Surface core-level shift of InSb(111)-2×2

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Surface core-level photoemission of InSb(111)-2×2 was performed using a synchrotron radiation light source. There were two surface components of the In $4d$ core level. A higher binding component of In $4d$ is attributed to the surface In bonded to Sb atoms. The lower binding component with smaller intensity is due to the surface In cluster atoms. On the other hand, we were not able to observe any surface components in the Sb $4d$ core level. This puzzling behavior is interpreted with a different contribution of surface and bulk Madelung potential to the surface core-level shifts in relation with the atomic geometry. [S0163-1829(96)01331-8]

The surface electronic properties of III-V compound semiconductors have been interesting topics in relation to their atomic geometry. Among the III-V semiconductor surfaces, polar {111} surfaces have not attracted much attention, because their preparation was not accessible by the natural cleavage unlike nonpolar {110} surfaces. Two kinds of {111} surfaces [group-III-terminated (111) and group-V-terminated ($\overline{111}$) surfaces] revealed various reconstructions[1,2] dependent upon the surface preparation condition. For the (111)-2×2 surface, a group-III-vacancy buckling model is believed to describe the atomic geometry experimentally[3–5] and theoretically.[6,7] Ejection of one cation atom makes the (2×2) surface more stable and geometrically flat. The resultant electronic nature of the (2×2) is similar to that of the (110) buckled surface. For the case of GaAs(111)-2×2, upward As and downward Ga atoms demonstrate p-type and sp^2-type bonding geometry, respectively.

Surface core-level photoemission spectroscopy is one of the powerful techniques for the investigation of the surface electronic and geometric properties.[8] Recently, Thornton *et al.*[9] reported that the surface core-level shifts (SCLS's) of the GaAs(111)-2×2 surface are very similar to that of the (110) surface. Their study is a good example of the correspondence between the atomic structure and its electronic nature. Very recent results on the SCLS's of the InSb(111)-2×2 showed a somewhat different behavior, but suggested the consistency of the general (111)-2×2 surface atomic stucture.[10] In this report, we present the SCLS's of the InSb(111)-2×2 surface, using synchrotron radiation and discuss the different behavior from that of the GaAs(111) surface with the Madelung potential concept.

The photoemission experiments were carried out at beam line BL6A2 of UVSOR at the Institute for Molecular Science in Okazaki of Japan and a detailed description of the equipment is presented elsewhere.[11] The photon incident angle was 45° off from surface normal and the emission angle of

photoelectrons was set to 10°. The overall energy resolution was 0.15 ~ 0.25 eV dependent upon the photon energy. The p-type InSb(111) was degreased in organic solvents and loaded in an UHV chamber. The cleaning of the surface was performed by repeated cycles of Ar$^+$ sputtering ($E=500$ eV) at 200 °C and a final annealing to about 350 °C. We obtained a distinct (2×2) diffraction pattern[12] and found no impurities such as O and C in the Auger electron spectroscopy spectrum.

Figure 1 shows the atomic structure of the In-vacancy buckling model for the InSb(111)-2×2 surface.[4] In a (2×2) unit cell, there are three In and four Sb atoms. Each surface In (A) has a coordination number of three with the neighboring Sb. Three Sb atoms (B_1), respectively, bond to three neighbor In atoms, while one Sb atom (B_2) bonds to four In atoms. There is vertical and lateral displacement of the surface atoms from ideal bulk termination. Particularly, the surface In-Sb bond distance is lengthened and the surface bilayer becomes nearly flat.
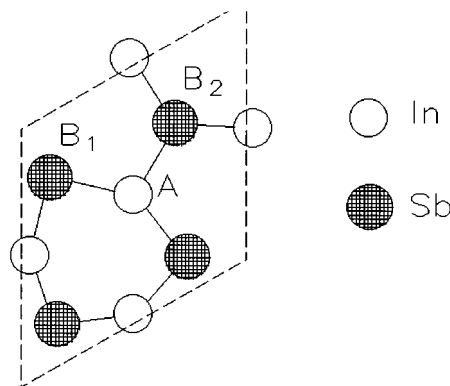

FIG. 1. The In-vacancy buckling model for InSb(111)-2×2 (plane view). There are three In atoms (A) and four Sb atoms (B_1 and B_2) in a unit cell.

FIG. 2. In $4d$ core-level spectra. The photon energy is 54 eV, except for (c). (a) sputtered surface ($E = 500$ eV and $T = 200$ °C); (b) clean InSb(111)-2×2 surface; (c) the same as (b), but $h\nu = 40$ eV; (d) after 1000 L O_2 exposure.
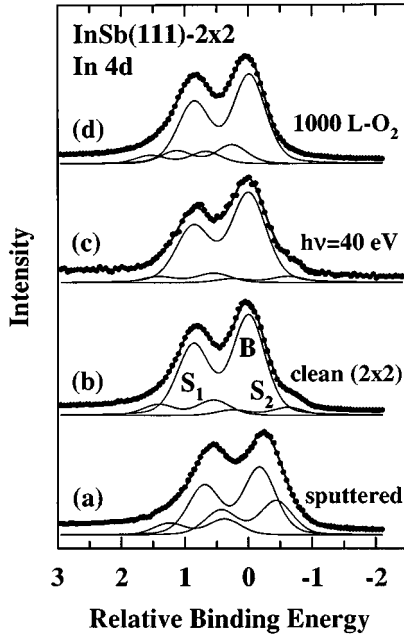

FIG. 3. Sb $4d$ core-level spectra. The photon energy is 72 eV, except for (c). (a) sputtered surface ($E = 500$ eV and $T = 200$ °C); (b) clean InSb(111)-2×2 surface; (c) the same as (b), but $h\nu = 54$ eV; (d) after 1000 L O_2 exposure.

Figures 2 and 3 are the core-level spectra of In $4d$ and Sb $4d$ of InSb(111) surfaces. The binding energy scale is referenced to each bulk $4d_{5/2}$ level of a clean (2×2) surface. In order to fit the core-level spectra, a nonlinear least square routine[13] was used after the subtraction of the cubic polynomial background. The fitting parameters and their results for the In $4d$ and Sb $4d$ levels are listed in Tables I and II. The binding energy difference between bulk In $4d_{5/2}$ and Sb $4d_{5/2}$ level was kept constant during the fitting procedure. Both the Lorentzian width and spin-orbit splitting are consistent with previous results.[14,15] In Fig. 2(a) for
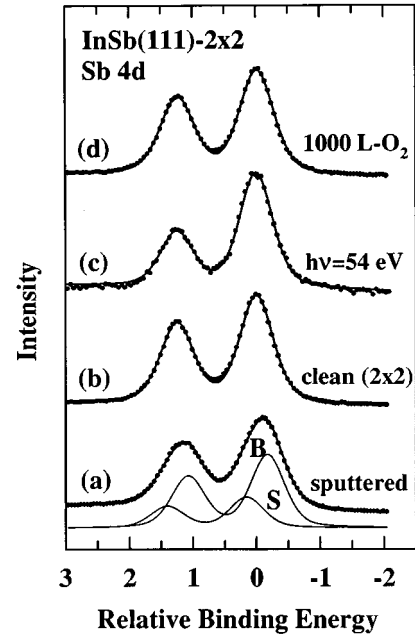
not-ordered surface, there are two surface components at $\Delta E_b = -0.26$ and 0.55 eV. After (2×2)-ordering induced by further annealing, the intensity of the surface components is reduced and the low binding component shifts to a lower position, as in Fig. 2(b). In the clean (2×2) surface of Fig. 2(b), the higher binding component, S_1 ($\Delta E_b = -0.62$ eV), is assigned to the surface In atoms (A in Fig. 1). The lower binding component S_2 ($\Delta E_b = 0.55$ eV) is due to the surface In cluster.[16] Upon sputtering, the amount of In cluster is much larger than that of the annealed (2×2) surface, as shown in Figs. 2(a) and 2(b). After annealing, the In cluster

TABLE I. Fitting parameters for the components used to fit the In $4d$ core-level spectra shown in Fig. 2. All the energies are in eV. The Lorentzian and Gaussian widths refer to full width at half maximum. The intensity ratio R is defined as the area of the surface component/total area. (Lorentzian width = 0.14, spin-orbit splitting = 0.87).

	(a) Sputtered	(b) clean (2×2)	(c) clean (2×2) $h\nu = 40$ eV	(d) O_2 exposed
Branching ratio	0.73	0.70	0.62	0.69
Bulk component				
core-level position	0.17	0	0	0.01
Gaussian width	0.52	0.52	0.56	0.52
Surface component S_1				
core-level shift	0.55	0.55	0.55	0.69
Gaussian width	0.51	0.52	0.55	0.49
intensity ratio R	0.14	0.13	0.09	0.10
Surface component S_2				
core-level shift	−0.26	−0.62	−0.62	0.28
Gaussian width	0.52	0.51	0.53	0.50
intensity ratio R	0.29	0.07	0.06	0.16

TABLE II. Fitting parameters for the components used to fit the Sb $4d$ core-level spectra shown in Fig. 3 (Lorentzian width = 0.19, spin-orbit splitting = 1.25).

	(a) Sputtered	(b) clean (2×2)	(c) clean (2×2) $h\nu$ = 54 eV	(d) O_2 exposed
Branching ratio	0.70	0.74	0.48	0.73
Bulk component				
core-level position	0.17	0	0	0.01
Gaussian width	0.51	0.50	0.50	0.52
Surface component S				
core-level shift	0.33			
Gaussian width	0.51			
intensity ratio R	0.31			

with reduced intensity remains, since most sputter-annealed III-V semiconductor surfaces contain some fraction of group-III metal clusters by segregation.[17] In addition, the In particle becomes larger in size, because the binding energy shifts to lower position in Fig. 2(b). The more bulk sensitive spectra in Fig. 2(c), the smaller the intensity of the S_1 and S_2 becomes. It indicates that both the S_1 and S_2 species are localized only at the surface. The bulk position of the In $4d$ level shifts to +0.17 eV after the sputtered surface is annealed. Because the Fermi level of the InSb(111)-2×2 is known to lie on the bottom of the conduction band,[18] the Fermi level position of not-ordered surface must be lower than that of the (2×2) surface.

The Sb $4d$ core-level spectra is shown in Fig. 3. In contrast with the In $4d$ core level, there is no observable surface component on the clean (2×2) surface in Figs. 3(b) and 3(c). In bulk sensitive [Fig. 3(c)] and surface sensitive [Fig. 3(b)] spectra, there are no SCLS's in the Sb $4d$ level, but there are some changes in Gaussian width and branching ratio. The absence of the anion SCLS's on the (2×2) surfaces was also reported before.[10,19] Only after sputtering, the surface component at ΔE_b = 0.33 eV appeared as in Fig. 3(a). It must be the surface Sb cluster not bonded to In, and disappears after annealing at 350 °C.

There have been two approaches to the interpretation of the SCLS's in III-V semiconductors. Priester et al. predicted the SCLS's and compared them with the experimental values by the tight-binding calculation.[20] They found that there is an excess charge in surface group-V atoms relative to bulk in (110) surfaces, and could explain many experimental observations. However, their study resulted in some deviation from the later experimental data, especially for InP(110) surface.[21]

Another approach is the Madelung potential effect proposed by Davenport et al.[22] or Mönch.[23] They suggested that

there is nearly no difference between the surface and bulk in charge transfer for most III-V (110) surfaces. The binding energy shift is approximately the summation of the charge transfer and ion interaction (Madelung potential), neglecting the final state effects. The SCLS's, ΔE_{sb} of the cation (group-III metal) is expressed by the equation,[2,23]

$$\Delta E_{sb} = E_b - E_s = (e_0^2/4\pi\epsilon_0)(A_{cd}/d_m - \alpha_s/d_{nn})\Delta q_s$$
$$- [E_m - E_b]. \qquad (1)$$

The A_{cd} is the charge distribution constant 3.32, d_m the nearest neighbor distance of the group-III metal, α_s the surface Madelung constant, which is 0.85±0.06 times the bulk value,[22,24] d_{nn} the nearest neighbor distance of the compound, and Δq_s the charge transfer of surface. The parameters and calculated results are presented in Table III. The result for the GaAs(111)-2×2 surface[9] is compared with ours. For the GaAs(111), the charge transfer of bulk and surface is nearly the same. This is more evidence that the (2×2)-GaAs surface has a similar electronic property to the (110) buckled surface. The valence charge density of the surface Ga atom on the GaAs(111)-2×2 seems to be the same as that in bulk.[7] On the contrary, the charge density near surface As is lower than that in bulk, reasonably because the surface stoichiometry is not satisfied. However, in the case of InSb, surface In loses excess charge, about 0.04 e_0, as shown in Table III. These different results between GaAs and InSb can be explained by considering their structural or electronic characters. As published by Bohr et al.,[4] the surface property of (2×2)-GaAs and InSb is somewhat different. The bond distance of surface In-Sb (A-$B_{1,2}$ in Fig. 1) is lengthened and the bond angle of In (A in Fig. 1) is small, while the bond length of surface Ga-As is unchanged or shortened from the bulk value. The bond angle of surface

TABLE III. Calculating parameters and results for a surface charge transfer of group-III atoms by the Madelung potential. The $E_m - E_b$ is the binding energy difference between the metal and compound bulk, the ΔE_{sb} the surface core-level shift of (111)-2×2 surface. The d_{nn} is the nearest neighbor distance of the compound, the Δq_b and Δq_s the charge transfer of bulk and surface, respectively. The calculation error in Δq_s is estimated by considering the surface relaxation and uncertainty of α_s.

Compound	$E_m - E_b$ (eV)	ΔE_{sb} (eV)	d_{nn} (nm)	Δq_b	Δq_s
InSb	0.98	0.55	0.281	0.166	0.21±0.03
GaAs	1.66	0.31	0.245	0.205	0.20±0.02

Ga is also larger than that of In. Making a comparison, the surface In atom loses its charge and Sb has the excess charge and more p character in InSb(111) than As in the GaAs(111) surface. No observable SCLS of the Sb $4d$ level in Fig. 3(b) and (c) results from the cancelation of decreased Madelung potential (negative shift) and the lack of valence charge density of the surface Sb atom, due to a nonstoichiometry (positive shift).

Upon O_2 exposure at room temperature, two surface In components appear at $\Delta E_b = 0.28$ and 0.69 eV in Fig. 2(d). The surface components S_1 and S_2 of the clean (2×2) disappear. However, there is no change, except for a little broadening in Sb $4d$ core level in Fig. 3(d). The higher binding In species must be the series of oxidized ones. Therefore, the initial oxidation of the InSb(111)-2×2 surface prefers the selective reaction to the surface In.

In conclusion, the SCLS of the InSb(111)-2×2 shows two surface components of the In $4d$ core level, but nothing of Sb $4d$ level. The surface components of cations of InSb and GaAs(111)-2×2 are calculated by the Madelung potential concept. In the case of the InSb(111) surface, an excess charge is transferred from In to Sb and surface Sb has more p-type bonding character. In comparison, the charge distribution of the GaAs surface is similar to that of bulk to the contrary. The different behavior of InSb and GaAs could be explained by the difference in structural and electronic characters of the cation-vacancy buckling model.

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