Large anisotropy in thermal atomic vibrations at the InSb(111)A-(2×2) surface

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Transmission electron diffraction and reflection high-energy electron diffraction have been used to study thermal vibrations at the InSb(111)A-(2×2) surface. The surface In and Sb atoms show a large anisotropy in their vibrational amplitudes. In particular, contrary to common belief, the Debye temperature of surface In (Sb) atoms is larger than the corresponding bulk value in the directions normal (parallel) to the surface. We show that thermal vibrations in these directions are suppressed so as to maintain the sp^2-type (p^3-type) bonding character of surface In (Sb) atoms with their nearest neighbors.

Thermal vibrations at solid surfaces are an important issue in surface science, because they relate closely with the dynamical processes on the surfaces, such as phase transition, adsorption/desorption, and epitaxial growth. It is generally assumed that thermal fluctuations are enhanced at surfaces, because surface atoms are usually less coordinated. Demuth, Marcus, and Jepsen performed a low-energy electron-diffraction analysis for Ni surfaces, and found that surface Debye temperatures are $\sim$70% of the bulk value.[1] Similar trends were reported for (001) surfaces of NaCl and KCl.[2] In these studies isotropic Debye temperatures are reasonably assumed.

Reduced surface Debye temperatures in the direction normal to the surface were also found for semiconductors such as Ge(111) (Ref. 3) and Si(111).[4] On the other hand, anisotropy in thermal vibrations at semiconductor surfaces, which is due to strong directional properties of the covalent bond, was confirmed theoretically[5] and experimentally.[6,7] Thus, thermal vibrations on semiconductor surfaces could not be described in a way similar to the case for metals and ionic crystals, and require a more appropriate description. In addition, what makes the situation more complex is a surface reconstruction, which occurs on the majority of semiconductor surfaces. Indeed, different values of vibrational amplitudes were reported for different surface atomic geometries.[5,7]

This paper reports evidence that the atomic geometry of the InSb(111)A-(2×2) surface causes a large anisotropy in the atomic vibrations. We found that the surface In(Sb) atoms have larger (smaller) and smaller (larger) vibrational amplitudes than in the bulk in the directions parallel and normal to the surface, respectively. The present results are closely related to the atomic arrangement of this surface: the InSb(111)A-(2×2) surface has the In-vacancy buckling structure,[8–10] as shown in Fig. 1. We show that the sp^2-type (p^3-type) bonding configuration of surface In (Sb) atoms with their nearest neighbors plays a key role in the reduction in the vibrational amplitude at this surface.

We used transmission electron diffraction (TED) and reflection high-energy electron diffraction (RHEED) in this study. The TED analysis enables us to obtain vibrational amplitudes in the lattice planes perpendicular to an incident electron beam, i.e., in the directions parallel to the surface. It is of great advantage that TED intensities can be interpreted by kinematical approximation:[11] Debye temperatures of reconstructed surface layers can be derived from the analysis using fractional-order reflections without considering possible contributions from the bulk. On the other hand, in the RHEED analysis, it is possible to choose the orientation of the incident electron beam at which electrons are diffracted mainly in lattice planes parallel to the surface (the so-called one-beam condition).[12] Thus, information about atomic vibrations along the surface-normal direction can be selectively obtained at this condition.

The TED measurements were performed using an ultrahigh-vacuum transmission electron microscope, for which a detailed description has been given in our previous papers.[10,13,14] The ultimate pressure in the specimen chamber was less than 3×10^{-10} Torr. The (111)A-oriented InSb substrates (nondoped) were chemically etched with a mixture of HNO_3 and lactic acid (1:10) to form a round hole of about 0.1-mm diameter with electron-transparent peripheries. The native oxide was removed from the substrate surfaces by heating the specimens at 730 K with Sb_4 molecular beams in the specimen chamber. Then, a few hundred Å of InSb films were grown homoepitaxially on the surfaces at 570 K. After the subsequent annealing at 670 K with Sb_4 beams, the surface showed sharp TED patterns corresponding to the In-stabilized (2×2) structure. TED patterns were recorded by a direct exposure of the electron beam onto an imaging plate (Fujifilm FDL-UR-V). The sample was tilted by 5° away from the [111] zone axis toward the [1$\bar{1}$0] azimuth in order to suppress dynamical scattering. The tilt angle was determined with sufficient accuracy by the position of the Kikuchi pattern. Slight asymmetry of the sixfold (2×2) reflections, caused by the tilt, was eliminated by being averaged over C_{6v} symmetry. By using these two techniques, the dynamical effect is reduced to a random error of less than 15%.[11]

The RHEED experiments were performed in a molecular-beam epitaxy system.[15] Clean surfaces of InSb(111)A-(2×2) were obtained using the procedures given in our previous papers.[9,16] RHEED rocking curves of the InSb(111)A surface were measured at the azimuthal angle of 7.2° off
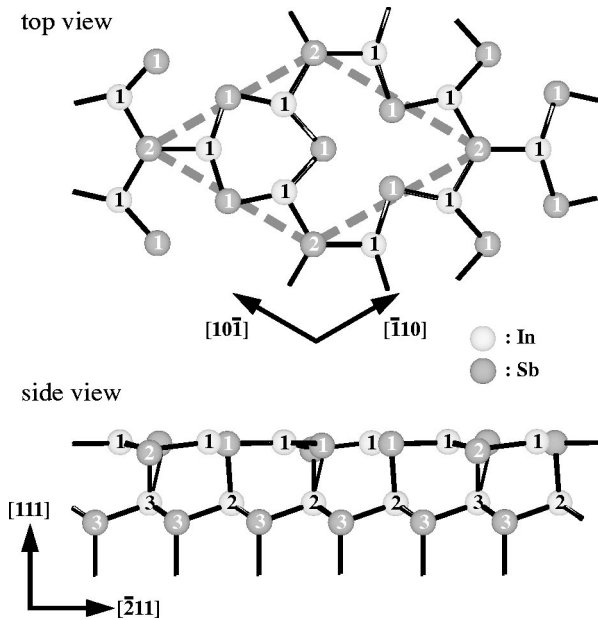
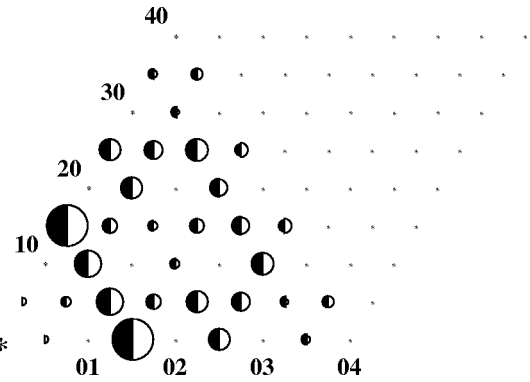FIG. 1. The In-vacancy buckling model for InSb(111)A-(2 ×2). The atom numbers are referred to in Table I.

FIG. 2. Schematic drawing of measured (closed semicircles) and calculated (open semicircles) intensities from the optimized structure model. The area of the semicircle is proportional to the diffraction intensity.

from the $[2\bar{1}\bar{1}]$ direction with an electron energy of 15 keV. At this azimuth, multiple scattering due to the potential variation parallel to the surface is suppressed.[12] The glancing angle of the incident electron beam was changed using the extended beam-rocking facility (Staib, EK-35-R and k-Space, kSA400) with intervals of ~0.025°. The RHEED measurements were performed in a good UHV condition of ~5×10⁻¹¹ Torr.

Surface Debye temperatures of InSb(111)A in the direction parallel to the surface have been determined using the TED analysis. Figure 2 depicts the intensities of fractional-order reflections measured from the InSb(111)A-(2×2) surface (closed semicircles). The intensity ratios hardly changed between 303 and 573 K, which assures us that the surface structure is preserved in this temperature range.

In order to estimate surface Debye temperatures, kinematical TED calculations were performed. At first, TED intensities were calculated using the structural parameters given in Ref. 8 and Debye temperatures of 147 K for In and 158 K for Sb.[17] Then the atomic coordinates of two surface bilayers were least-squares refined so as to fit the TED data obtained at 303 K (closed semicircles in Fig. 2). The refinement processes were guided with the R factor used in x-ray crystallography. Using the optimized atomic coordinates, the Debye temperatures of In1 and Sb1 atoms (Fig. 1) were op-

TABLE I. Debye temperatures (mean-square vibrational amplitudes at 300 K) for the InSb(111)A-(2×2) surface.

Atom	TED (in plane)	RHEED (out of plane)
In1	127±20 K (0.154 Å)	171±18 K (0.114 Å)
Sb1	225±35 K (0.087 Å)	120±18 K (0.163 Å)
In2 and In3	151±19 K (0.130 Å)	140±12 K (0.140 Å)
Sb2-Sb4	151±19 K (0.130 Å)	160±12 K (0.122 Å)

timized for the data obtained at 303, 373, 433, 473, 533, and 573 K. These procedures were repeated three times.

As shown in Fig. 2, the calculated TED intensities (open semicircles) from the In-vacancy buckling model are in very good agreement with the measured ones, the averaged R factor being 12%. The optimized atomic coordinates agree well with those reported in Ref. 8: differences in absolute coordinates are typically less than 0.05 Å. As shown as part of Table I, averaged surface Debye temperatures of In1 and Sb1 atoms are 127±20 K and 225±35 K, respectively. On the other hand, a value of 151±19 K was obtained for bulk InSb from the temperature dependence of the 660 and 880 spots, which falls in the range of the values in the literatures (140–160 K).[17,18] Thus, the TED analysis indicates that In1 (Sb1) atom has a larger (smaller) vibrational amplitude than that in bulk InSb in the direction parallel to the surface.

Figure 3 shows a series of RHEED rocking curves measured in a temperature range of 323–573 K. Peaks associated with the bulk Bragg reflections are indicated by the arrows with their indices, considering the refraction of the electrons due to the mean inner potential. Peaks at high glancing angles decrease their intensities with increasing temperature. Also, it is seen that the position of the dip at ~1° is shifted to higher angles as the temperature is increased. These behaviors can be explained by the enhancement of thermal vibrations at high temperatures without considering structural change of the InSb(111)A-(2×2) surface, as we will show below.

RHEED intensities were calculated by the multislice method proposed by Ichimiya.[19] Fourier coefficients of the elastic-scattering potential were obtained from the atomic scattering factors for free atoms calculated by Doyle and Turner.[20] A correction due to condensation was made to fit the positions of bulk Bragg peaks at large glancing angles. For instance, the resulting mean inner potential of bulk InSb was 14.3 eV. The imaginary part of the potential for inelastic scattering of In and Sb was represented by a set of Gaussians for Sn.[21] The magnitude of the imaginary potentials was adjusted so as to reproduce the peak width of the measured rocking curves. The resulting mean imaginary potential is 2.7 eV. The thickness of a slice, in which scattering potential was
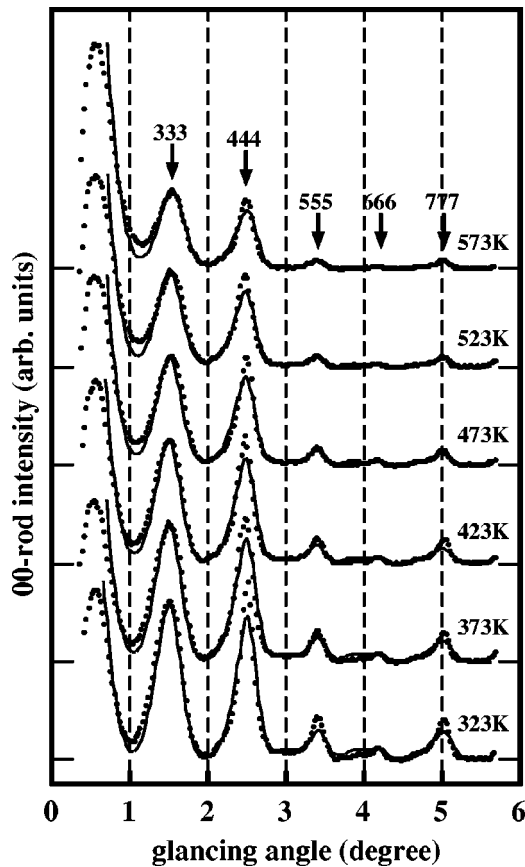
FIG. 3. RHEED rocking curves (solid circles) measured from the InSb(111)A-(2×2) surface at a temperature range of 323–573 K. The solid curves are calculated for the optimized structure of the In-vacancy buckling model.
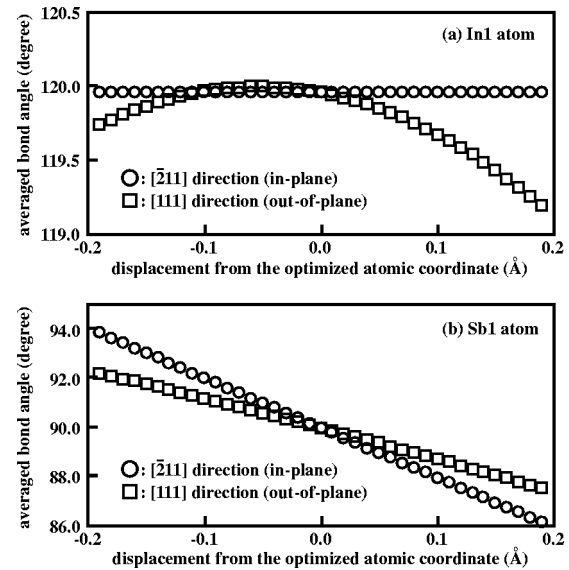

FIG. 4. The averaged bond angles of In1 (a) and Sb1 (b) with their nearest-neighbor atoms plotted as a function of the displacement from the optimized atomic coordinates.

approximated to be constant toward the direction normal to the surface, was about 0.1 Å. In order to quantify the agreement between the calculated rocking curves and the experimental ones, the R factor defined in Ref. 22 was used for the glancing-angle range of $0.8°$–$5.8°$. The calculated rocking curves were convoluted with a Gaussian which has a full width at half maximum of $0.1°$, corresponding to the experimental resolution.

Debye temperatures and atomic coordinates were optimized as follows. First, the Debye temperatures of In1 and Sb1 atoms and bulk layers were changed holding the atomic coordinates at those in Ref. 9, so as to minimize the R factor. Second, the atomic coordinates of the first and second bilayers were refined one after another. Finally, the resulting optimized structure was set as the starting point of the next refinement. This procedure iteratively minimizes the R factor. In the optimized structure model, In1 atoms are displaced by 0.78 Å towards bulk, while atomic displacements from bulk positions for other atoms are typically less than 0.1 Å. We note that the atomic coordinates did not show any significant changes from the initial values[9] after the structure optimization.

The calculated rocking curves are shown by solid lines in Fig. 3. In this calculation, five beams of (0 0), $\pm(\frac{1}{2}\frac{1}{2})$, and $\pm(1\ 1)$, were used. We note that the calculations including

higher-order reflections yielded almost the same results. An averaged R factor is 2.2%, showing an excellent agreement with experiments and calculations: the relative intensities and the position of the dip at $\sim1°$ are well reproduced by the calculations. The surface Debye temperatures for In1 and Sb1 atoms are estimated to be 171 ± 18 K and 120 ± 18 K, respectively (Table I). On the other hand, we confirmed that the bulk values for In and Sb are 140 and 160 K, in good agreement with the TED results. The present RHEED results clearly indicate that thermal vibrations of In1 and Sb1 atoms in the surface-normal direction are suppressed and enhanced, respectively.

Comparing the TED and RHEED results, we found that the surface Debye temperature of InSb(111)A has a large anisotropy. In particular, it is interesting to note that the vibrational amplitude of the surface In (Sb) atoms in the direction normal (parallel) to the surface is smaller than those in bulk InSb. At first sight, such a behavior might be somewhat surprising because the surface atoms are less coordinated and, therefore, are expected to have larger vibrational amplitudes than in the bulk. However, the present results are well explained by considering the atomic arrangement of the InSb(111)A-(2×2) surface: as mentioned earlier in this paper, the InSb(111)A-(2×2) surface has the In-vacancy buckling structure[8–10] (Fig. 1). In this structure model, the In1 atoms are displaced downward by a large amount of ~0.8 Å to form a planar sp^2-type bonding configuration with surface Sb atoms, while Sb1 atoms produce p^3-type bonds with their In nearest neighbors. The averaged bond angle of the In1 atom (Sb1 atom) is 119.9° (89.9°), which compares with the value expected for the ideal sp^2 (p^3) arrangement. Such an atomic configuration eliminates all of the In1 and Sb1 dangling bonds by transforming the Sb dangling bonds into s-type occupied states and the In dangling bonds into p_z-type empty states, so that the surface is electrically stabilized.[23] In Fig. 4, the averaged bond angles of

In1 and Sb1 atoms are plotted as a function of the atomic displacement from the optimized coordinate. As seen in this figure, the deviation in the averaged bond angle of In1 (Sb1) from the sp^2 (p^3) geometry is more noticeable for the atomic displacement in the $[111]$ ($[\bar{2}11]$) direction than in the $[\bar{2}11]$ ($[111]$) direction. This means that the atomic displacement of In1 (Sb1) in the $[111]$ ($[\bar{2}11]$) direction is energetically unfavorable. Thus, we conclude that the thermal vibration of In1 (Sb1) in the direction normal (parallel) to the surface is suppressed so as to preserve the bonding characters of surface In (Sb) atoms.

In conclusion, we have determined the surface Debye temperatures at the InSb(111)A-(2×2) surface using TED and RHEED. The results show that the thermal vibration of the surface In (Sb) atoms in the direction normal (parallel) to the surface is more suppressed than those in bulk InSb. The reduced vibrational amplitudes are explained well by considering the sp^2-type (p^3-type) bonding configuration of surface In (Sb) atoms in the In-vacancy buckling structure.

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