Sb Trimer Structure of the InSb(111)*B*-(2×2) Surface as Determined by Transmission Electron Diffraction

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We have proposed a new model for the Sb-stabilized InSb(111)*B*-(2×2) reconstructed surface prepared by molecular-beam epitaxy. Adsorption of Sb trimers at a fourfold atop site of the outermost Sb layers is confirmed by intensity analysis of transmission-electron-diffraction patterns obtained from the reconstructed surface. Also, Auger electron spectroscopy measurements provided a satisfactory surface composition for the InSb(111)*B*-(2×2) surface.

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The (111)*A* and (111)*B* polar surfaces of III-V compound semiconductors exhibit a considerable number of reconstructions, depending on temperature and surface compositions. In order to obtain details on the surface reconstructions and the related surface phase transitions, first the atomic structures of both polar surfaces have to be determined. Recently, for the (111)*A* surface of GaAs, Tong, Xu, and Mei [1] proposed the vacancy buckling model which has been widely accepted because the structure has been confirmed by a variety of investigations: diffraction experiments [1,2], theoretical calculations [3,4], and scanning tunneling microscopy (STM) [5]. On the other hand, for the (111)*B* surface a similar (2×2) structure has been observed on the molecular-beam-epitaxy- (MBE-) grown surface under group-V-element stabilized conditions. However, no well-established model for the (111)*B* surface has been reported. For example, although for the GaAs(111)*B*-(2×2) structure total energy calculations led to a multivacancy model [6] and a staggered As vacancy model [7], both failed in low-energy electron-diffraction (LEED) tests [8].

We use transmission electron diffraction (TED) in a structure analysis for the (111)*B* surface of InSb. The reason is that information obtained by this method can be interpreted by kinematical approximation under a given diffraction condition, similar to general x-ray diffraction [9,10]. While other electron-diffraction methods, such as LEED and reflection high-energy electron diffraction (RHEED), are useful for surveying surface symmetry, in their interpretations dynamical scattering effects always have to be taken into account. TED can be also complementary to STM, which gives information on the top layer of a surface.

In this paper, we present the first quantitative TED analysis of the InSb(111)*B*-(2×2) surface structure and propose a structural model which explains other experimental and theoretical works.

Experiments were performed with a modified JEM-7A transmission electron microscope (100 kV). A detailed description of the experimental apparatus was presented in our earlier papers [11,12]. The ultimate pressure in the specimen chamber was less than 5×10^{-10} Torr and the pressure during evaporation was below 2×10^{-9} Torr. Samples of (111)*A*- and (111)*B*-oriented InSb (nondoped) were chemically etched with a mixture of HNO_3 and lactic acid (1:10) to form a round hole about 0.1 mm diameter with electron-transparent peripheries. The native oxide was removed from both types of substrate surfaces by heating at 460 °C with Sb_4 beams in the specimen chamber. Immediately after the cleaning, homoepitaxial growth of InSb was performed on InSb(111)*A* and InSb(111)*B* surfaces at 300 °C under Sb-stabilized conditions [11,12]. Cooling down to room temperature, followed by the growth of a few hundred Å of InSb, both the (111)*A* and (111)*B* specimens showed a sharp (2×2) TED pattern. Reheating of these specimens at 400 °C gave patterns characteristic of each specimen surface: For (111)*A* the (2×2) structure remained unchanged, whereas for (111)*B* the structure changed to the (3×3) [13]. Additionally, as far as the pressure in the chamber was preserved within the range of 10^{-10} Torr, no change in these extra reflections was observed. However, when air was admitted slowly through a variable leak valve until a pressure of 1×10^{-7} Torr was reached, the extra reflections became weakened and soon disappeared entirely.

Figure 1(a) shows a typical TED pattern taken from the InSb(111)*B* homoepitaxially grown films. The samples were slightly tilted about 5° away from the [111] zone axis to suppress dynamical scattering [9,14]. Slight asymmetry of the sixfold (2×2) reflections, caused by the tilt, was eliminated by being averaged over C_{6v} symmetry in order to further lower the dynamical effect. By using these two techniques, as evidenced in the multislice analysis example for a Si(111)-(7×7) surface, the dynamical effect is reduced to a random error of less than 10% [14]. Similar multislice calculations for the (2×2) surface of the InSb(111)*A* specimen having a thickness of 1000 Å resulted in a less dynamical effect less than 15% by using the specimen tilt and the averaged reflection intensities. In addition, the measured intensities for InSb(111)*A*-(2×2), which were quite different from those for InSb(111)*B*-(2×2), agreed well with the kinematically calculated ones for the surface structure

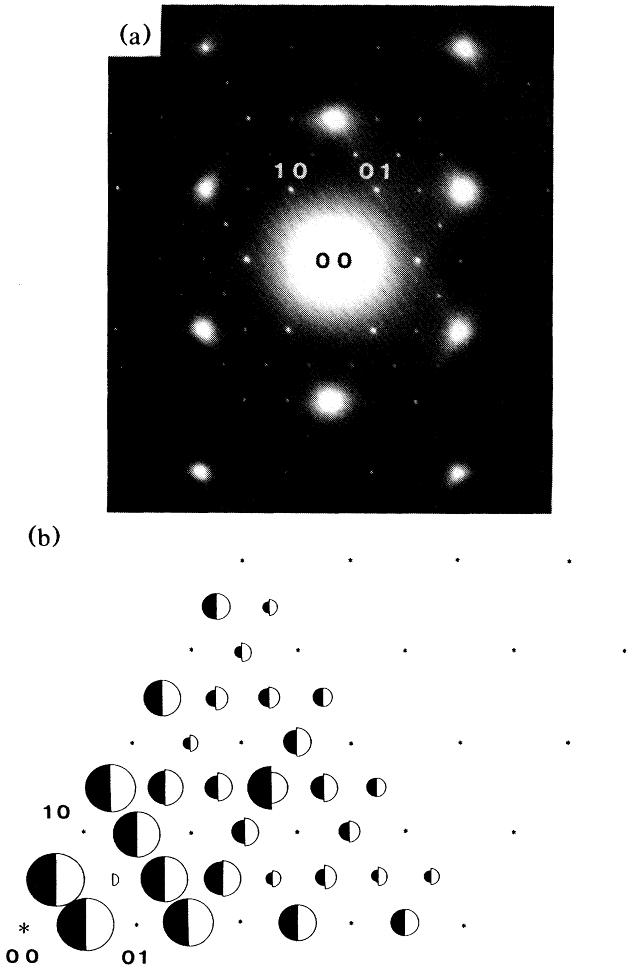

FIG. 1. (a) TED pattern of the InSb(111)B-(2×2) reconstructed surface at room temperature. (b) Schematic drawing of observed (open semicircles) and calculated (solid semicircles) intensities from the model for the surface structure of InSb(111)B-(2×2) in Fig. 4(a). The area of the semicircle is proportional to the diffracted intensity.

referring to the vacancy buckling model [2].

TED patterns were recorded by a direct exposure of the electron beam onto a photographic plate (Fuji FG) in the linear-response region of the emulsion. We measured relative intensities of 156 superlattice reflections by photodensitometry with an accuracy of a few percent and reduced the 156 to 16 crystallographically independent values. We also measured superlattice intensities from many specimens with a reproducibility of 13%, which is responsible for the overall systematic error. Figure 1(b) depicts the measured intensities of the superlattice reflections from the InSb(111)B-(2×2) surface.

Information about the atomic arrangement of a solid can be obtained from the Fourier inversion of observed intensities, $|F_{hk}^{\text{obs}}|^2$, giving the so-called Patterson (pair-correlation) function [15]

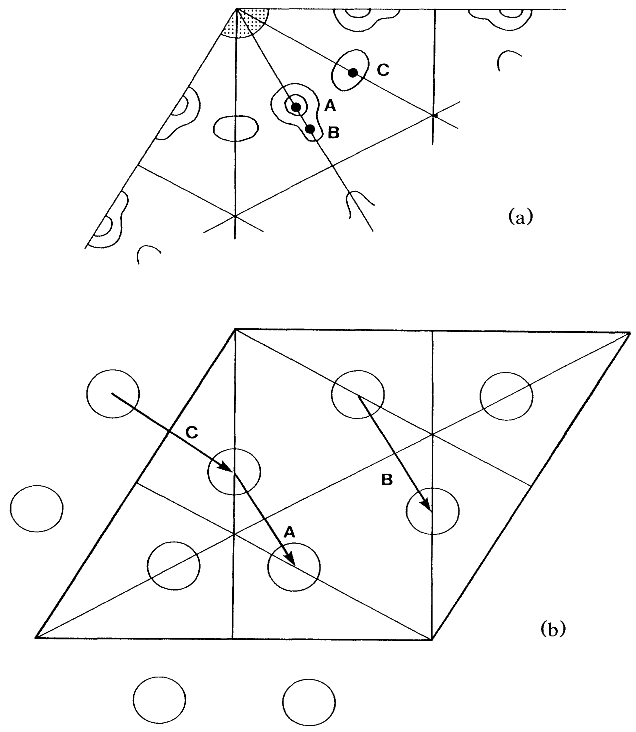

FIG. 2. (a) Contour plot of the Patterson function based on the observed intensities in Fig. 1(b). Positive contour indicates levels above zero, shaded circle the origin peak conveniently representing twenty contour levels, and solid circles (labeled A-C) the peak position corresponding to interatomic vectors in the InSb(111)B-(2×2) surface structure. (b) Arrangement of surface atoms (open circles) present at the three peaks in (a), which cannot be determined to be either In or Sb at this stage. The surface interatomic vectors compatible with (a) are shown by arrows.

$$P(x,y)=\sum_{hk}|F_{hk}^{\text{obs}}|^2\cos 2\pi(hx+ky)\,.$$

A contour plot based on the fractional-order reflections of InSb(111)B-(2×2) is shown in Fig. 2(a). In this figure, it should be noted that three peaks near the origin are in a nonsymmetrical relationship, whereas, if the peaks originate from the bulk, they have to hold a symmetrical configuration. When the fractional-order reflections in Fig. 1(b) are taken in the Fourier synthesis, the map obtained involves atoms located at the unique position of the superlattice unit cell which corresponds to the reconstructed region of the surface. Figure 2(b) shows the arrangement of atoms in the (2×2) unit cell with C_{3v} symmetry. However, at this stage of the analysis the arrangement has several possible structure models as shown in Figs. 3(a)-3(c).

A structure-factor calculation was then performed with these models by using the scattering factor for Sn ($Z=50$) instead of In ($Z=49$) and Sb ($Z=51$), because

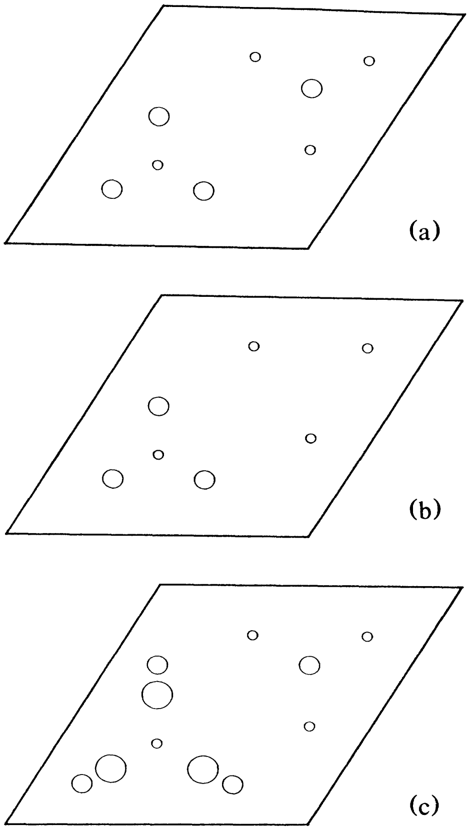

FIG. 3. Possible models for the InSb(111)B-(2×2) surface. (a) Buckling model; (b) vacancy buckling model; (c) T_4 site trimer model.

these scattering factors are extremely close, within the accuracy of the calculation [2]. Each structure in Figs. 2 and 3 was least-squares refined so as to fit the TED data in Fig. 1(b). The models in Figs. 2(b), 3(a), and 3(b) revealed clear minima in R factors of 25%, 38%, and 18%, respectively. However, they did not reach the level of experimental errors (13%). Only when a fourfold atop (T_4) site trimer configuration in Fig. 3(c) was tested was the best fit of $R=13\%$ found. Although least-squares refinements were also made for previous structure models of GaAs(111)B-(2×2) [6–8,16], they resulted in an R factor above 20%: For example, a hollow (H_3) site trimer model for GaAs(111)B-(2×2) [16] gives a large R factor of 29%, even after the refinement. Consequently, the Patterson function from these models did not explain the present result [Fig. 2(a)]. Thus, it is most likely that the T_4 site trimer model shown in Fig. 3(c) is the structure for the InSb(111)B-(2×2) surface. Our analysis, however, still remains to assign the trimer adatom to In and Sb atom types. When the atomic number of the adatoms is allowed to vary from 45 to 55, the best agreement is for $Z=51$. This result suggested that the atom type of the trimer might be Sb. However, since In and Sb are isoelectronic in InSb, it is difficult to distinguish between them by using only TED.

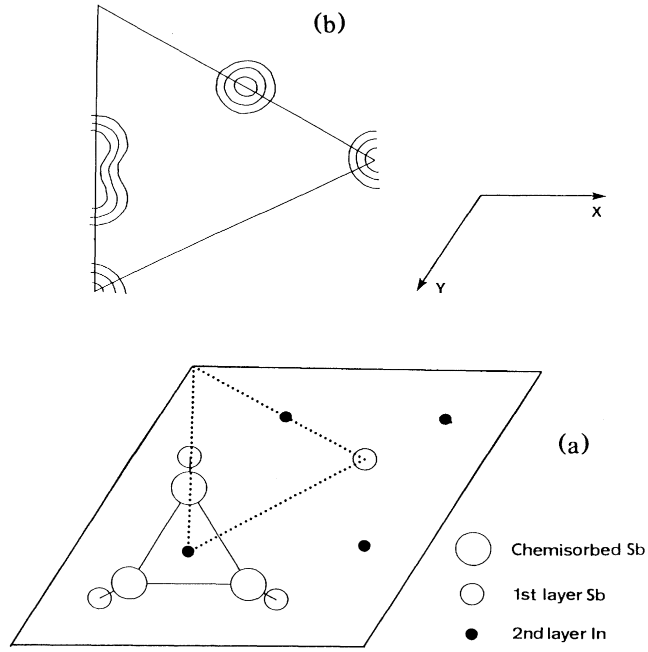

FIG. 4. (a) T_4 site Sb trimer model for the InSb(111)B-(2×2) surface. (b) Contour plot of the Fourier synthesis obtained from the observed scattering factor and the assumed phase by model (a).

Auger intensity measurements, which were performed in another UHV chamber, revealed, as expected, a high surface Sb concentration of $\sim\frac{3}{4}$ monolayer. In this measurement, a relative sensitivity factor was estimated to be 0.7 from that required for an InSb(111)A-(2×2) surface structure already established [2]. The InSb(111)B-(2×2) surface gave an Auger intensity ratio of $I_{\mathrm{Sb}}/I_{\mathrm{In}}=1.2$. Taking account of an exponential absorption law for electrons and numerical values for the electron escape depth, the Auger intensity ratios assigned to the Sb trimer and the In trimer models are 1.2 and 0.6, respectively [17]. Thus, the result allows us to conclude that an Sb trimer is chemisorbed on the top layer. The final structure model with assignment of atoms ends up as shown in Fig. 4(a). The last least-squares refinement for this structure arrived at an R factor of 12.3%, which coincides with errors of measurement, yielding a good one-to-one correspondence between the observed and calculated structure factors displayed in Fig. 1(b).

We performed Fourier synthesis to further validate the results using the observed scattering amplitudes F_{hk}^{obs} and assumed phases $\alpha_{hk}^{\mathrm{cal}}$ given by the model in Fig. 4(a),

$$V(x,y)=\sum_{hk}F_{hk}^{\mathrm{obs}}\exp(i\alpha_{hk}^{\mathrm{cal}})\,.$$

As a result, all peaks lead to the structure model as

TABLE I. Structure parameters for ideal and Sb trimer models of the reconstructed (111)*B*-(2×2) surface of InSb. The (*x*,*y*) coordinates are given as fractions of the unit cell along the [10] and [01] directions in Fig. 4(a).

		Ideal		Reconstructed	
		x	*y*	*x*	*y*
1	Sb	···	···	0.438	0.876
2	Sb	1.333	0.667	1.333	0.667
3	Sb	0.333	0.667	0.322	0.644
4	In	0.667	0.333	0.704	0.352
5	In	0.667	1.333	0.667	1.333

shown in Fig. 4(b). Moreover, drawing a differential Fourier map with the new calculated structure factors,

$$D(x,y)=\sum_{hk}(F_{hk}^{\mathrm{obs}}-|F_{hk}^{\mathrm{cal}}|)\exp\{i[\alpha_{hk}^{\mathrm{cal}}-2\pi(hx+ky)]\}\ ,$$

generated only noise. The final structure parameters are given in Table I. The Sb-Sb bond length in the trimer is 3.14 Å and is significantly (9.4%) larger than in bulk Sb (2.87 Å). One-half of the measured value (1.57 Å) is very close to the metallic radius (1.59 Å) [18] of Sb in a 12-coordinated system. Similar chemical trends have been also found for As dimers chemisorbed on As atoms in a GaAs(100)-*c*(4×4) surface [19]. The existence of the trimer adatom associated with the (111)*B*-(2×2) surface of III-V compound semiconductors has been already suggested in some papers [16,20]: In one of them [20], STM experiments indicate that the adatom structure for GaAs(111)*B*-(2×2) surfaces looks consistently triangular. However, our analysis directly derived a trimer adatom structure including information on atom location, atom types, and bond length.

In summary, we have used the Patterson function, Fourier analysis, and least-squares refinement to determine atomic structures of the InSb(111)*B*-(2×2) reconstructed surface. The proposed Sb trimer model sufficiently explained the experimental data from transmission electron diffraction and Auger electron spectroscopy. The new structure consists of an Sb trimer which has a Sb-Sb bond length of 3.14 Å and is located with threefold symmetry above substrate Sb atoms consisting of the (2×2) structure.

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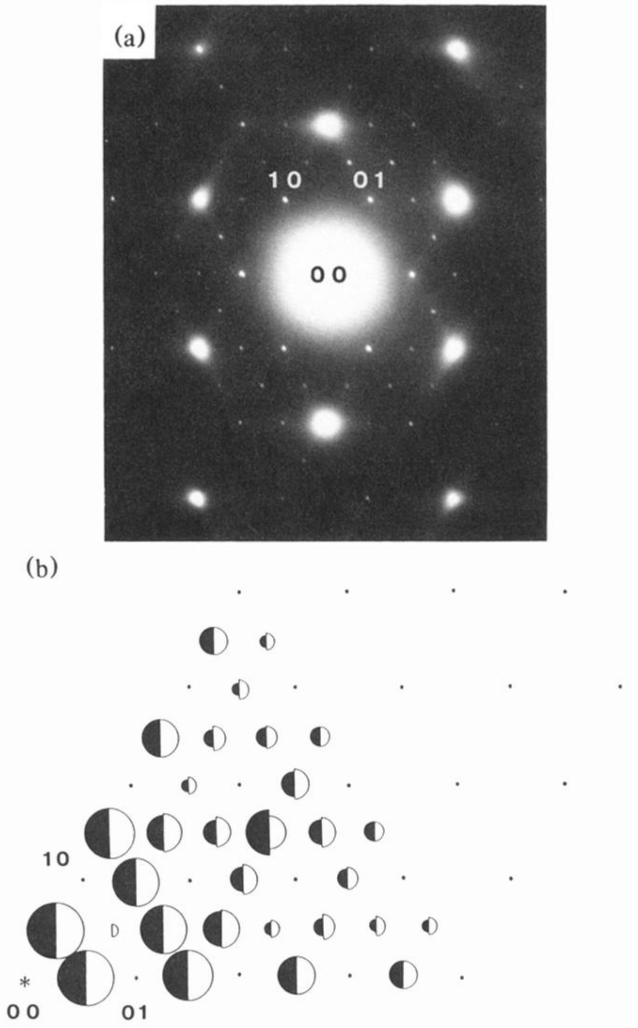

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