atoms on the GaAs (001) surface. Maeda, Watanabe, and Oshima[1] reported the surface reconstruction and the chemical bonding change on an Sb/GaAs (001) surface prepared by depositing Sb on As-terminated GaAs(001) at room temperature and annealing it up to the Sb desorption temperature. They found that the reflection high-energy electron diffraction (RHEED) pattern changes from 1$\times$4 with high halo, via 1$\times$4, 1$\times$3, and 2$\times$4, to 4$\times$6 as the substrate temperature is increased. Furthermore, photoelectron spectra showed that only single Sb-Ga and As-Ga chemical states exist in Sb and As atoms, respectively, for the 2$\times$4 reconstructed surface. This suggests that Sb atoms are located only at the surface layer and As atoms are located only at the bulk positions. The surface atomic arrangement of this Sb-terminated surface is thought to be very similar to the As-terminated GaAs(001) surface except that the dimer consists of Sb atoms instead of As atoms.

The x-ray standing-wave (XSW) technique is capable of locating the position of particular atomic species at a crystal surface.[2,3] After the advantages of a back reflection x-ray standing-wave technique by scanning the photon energy were pointed out by Woodruff *et al.*,[4] several studies utilizing this technique have been reported.[5–9] Kendelewicz *et al.* have performed back reflection XSW experiments for the Sb/GaAs (110) surface.[8,9] There have been many experimental[8–12] and theoretical[13–15] structure analysis studies of the Sb/GaAs(110) surface; however, no structural study of the Sb/GaAs(001) surface has been reported until now to our knowledge. When structures of the adsorbates on III-V compound semiconductor surfaces are analyzed by XSW, the group-III atomic site and the group-V atomic site can be distinguished by using noncentrosymmetric $\{111\}$ reflections. Therefore, two different XSW experiments of (111) and $(1\overline{1}1)$ reflections are thought to be suitable for the analysis of the GaAs(001) surface.[16] In this study, the Sb 3*d* core-level photoelectron collection mode of back reflection XSW analysis using (111) and $(1\overline{1}1)$ reflections were performed to investigate the Sb-Sb dimer structure of the 2$\times$4 reconstructed Sb-terminated GaAs(001) surface.

The 2$\times$4 reconstructed Sb/GaAs(001) sample was prepared as presented by Maeda, Watanabe, and Oshima.[1] After the chemical treatment, the *n*-type GaAs(001) wafer was attached to a Mo sample holder with In solder and transferred to a molecular-beam-epitaxy (MBE) growth chamber. The sample surface was flashed to 620 °C and then annealed for 15 min at 590 °C under an As flux to remove surface oxides and contamination. Next, the substrate temperature was immediately decreased to 560 °C and then GaAs was grown homoepitaxially. After the growth, the sample showed a sharp, streaky 2$\times$4 RHEED pattern. Several monolayers of Sb atoms were deposited on the As-stabilized GaAs(001) surface at room temperature from an effusion cell. The substrate temperature was increased to 500 °C and a well-defined 2$\times$4 reconstructed Sb/GaAs(001) surface was obtained. Then the sample was transferred from the MBE chamber to the x-ray standing-wave analysis chamber through ultrahigh vacuum.

The XSW experiments were carried out at the NTT beamline 1A of the Photon Factory at the National Laboratory for High Energy Physics.[17] We developed an ultrahigh vacuum three-axis goniometer system to perform the XSW experiment. In order to determine the three-dimensional arrangement of the Sb atoms, the back reflection XSW experiments of both GaAs $(1\overline{1}1)$ and (111) reflections were performed by scanning a pair of InSb(111) crystals through the GaAs $(1\overline{1}1)$ and (111) normal incidence Bragg reflection condition, which occurs at around 1.9 keV. For the GaAs(001) substrate, both the $(1\overline{1}1)$ and (111) diffraction planes were inclined at about 54° to the (001) surface. Thus, the (111) experiment could be set up by rotating the ϕ axis of the goniometer 90° after the $(1\overline{1}1)$ reflection experiment. Therefore, these two XSW experiments were performed using the same arrangement. The intensities of Ga 2*p*, As 2*p*, and Sb 3*d* core-level photoelectron spectra were measured with the electron energy analyzer as a function of photon energy.

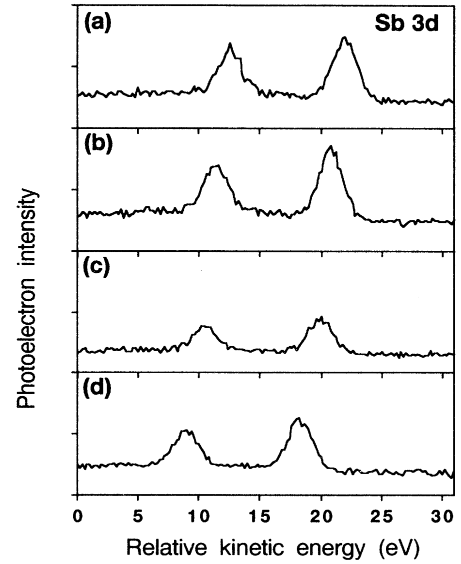

FIG. 1. Sb 3*d* photoelectron spectra collected at the four different Bragg conditions in the (111) XSW experiment. Integrated intensities of these Sb 3*d* spectra (a)–(d) are shown in Fig. 2 as the (111) XSW data points (a)–(d). The photon energies of the spectra (a), (b), (c), and (d) were about 1901.3, 1900.1, 1899.3, and 1897.7 eV, respectively.

In the correction of photoelectron intensity, we should pay attention to the very high background of the photoelectron spectra. Kendelewicz *et al.*[9] used the constant initial state mode both at the exact photoelectron peak and at the background by scanning the cylindrical mirror analyzer kinetic energy simultaneously with the monochromator. In our study, photoelectron spectra of the Ga 2*p*, As 2*p*, and Sb 3*d* core level were collected in all data points with a 100-mm mean radius hemispheircal electron energy analyzer (CLAM2) with a lens unit. Figure 1 shows electron energy scanned Sb 3*d* spectra in four different conditions around the (111) reflection. The background of these spectra was subtracted after the measurement. In order to obtain reliable Sb 3*d* photoelectron intensity profiles, Sb 3*d* spectra were fitted by fixing the intensity ratio and separation of the doublet (Sb $3d_{3/2}$ and Sb $3d_{5/2}$).

The photon-energy-dependent secondary emission yield profile $Y_{(E)}$ is given by

$$Y_{(E)} = 1 + R_{(E)} + 2F\sqrt{R_{(E)}}\cos(2\pi P - \delta_{(E)}) , \qquad (1)$$

where $R_{(E)}$ is the intrinsic reflectivity and $\delta_{(E)}$ the phase between the two plane waves that form the interference field. Here, $R_{(E)}$ in back reflection condition and $\delta_{(E)}$ can be computed as a function of photon energy *E*.[18] We used the anomalous atomic scattering factors reported by Henke *et al.*[19] and the room-temperature Debye-Waller factors of the Ga and As atoms calculated from $B = 0.91$ Å^2.[20] The two parameters *P* and *F* in Eq. (1), which can be determined by the XSW analysis, are called the coherent position and the coherent fraction, respectively. These parameters contain structural information about target atoms. The coherent position *P* gives the position of the target atoms with respect to the specific bulk-extrapolated reflection planes. In our case, the coherent position *P* is defined as the normal distance in units of the GaAs {111} *d* spacing from the {111} net planes, which lie at the midpoint of the Ga-As double layers. The coherent fraction *F* includes both the Debye-Waller factor and the fraction of the atoms at the actual lattice sites defined by the coherent position *P*. In other words, the coherent fraction *F* acts as a measure of the degree of ordering. A highly disordered or amorphous distribution corresponds to *F* of 0. On the other hand, *F* close to 1 indicates that all target atoms are almost at identical positions. Multiple locations of target atoms can also be analyzed based on the reduction of *F* values.[21,22] Fontes, Patel, and Comin investigated the asymmetric dimer buckling of Ge on the Si(001) surface where there are two different Ge atomic positions.[22] They pointed out that structural information can be derived from the ratio of *F* values for several different XSW results. Recently, Franklin *et al.* demonstrated the determination of the bond length and height of the symmetric As dimer in the As/Si(001)-(2×1) surface.[23]

Figure 2 shows two types of XSW results for the 2×4 reconstructed Sb/GaAs(001) surface. Both Ga 2*p* and As 2*p* photoelectron intensity profiles are thought to agree with the theoretical curves based on the ideal distribution in GaAs bulk crystal, because the kinetic energy of Ga 2*p*

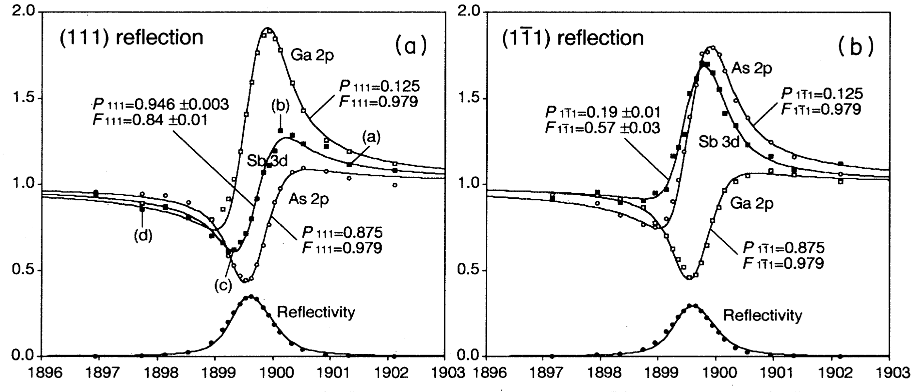

FIG. 2. Back reflection XSW results of two reflections: (111) and ($1\bar{1}1$). The horizontal axis is incident photon energy. The solid circles are the Bragg reflection. The open circles and open squares are the photoelectron intensity data points of As 2*p* and Ga 2*p*, respectively. The solid squares are Sb 3*d* data points. Sb 3*d* data points (a)–(d) in the (111) result are the integrated intensities of the Sb 3*d* spectra (a)–(d) in Fig. 1.

and As $2p$ photoelectrons of about 780 and 575 eV, respectively, has long escape length. The XSW result gives the normal distance from the specific bulk or bulk-extrapolated reflection net planes. We defined that the (111) and $(1\bar{1}1)$ net planes lie at the middle position of the As-Ga and Ga-As double layer, respectively. The ideal Ga and As profiles for (111) reflection can be calculated with the coherent position P_{111} of 0.125 and 0.875, respectively. On the other hand, those for the $(1\bar{1}1)$ reflection can be calculated with the coherent position $P_{1\bar{1}1}$ of 0.875 and 0.125, respectively. Theoretical curves of Ga and As convoluted by an instrumental resolution function of 80% Gaussian and 20% Lorentzian whose full width at half maximum is 0.5 eV show very good agreement with experimental data points of Ga $2p$ and As $2p$ photoelectron yields, respectively. Therefore, this resolution function was used for the analysis of Sb $3d$ photoelectron intensity profiles. The coherent position P and the coherent fraction F were determined for Sb $3d$ photoelectron intensity profiles from least-square fits to the theoretical profiles. The (111) results yielded a P_{111} of 0.946 ± 0.003 and an F_{111} of 0.84 ± 0.01, whereas the $(1\bar{1}1)$ results yielded a $P_{1\bar{1}1}$ of 0.19 ± 0.01 and an $F_{1\bar{1}1}$ of 0.57 ± 0.03.

Figure 3 shows the Sb adsorption configuration on the Ga-terminated GaAs(001) surface. This surface has a 2×4 reconstruction according to the RHEED pattern. The origin of this $2\times$ periodicity is thought to be symmetric Sb-Sb dimers lining up in the $[1\bar{1}0]$ direction. Considering the crystal symmetry of this system, the $P_{1\bar{1}1}$ and P_{111} should be equal to the $P_{\bar{1}11}$ and $P_{\bar{1}\bar{1}1}$, respectively. Therefore, the average position of Sb atoms projected onto the (110) plane (side view 1 in Fig. 3) can be obtained only from $P_{1\bar{1}1}$, and the position of Sb atoms projected onto the $(1\bar{1}0)$ plane (side view 2 in Fig. 3) can be obtained only from P_{111}. The surface normal distance $D_{\text{Sb-Ga}}$ between the position of Sb atoms forming Sb-Sb dimers and the bulk lattice position of the underlying Ga atoms, can be obtained from either P_{111} or $P_{1\bar{1}1}$ and is given by

$$D_{\text{Sb-Ga}}=d_{111}\sqrt{3}(P_{111}-\tfrac{5}{8})=d_{111}\sqrt{3}(P_{1\bar{1}1}+\tfrac{1}{8}) , \quad (2)$$

where d_{111} is the d spacing of the GaAs $\{111\}$ net plane (3.264 Å). The distance can be independently obtained by using P_{111} or $P_{1\bar{1}1}$. $D_{\text{Sb-Ga}}$ determined from P_{111} and $P_{1\bar{1}1}$ is 1.81 ± 0.02 and 1.78 ± 0.06 Å, respectively. The slight difference is thought to be due to experimental errors. In this study, $D_{\text{Sb-Ga}}$ determined from P_{111} is thought to be more reliable than that from $P_{1\bar{1}1}$, because its deviation is small. The larger deviation of the $P_{1\bar{1}1}$ value might be caused by the smaller $F_{1\bar{1}1}$ value of the $(1\bar{1}1)$ results.

As shown in Fig. 3, there are two different positions for Sb atoms that form dimers in the (110) plane (side view 1 in Fig. 3). $F_{1\bar{1}1}$ gives a one-dimensional distribution of Sb atoms in the $[1\bar{1}1]$ direction that depends on the dimer formation. On the other hand, F_{111} gives a distribution in the [111] direction that is independent of the dimer formation. The experimentally determined F_{111} value of 0.84 suggests that well-ordered Sb atomic layer is formed on this surface. A significantly smaller experimental $F_{1\bar{1}1}$ value of 0.57 than the F_{111} value of 0.84 indicates the existence of the Sb-Sb dimer on the surface. When there are two different atomic positions as shown in Fig. 3, the resulting coherent fraction $F_{1\bar{1}1}$ is given by the following equation:

$$F_{1\bar{1}1}=f\cos[\pi(P_{1\bar{1}1_A}-P_{1\bar{1}1_B})] , \quad (3)$$

where $P_{1\bar{1}1_A}$ and $P_{1\bar{1}1_B}$ are the discriminated coherent positions as shown in Fig. 3 and f is the intrinsic value of the coherent fraction, which includes both an ordered fraction and a Debye-Waller factor,[23] ranging between 0 and 1. The following cosine term is a geometrical factor.[23] If the ordering degree of both Sb atomic positions along the $(1\bar{1}1)$ direction is assumed to be the same as that along the [111] direction, we can use the f of 0.84, which is the experimentally determined F_{111} value. This indicates that the ratio of $F_{1\bar{1}1}$ and F_{111} is only affected by the symmetric dimer formation of Sb atoms, and that the isotropical distribution caused by the thermal vibration and the disordering of Sb atoms can be canceled in the analysis. Therefore Eq. (3) can be used to estimate the difference between $P_{1\bar{1}1_A}$ and $P_{1\bar{1}1_B}$. When the symmetric Sb-Sb dimer forms as shown in Fig. 3, the Sb-Sb bond length $L_{\text{Sb-Sb}}$ is given by

$$L_{\text{Sb-Sb}}=d_{111}\sqrt{3/2}\{1-(P_{1\bar{1}1_A}-P_{1\bar{1}1_B})\} . \quad (4)$$

$L_{\text{Sb-Sb}}$ was calculated to be 2.95 ± 0.06 Å by using Eq. (4). Furthermore, if surface relaxation of second-layer Ga atoms is neglected, the Sb-Ga bond length is 2.75 ± 0.03 Å, which is not far from 2.64 Å, the Sb-Ga bond length in the GaSb bulk crystal. The Sb-Sb dimer bond length $L_{\text{Sb-Sb}}$ (2.95 Å) is found to be slightly longer than the sum of the covalent radii (2.72 Å), Sb bulk bond length (2.87

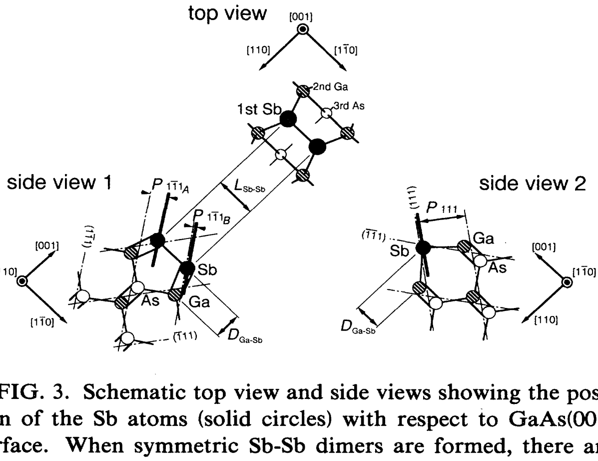

FIG. 3. Schematic top view and side views showing the position of the Sb atoms (solid circles) with respect to GaAs(001) surface. When symmetric Sb-Sb dimers are formed, there are two different Sb atomic positions of $P_{1\bar{1}1_A}$ and $P_{1\bar{1}1_B}$ relative to the $(1\bar{1}1)$ net plane as shown in side view 1. On the other hand, there is only a single position relative to the (111) net plane as shown in side view 2.

Å), and the Sb-Sb bond length (2.77–2.80 Å) in the reported atomic geometry of Sb/GaAs(110).[8–15] The difference in the Sb-Sb bond length between Sb/GaAs (001) and (110) is thought to be caused by the different local bonding geometry around Sb atoms. On the other hand, the Sb-Sb bond length in Sb/Ge(001) revealed by x-ray diffraction is 2.90 Å,[24] which is close to the determined value of 2.95 Å in the Sb/GaAs(001) system.

In this study, a simple symmetric Sb-Sb dimer model was assumed to estimate the dimer bond length from the XSW results, though it was not sure that every Sb dimer in 2×4 unit cell has exactly the same symmetric dimer arrangement. This study demonstrated that structural information can be derived from the ratio of F values for several different XSW results as pointed out by Fontes, Patel, and Comin.[22]

In conclusion, the Sb-Sb dimer structure of the 2×4 reconstructed Sb/GaAs(001) surface was investigated by core-level photoelectron collection mode of back reflection XSW analysis using two different asymmetric (111) and $(1\bar{1}1)$ reflections. The F_{111} value of 0.84 suggests that Sb atoms are well ordered, and the difference between F_{111} of 0.84 and $F_{1\bar{1}1}$ of 0.57 can be explained by the dimer formation of Sb atoms. These results were consistent with the previous photoemission results reported by Maeda, Watanabe, and Oshima.[1] The first-layer Sb atomic plane is estimated to be 1.81 ± 0.02 Å above the second-layer Ga lattice plane. The bond length of the symmetric Sb-Sb dimer on GaAs(001) surface was estimated to be 2.95 ± 0.06 Å. To our knowledge, this is the first structural investigation of the Sb/GaAs(001) surface. We expect many more experimental and theoretical studies of this structure.

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