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Growth of an α-Sn film on an InSb(111) A-(2×2) surface

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We have investigated the initial growth process of α-Sn films on the In-terminated InSb(111)A-(2×2) surface using low-energy electron diffraction (LEED) and high-resolution core-level photoelectron spectroscopy. Taking the LEED observation and the Sn coverage-dependent integrated intensities of the In 4*d*, Sb 4*d*, and Sn 4*d* core-level spectra into account, we conclude that the α-Sn film grows epitaxially by a bilayer mode and that there is no interdiffusion of the substrate atoms as suggested in the literature. Furthermore, the coverage-dependent In 4*d* and Sn 4*d* core levels indicate that the In vacancy site of InSb(111)A-(2×2) surface is not the preferable Sn absorption site.

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Thin films grown on III-V compound semiconductors (GaAs and InSb) are quite interesting systems, due to their possibilities of application as high electron mobility transistors and semiconductor laser devices. Sn film grown on InSb surfaces[1,2] is one of such systems. In contrast to bulk Sn, which is known to show a semiconducting α phase with a diamond structure below 13.2 °C and a metallic β phase with a tetragonal structure above this temperature, Sn films grown on InSb(111) surfaces are reported to have an α phase at room temperature.[2–5] The stability of the α-Sn films grown on InSb(111) surfaces was reported to depend on the film thickness.[3] An α-Sn film with a thickness of 8 monolayers (ML) was reported to be stable up to approximately 200 °C, and a film of 50 ML to be stable up to approximately 160 °C. The origin of this difference was proposed to result from a strong chemical bonding between Sn and In atoms at the interface. However, there is no strong evidence so far to confirm this mechanism.[3]

The (111) surface of the α-Sn film grown on an InSb(111)A-(2×2) was reported to show different reconstructions depending on the cleaning methods of the substrate. That is, 2×2 and 3×3 reconstructions of the α-Sn(111) surface were observed by cleaning the InSb(111)A surface using the molecular beam epitaxy (MBE) method,[3] while only a 1×1 reconstruction was observed in the case of repeating sputtering and annealing.[2,4,5] This difference was proposed to result from the interdiffusion of In atoms into the Sn overlayer and/or from the presence of only small 2×2 or 3×3 domains[2,4,5] that lead to invisible 2×2 (3×3) spots in reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED) using the latter cleaning method. Regarding the very initial stage of Sn film growth, the 2×2 pattern of the clean InSb(111)A surface was reported to change into a 1×1 pattern at a Sn coverage of 0.25 ML in RHEED and LEED studies.[3–5] This change was proposed to result from the adsorption of Sn atoms on the In vacancy site of the In-vacancy buckling structure[7] of the InSb(111)A-(2×2) clean surface. Although this proposition is supported theoretically,[3,6] there is no experimental evidence for this, except the change in diffraction patterns. Since the understanding of the initial growth process of an Sn film is essential to comprehend the origin of the presence of an α phase even above 13.2 °C, we have investigated the process using LEED and high-resolution core-level spectroscopy.

In this paper, we report LEED and core-level photoemission measurements of Sn films grown on the InSb(111)A-(2×2) surface. The coverage-dependent LEED patterns and integrated intensities of the In 4*d*, Sb 4*d*, and Sn 4*d* core levels indicate that the α-Sn film grows epitaxially by a bilayer (double layer by double layer) mode and that no substrate atoms diffuse into the Sn film as suggested in the literature.[5] Furthermore, the coverage-dependent intensities of the four In 4*d* components and those of the three Sn 4*d* components indicate that the In vacancy site is not the preferable Sn adsorption site. The present results provide a detailed understanding of the fundamental properties at the interface of an α-Sn film and the InSb surface.

The high-resolution core-level photoemission and LEED measurements were performed at beamline BL-1C at the Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The photoemission spectra were obtained using an angle-resolved photoelectron spectrometer with a total energy resolution of 75 meV for all photon energies. An undoped InSb(111)A sample was cleaned by repeating Ar^+ ion sputtering (500 eV) and annealing (370 °C) until a sharp 2×2 LEED pattern was observed. After the cleaning, surface states were observed in the valence-band spectra, and neither the In 4*d* core-level spectra nor the Sb 4*d* core-level spectra showed any indication of contamination. Sn adsorption was performed using a Knudsen cell after cooling down the samples to room temperature. The deposition rate, which was measured to be 0.32 ML/min by monitoring a quartz crystal oscillator microbalance, was calibrated using the core-level spectra. All LEED and core-level measurements were performed at room temperature.

The Sn coverage-dependent integrated intensities of the In 4*d*, Sb 4*d*, and Sn 4*d* core levels are shown in Fig. 1. The

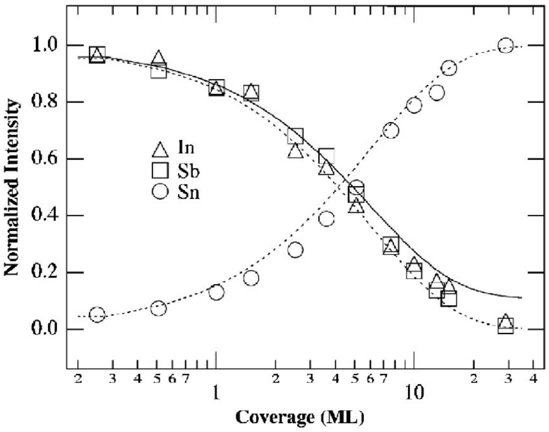

FIG. 1. Sn coverage-dependent integrated intensities of the In 4*d*, Sb 4*d*, and Sn 4*d* core levels. Each core level is normalized to its maximum intensity. The two dashed lines are the fitting results obtained using a bilayer growth model and the solid line is obtained using the interdiffusion model.

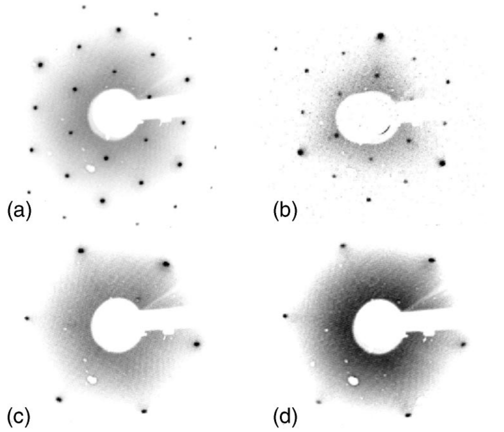

FIG. 2. LEED patterns obtained at different Sn coverages. (a) shows the LEED pattern of a clean InSb(111)A-(2×2) surface. The Sn coverages in (b), (c), and (d) are 1.0, 3.6, and 7.6 ML, respectively. Primary electron energies are (a) 35 eV, (b) 40 eV, (c) 36 eV, and (d) 34 eV. The azimuthal angle of the sample holder in (c) and (d) was rotated 90° with respect to that of the sample holder in (a) and (b).

triangles, squares, and circles represent the integrated intensities of the In 4*d*, Sb 4*d*, and Sn 4*d* core levels, respectively. The intensity of each core level is normalized to its maximum intensity. To obtain more information about the growth process of the Sn film, we have analyzed the coverage-dependent integrated intensities of the core levels using a bilayer growth model[8] (dashed lines) and an interdiffusion model (solid line). The solid line is obtained by considering that the Sn film grows by a bilayer mode but with 1.6% of In atoms at the Sn surface, i.e., a percentage proposed in Ref. 5. As shown in Fig. 1, the dashed lines show good agreement with the experimental result, while the solid line does not agree with the experimental result at coverages higher than 10 ML. The good agreement between the experimental result and dashed lines indicates that Sn film grows by a bilayer on an InSb(111)A-(2×2) surface, and therefore supports the growth mode reported in Ref. 3. Furthermore, since the In 4*d* and Sb 4*d* core levels show the same decrease in intensity, we conclude that In and Sb atoms do not diffuse into the Sn film.

The LEED pattern of an InSb(111)A-(2×2) clean surface is displayed in Fig. 2(a), and the LEED patterns obtained after Sn adsorption are displayed in Figs. 2(b)–2(d). The Sn coverages in (b), (c), and (d) are 1.0, 3.6, and 7.6 ML, respectively. Here we notice that the azimuthal angle of the sample holder in (c) and (d) was rotated 90° with respect to that of the sample holder in (a) and (b), and thus the 30° rotated ×1 LEED spots observed in (c) and (d) indicate that the vectors of the reciprocal unit cell of the Sn film are the same as those of the InSb(111) surface. Furthermore, the lattice constant of α-Sn ($a=6.489$ Å) is almost the same as that of InSb ($a=6.4798$ Å), while the lattice constant of a β-Sn ($a=5.831$ Å, $b=3.182$ Å) is quite different. By considering the rotation of the sample holder and the almost identical distances between two ×1 fundamental spots in all patterns shown in Fig. 2, we conclude that an α-Sn film has epitaxially grown on the InSb(111)A-(2×2) in the present study as well as in the previous reports. The clear 2×2 spots of the clean surface in Fig. 2(a) become weaker after a 1.0 ML Sn adsorption, and only 1×1 patterns are observed in Figs. 2(c) and 2(d). Taking into account that an α-Sn film grows by a bilayer process, a 1.0 ML coverage means that approximately half of the surface of Fig. 2(b) is covered by Sn. A 1×1 LEED pattern was also observed at a Sn coverage of 2.4 ML, i.e., a coverage that corresponds to a surface which is fully covered by a Sn double layer. Since the thickness of the 2.4 ML Sn overlayer is shorter than the electron mean free path (approximately 7 Å at electron energies used in the present study), both the structure of the Sn overlayer and the structure of the InSb surface should contribute to the LEED pattern at this coverage. We therefore conclude that the coverage used in the previous reports, in which the 2 ×2 LEED pattern was reported to disappear at 0.25 ML,[4,5] was underestimated. Moreover, since a 1×1 LEED pattern was observed at a 29 ML Sn coverage, where there is no In and no Sb atoms in the surface region, we conclude that the origin of the difference in Sn surface reconstructions is not the interdiffusion of In atoms.

The Sn coverage-dependent In 4*d* core-level spectra are shown in Fig. 3. The spectrum of the InSb(111)A-(2×2) clean surface is displayed in (a), and the Sn coverages in (b)–(e) are 0.25, 1.0, 2.5, and 3.6 ML. An emission angle (θ_e) of 0°, i.e., the surface normal direction, and a photon energy ($h\nu$) of 70 eV were used for all spectra. In order to obtain information about the In 4*d* components that contribute to the spectral shape, we have analyzed the spectra by a standard least-squares-fitting method using spin-orbit split Voigt functions. The solid lines overlapping the data points (open circles) are the fitting results. We used 0.86 eV for the spin-orbit splitting and a 0.18 eV full width at half maximum (FWHM) for the Lorentzian contribution for all In 4*d* components in the fitting procedure. The Gaussian widths of the bulk components are 0.50 eV, and those of the surface components are 0.50–0.55 eV. A polynomial background was subtracted before the decomposition of each spectrum, and each component is indicated by different hatching. The num-

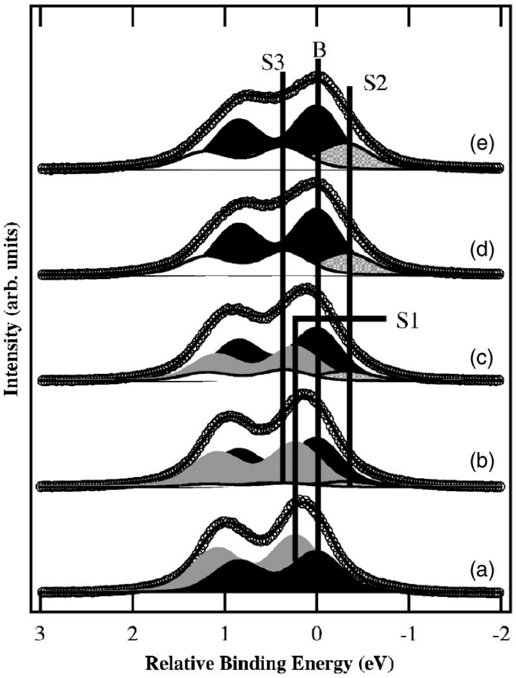

FIG. 3. Sn coverage-dependent In 4*d* core-level spectra. (a) shows the spectrum of an InSb(111)A-(2×2) clean surface, and (b)–(e) are the spectra after Sn adsorption. The Sn coverages in (b)–(e) are 0.25, 1.0, 2.5, and 3.6 ML. The zero of the binding energy is taken at the position of the bulk component (B) in each spectrum. Each component is indicated by different hatching.

ber of components and their binding energies were confirmed by measuring the same samples as those used in Fig. 3 using different $h\nu$ and θ_e that give a difference in the surface sensitivity.

The In 4*d* core-level spectrum of the InSb(111)A-(2×2) clean surface is well reproduced using two components whose difference in binding energy is 0.23 eV. This result is in good agreement with the previous In 4*d* core-level studies,[5,9] in which two components with a difference in binding energy of 0.23–0.24 eV were observed for the InSb(111)A-(2×2) clean surface. Taking into account that the intensity of the component with lower binding energy (B) becomes larger using a bulk sensitive measurement condition, while the intensity of the higher-binding-energy component (S1) becomes smaller, we attribute B to bulk In atoms and S1 to surface In atoms of the (2×2) reconstructed structure. Within the limit of the initial-state effect, this attribution is consistent with the STM observation,[11] in which the charge state of the surface In atoms was reported to be more positive than the charge state of bulk In atoms, and also consistent with the attributions performed in the previous In 4*d* core level studies.[5,9] The binding energy of the In 4*d* core level of In clusters that might be produced during the Ar^+ ion sputtering is reported to be 0.62 eV lower than that of the bulk component.[10] However, no structure is observed at this energy in Fig. 3. This indicates that there is no In cluster on the surface used in the present study.

After the 0.25 ML Sn adsorption, the intensity of S1 decreases, and two new components (S2 and S3) appear at binding energies of -0.21 and 0.33 eV related to the bulk component. S2 is revealed by the tail on the low binding energy of the B component, and the presence of S3 is obvious from the shallower valley between the two peaks observed in the spectrum. At higher Sn coverages, the intensities of both the S2 and S3 components increase together with the decrease in intensity of S1. Taking into account that the electronegativities of In, Sn, and Sb are 1.78, 1.96, and 2.05 in the Pauling scale, the In-Sn bonding should be less ionic than the In-Sb bonding, and the charge state of In atoms bonded to Sn atoms should be more negative than the charge state of In atoms in the bulk phase. This means that the binding energy of the 4*d* component of In atoms bonded to Sn should be lower than that of the bulk component within the initial-state effect, and we therefore attribute the S2 component to In atoms that bond directly to Sn atoms at the interface. The S3 component was not observed in the former core-level study (Ref. 5). In Ref. 5, a He II resonance line was used in the measurement and an overlap of the Sn 4*d* core level to the In 4*d* core level, which originates from the He II_β satellite photon, was observed in the spectrum. This overlap might be the reason why S3 was not identified in this former study. The origin of S3 should be In atoms of the InSb substrate since In does not diffuse into the Sn overlayer. Thus we propose that S3 originates from In atoms of the second bilayer, by assuming that Sn adsorption affects the charge state of the second In layer.

The observation of S2 at 0.25 ML Sn coverage indicates that Sn atoms do not adsorb preferably on the In-vacancy sites of the InSb(111)A-(2×2) structure as suggested in the literature.[3–6] In order to obtain further information about the initial growth process of the α-Sn film on an InSb(111)A-(2×2) surface, we consider the coverage-dependent intensities of the Sn 4*d* core level. Figure 4(a) shows the fitting result of the Sn 4*d* core level of a 3.6 ML Sn adsorbed InSb(111)A surface, and (b) displays the coverage-dependent intensities of the Sn 4*d* components obtained by analyzing the core-level spectra. As shown in Fig. 4(a), the Sn 4*d* core-level spectra are well reproduced using three components (Sn1–Sn3). The solid line overlapping the data points (open circles) is the fitting result. We used 1.07 eV for the spin-orbit splitting and a 0.18 eV FWHM for the Lorentzian contribution for the three Sn 4*d* components in the fitting procedure. A Gaussian width of 0.60 eV was used for Sn1 and Sn3, and widths of 0.60–0.70 eV were used for Sn2.

The intensities of the Sn2 and Sn3 components increase at low coverage, saturate at approximately 2 ML, and continuously decrease at higher coverages. Taking the finite mean free path of the photoelectron into account, the intensity decreases of Sn2 and Sn3 indicate that the origins of these two components are Sn atoms that situate at the interface of the InSb substrate and α-Sn film. In order to make more detailed assignments of the origins of Sn1–Sn3, we pay attention to the intensity ratio of the three components that gives information about the number ratio of corresponding Sn atoms. As shown in Fig. 4(b), the intensity of Sn1 drastically increases at 2 ML, and $I_{\mathrm{Sn1}}:(I_{\mathrm{Sn2}}+I_{\mathrm{Sn3}})$ is approximately 1:1 at 4 ML (I_{Sn1}, I_{Sn2}, and I_{Sn3} are the intensities of Sn1, Sn2, and Sn3, respectively). These suggest that the origin of Sn1 is Sn atoms of the third and higher layers, and that the Sn2 and Sn3 components originate from Sn atoms of the first and

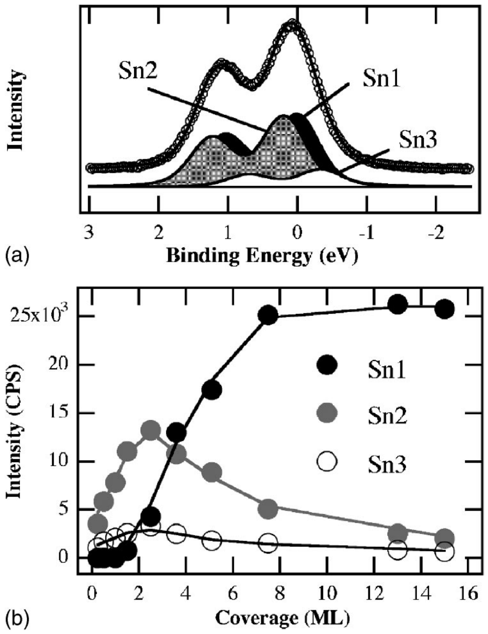

FIG. 4. (a) Decomposition of the Sn 4*d* core-level spectrum of a 3.6 ML Sn adsorbed InSb(111)A surface. The open circles are the experimental data, and the solid line overlapping the open circle is the fitting curve. Each component is indicated by different hatching. (b) Coverage-dependent intensities of the three Sn 4*d* components.

second layer. Furthermore, $I_{\mathrm{Sn2}}:I_{\mathrm{Sn3}}$ was approximately 3:1 in the full coverage range shown in Fig. 4(b). Taking the electronegativities of atoms into account, Sn atoms bonded to In should be negatively charged and those bonded to Sb should be positively charged. Thus, by assuming that Sn atoms of the second layer are positively charged to relax the charge distribution at the interface and by considering the In 4*d* core-level results (the bilayer growth mode and random Sn adsorption site), we assign Sn3 to originate from atoms bonded to In and Sn2 to originate from both the atoms bonded to Sb and the Sn of the second layer. The larger Gaussian width of Sn2 supports the assignment that this component consists of more than one origin. Since the Sn2 and Sn3 components are dominant at Sn coverages below 4 ML, we propose that the strong chemical bonding might be the origin of the stable α-Sn film on an InSb(111)A surface at room temperature.

Finally, we discuss briefly the origin of different reconstructions of the Sn(111) surface that depend on the cleaning methods. As mentioned above, this difference cannot result from the interdiffusion of In atoms into the Sn overlayer. Taking into account that the 2×2 and 3×3 reconstructions observed at room temperature transformed into a 1×1 pattern at higher temperatures,[3] one possible explanation is the disorder of the surface Sn atoms. This disorder can be produced by either the presence of only small 2×2 and 3×3 domains, or by the thermal vibration of surface Sn atoms. By assuming that the repeat of sputtering and annealing produces Sn domains whose phases are shifted, we propose that the first reason fits the case.

We have investigated the growth of α-Sn films on an In-terminated InSb(111)A-(2×2) surface at room temperature using LEED and high-resolution core-level photoelectron spectroscopy. In LEED, the 2×2 reconstructed pattern of the clean InSb(111)A surface was still observed after a 1.0 ML Sn adsorption, though the intensity of the $\times2$ spots becomes weaker. This observation means that the disappearance of the 2×2 LEED pattern at 0.25 ML reported previously was underestimated in terms of the coverage. The almost same distances between two $\times1$ fundamental spots in the LEED patterns of the InSb(111)A surface and of the Sn film indicate that the film grown on the substrate is α-Sn. Taking the integrated intensities of In 4*d*, Sb *d*, and Sn 4*d* core-level spectra into account, we conclude that the α-Sn film grows epitaxially by a bilayer mode, and that there is no interdiffusion of the substrate atoms. The coverage-dependent intensities of the In 4*d* and Sn 4*d* components indicate that the In vacancy site is not the preferable Sn adsorption site as suggested in the literature. The interface components, which originate from the strong chemical bonding between substrate atoms and Sn atoms, are dominant at Sn coverage below 4 ML. These bondings might be the origin of the stable α-Sn film on an InSb(111)A surface at room temperature.

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