Influence of Monomolecular Steps on the First-Order Structure Transition of an InAs(001) Surface

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The surface stoichiometry transition from As-covered 2×4 to In-covered 4×2 on InAs(001) misoriented surface is studied by reflection high-energy electron diffraction. The width of the hysteresis due to the first-order phase transition between these two structures is smaller with a surface misoriented toward the $[1\bar{1}0]$ direction than that with an exactly oriented surface. The results from Monte Carlo simulation indicate that this phenomenon can be explained by the finite size effect on the first-order surface stoichiometry transition caused by the existence of monomolecular steps.

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Recent advances in molecular beam epitaxy (MBE) are useful for studying surface physics as well as for fabricating optoelectric devices [1]. It has become possible not only to prepare clean surfaces but also to get important information about the surface physical phenomena by positively modulating the surface, for example, by depositing some species of atoms, slightly misorienting the surface axis, or introducing stress due to the formation of heterointerfaces. In particular, the surface is interesting as the stage for two-dimensional phase transitions [2]. Phase transitions are commonly observed in many physical systems, and studying the influence of surface modulation on a phase transition also provides important information about other physical systems as well as the surface physics. In this Letter, we report about finite size effects on a first-order phase transition, which is commonly discussed in phase-transition systems.

There are many theoretical studies on finite size effects on phase transition, for example, by Monte Carlo simulations and renormalization-group treatments [3, 4]. In general, a phase transition can occur in a system with infinite degrees of freedom. In a finite system, however, the physical quantity has no singularity as a function of temperature (or other parameters in general). The metastability associated with the first-order phase transition is broken by making the system size finite. For sufficiently large systems, the quantity has an abrupt dependence at the singular point and this abruptness increases when the system size increases. This influence on the phase transition of system size is theoretically well known, and has been also studied experimentally for a number of physical systems [4]. For example, for semiconductor surfaces finite size effects were reported for an irreversible transition from Si(111)-2×1 to 7×7 with the measurement of the LEED pattern and surface conductivity [5], and for the transition between Si(111)-7×7 and 1×1 with reflection electron microscopy [6] and high-temperature scanning tunneling microscopy [7].

Here, we discuss the phase-transition on InAs(001) surfaces with a fixed As pressure. As-covered 2×4 and In-covered 4×2 surfaces have been observed using the difference in surface stoichiometry [8]. The stoichiometry variation between these two surfaces was reported to be a first-order phase transition [9, 10]. With a fixed As pressure, the InAs surface changes discontinuously from one surface to the other as a function of the substrate temperature with hysteresis. This is not an ordinary order-disorder transition associated with the formation of surface reconstruction but a transition in the surface stoichiometry variation which can be peculiarly observed in a thermal equilibrium system between vapor and compound crystal surface. To our knowledge, there is no report on the influence of surface steps on the phase transition for such physically different equilibrium systems.

This Letter presents results for slightly misoriented InAs(001) surfaces. Periodic monomolecular steps are formed on the misoriented surface, and these monomolecular steps cut off the lateral interaction among surface atoms. This makes the system size along the misorientation direction finite. By observing the influences of this misorientation on phase transition, we can study the finite size effects experimentally.

The details of our experimental setup are explained elsewhere [10, 11]. Only the specific experimental procedure is explained here. Three types of undoped n-type InAs were used as the substrate. One was exactly oriented (001), one was 2° misoriented toward the [110] direction (called the A surface), and the other was 1° or 2° misoriented toward the $[1\bar{1}0]$ direction (the B surface). They were all etched in H_2SO_4:H_2O_2:H_2O=20:1:1 solution. A 200 nm thick InAs buffer layer was grown at 450 °C in the MBE chamber before the observations. Electron-beam specular reflectivity of these surfaces was measured under an As pressure of 2.6×10^{-6} Torr. The electron-beam incident angle was chosen to be about 1° and the incident azimuth was chosen to be [110] or $[1\bar{1}0]$. In particular, one of these two directions which is parallel to the surface monomolecular steps was used for misoriented surfaces. With misoriented surfaces, the specular beam splits due to the periodicity of the monomolecular steps [12]. We used a Faraday-cup-shaped electrode to detect the electron-beam intensity [11]. This electrode diameter is large enough to include both peaks of the split specular beam. A 2×4 surface structure, which corresponds to an As-covered surface, was observed at low substrate temperatures, and a 4×2 structure, which corresponds to an In-covered surface, was observed at high substrate temperatures. We initially increased the substrate temperature and then decreased it at a rate of 1 °C/min while measuring the electron-beam reflectivity during the transitions between these two surface structures.

Figure 1 shows the results for an exactly oriented surface. For the azimuths of both the [110] and $[1\bar{1}0]$ directions, the reflectivity changed discontinuously with a hysteresis of about 10 °C at the transition between As-covered and In-covered surfaces. This result was reproducibly obtained for different runs and no significant change was observed when the rate was changed in the range from 0.5 to 2 °C/min. This discontinuous change is not observed with a GaAs (001) surface, i.e., the electron reflectivity changed gradually for a similar thermal cycle [10]. This discontinuous change for InAs shows that the structure transition between As-covered and In-covered surfaces is a first-order phase transition.

Next, the finite size effect on this first-order transition was studied using misoriented surfaces. A (001) InAs 2° misoriented surface has an average terrace width of about 8 nm. Because the two-dimensional primitive cell of this surface forms a square lattice with a lattice constant of 0.4 nm, twenty arsenic atoms are in a row along the misorientation direction. Even if we assume that the desorption and adsorption of As occurs with the smallest unit, i.e., an As atom, the system size along the misorientation direction is limited to twenty units. This means that the existence of periodic monomolecular steps makes the system size finite. Figure 2 shows the results with 2° misoriented surfaces. The hysteresis for the *A* surface shows a width similar to the exactly oriented surface, but that for the *B* surface is 3.5 °C, which is smaller than for the exactly oriented surface. A similar observation was performed with a 1° misoriented *B* surface and the hysteresis width was found to be 5.3 °C for this surface. Therefore, the hysteresis width indicates a decrease with increasing misorientation angle. The decrease in hysteresis width indicates a drop in metastability associated with the first-order phase transition. This experimental result shows that an expected finite size effect was observed for the *B* surface, but was not significant for the *A* surface. To explain this finite size effect due to the surface misorientation and the difference between the *A* and *B* surfaces, we performed a Monte Carlo simulation taking into account the interaction between two neighboring As surface units. We made the following assumptions.

(a) The desorption and adsorption of As atoms occurs within units which form a rectangular lattice on the surface. The structure of an As-covered 2×4 has been reported to consist of three As dimers and one missing dimer [13]. This unit, therefore, can be As, an As dimer, or three As dimers.

(b) In the temperature range used for these experiments, the sticking coefficient of As atoms on an As-stable surface is very small. We assume that the adsorption of an As unit can occur only on an In-covered site. In other words, no As unit can adsorb at the As-covered

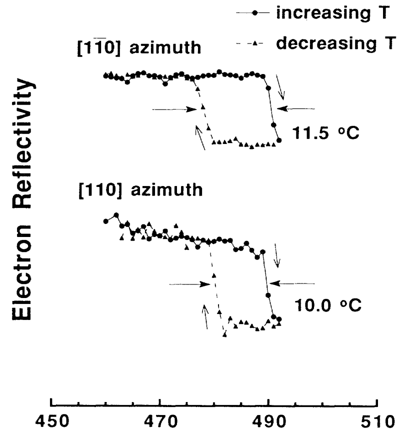

FIG. 1. Electron-beam specular reflectivity as a function of substrate temperature for InAs exactly (001) oriented surface with $[1\bar{1}0]$ and [110] azimuths. An As flux of 2.6×10^{-6} Torr was supplied during the measurement.

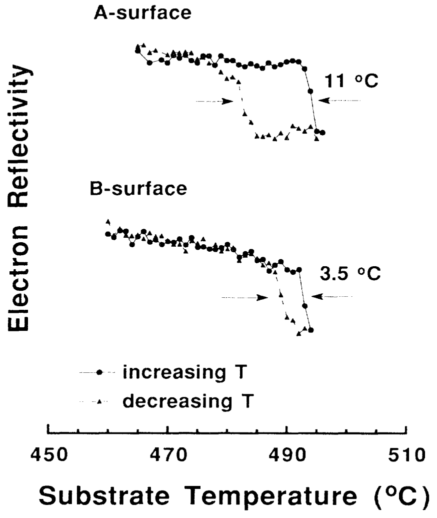

FIG. 2. Electron-beam specular reflectivity as a function of substrate temperature for InAs (001) surfaces misoriented toward the [110] (*A* surface) and the $[1\bar{1}0]$ (*B* surface) directions. An As flux of 2.6×10^{-6} Torr was supplied during the measurement, and $[1\bar{1}0]$ and [110] azimuths were used for the *A* and *B* surfaces, respectively.

site.

(c) This As unit interacts with the In atoms in the lower atomic layer and with neighboring As units. In the following, the former is referred to as an As-In interaction and the latter as an As-As interaction. Anisotropy in the As-As interaction along the surface was also assumed to explain the difference between A and B surfaces. We specify the two-dimensional surface site position by (n, m) (the positions along [110] and [$1\bar{1}0$] directions, respectively), and the existence of an As unit at this position is expressed by $\eta_{n,m}$, which takes the value of 1 for existence and 0 for absence. The Hamiltonian of the system is then given by

$$H = -\sum_{n,m} E_s\eta_{n,m} - \sum_{n,m} (E_{i1}\eta_{n,m}\eta_{n+1,m} + E_{i2}\eta_{n,m}\eta_{n,m+1}). \qquad (1)$$

Here, E_s is the energy of As-In interaction, and E_{i1} and E_{i2} give the energies of As-As interaction along the [110] and [$1\bar{1}0$] directions, respectively. In the isotropic case, i.e., $E_{i1} = E_{i2}$, this Hamiltonian is identical to that for the two-dimensional Ising model.

(d) The adsorption of an As unit to an empty site has a constant rate of R_{ad}, which is independent of the temperature. The value of $2s^{-1}$ was used for all calculations reported here.

(e) The desorption rate of the As unit existing at the site position (n, m), $R_{d:n,m}$, has the form

$$R_{d:n,m} = \nu \exp[-(E_s + N_{1:n,m}E_{i1} + N_{2:n,m}E_{i2})/kT], \qquad (2)$$

which is the simplest expression deduced from assumptions (c) and (d). In this expression, $N_{1:n,m} = \eta_{n+1,m} + \eta_{n-1,m}$ and $N_{2:n,m} = \eta_{n,m+1} + \eta_{n,m-1}$ give the numbers of existing nearest-neighbor As units along the [110] and [$1\bar{1}0$] directions. The value of 10^{17} s^{-1} was used for the parameter ν in all calculations reported here.

To reduce the computer time needed for simulations, we used a method suggested by Maksym which gives a new algorithm with a higher level group structure [14]. The change in As surface coverage when the temperature was changed at the rate of 1°C/min was calculated with these assumptions. The simulation started at a substrate temperature low enough to have a full surface coverage of As units and the temperature was increased up to the temperature at which the coverage becomes negligible and then the temperature was decreased at the same rate of 1°C/min. The calculation was performed with a lattice size of 72 × 72 units and a periodic boundary condition was used at the edge of the area.

Figure 3 shows the calculated As coverage for exactly oriented surfaces. For simplicity, an isotropic As-As interaction ($E_{i1} = E_{i2} \equiv E_i$) was used here. The average interaction energy, $E_s + 2E_i$, was fixed at 2.5 eV, which is the value obtained from the P-T phase diagram in Ref. [9] and the value for E_i was changed. For E_i less than 0.12 eV, As coverage changed gradually as a function of substrate temperature without hysteresis. In particular, when there was no As-As interaction, i.e., $E_i = 0$, the result coincided with the Langmuir isotherm,

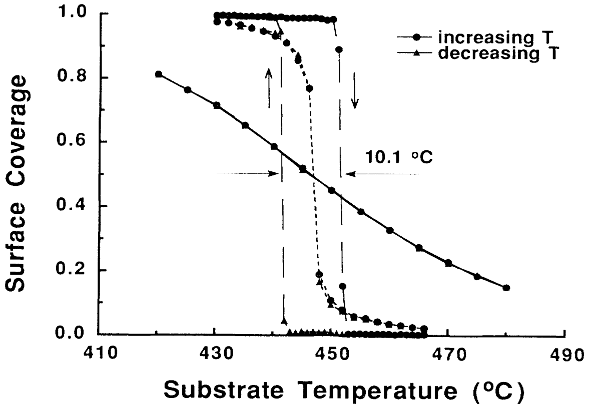

FIG. 3. Calculated coverage of As unit as a function of substrate temperature for E_i of 0 (solid curve), 0.1 (dotted curve), and 0.16 eV (dashed curve) with an exactly oriented surface.

$$R_d = [\theta/(1-\theta)]\nu \exp(-E_s/kT). \qquad (3)$$

On the other hand, for E_s larger than this value, the coverage changed discontinuously with hysteresis. A typical result for E_i=0.16 eV is shown in the figure. This indicates that the transition becomes first order when the As-As interaction is stronger than this critical energy. The value of the critical energy, 0.12 eV, is consistent with the exact solution by Onsager, which gives the critical energy of 0.115 eV for our model [15]. This coincidence in critical energy justifies our calculations. For GaAs, the structure gradually changes between the As-covered surface and the Ga-covered surface showing higher order or no phase transition. The ratio E_i/E_s is probably small for GaAs (001). On the other hand, the transition is first order for InAs because this ratio is comparatively large for this surface. A hysteresis width of about 10°C was obtained for the E_i of 0.16 eV, which gives a rough estimate for the strength of the As-As interaction with an InAs (001) surface.

Next, the simulation was performed for a InAs misoriented surface. We used the following boundary conditions at the step edge. An As unit on one side of the step edge has no interaction across the step edge and one on the other side of the step edge has an interaction with an energy of E_{i1} (or E_{i2}) across the step edge, regardless of the existence of the As unit on the opposite side. First, an isotropic As-As interaction was used to study only the influence of monomolecular steps, and then the anisotropic interaction was introduced to explain the experimental difference between A and B surfaces. Figure 4 shows the

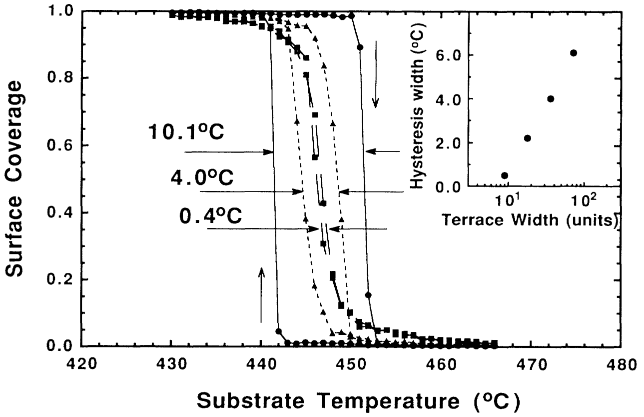

FIG. 4. Calculated As coverage for misoriented surfaces with several terrace widths. The solid curve corresponds to the exactly oriented surface, and the dotted and dashed curves correspond to the misoriented surfaces with terrace widths of 36 and 9 units, respectively. Inset: Plot of obtained hysteresis vs terrace width.

calculated hysteresis width with several terrace widths for E_s=2.18 eV and E_i=0.16 eV. As expected from the experimental results, the hysteresis width is smaller for a smaller terrace width. This finite size effect on the first-order transition is consistent with our experimental results. For misoriented surfaces, the As unit at the step edge has no interaction across the step. Therefore, the unit has less activation energy and can desorb from the surface more easily than one in a terrace. Then the metastability kept by the strong As-As interaction is broken and the hysteresis width becomes smaller. This provides a physical explanation of this phenomenon.

An anisotropic interaction was then introduced to explain the difference between A and B surfaces. In our experimental results, the finite size effect is stronger for the B surface than the A surface showing that the interaction along the $[1\bar{1}0]$ direction is stronger than that along the [110] direction. Here, we simply mention a typical result with E_{i1} of 0.03 eV and E_{i2} of 0.15 eV. The terrace width of eighteen units, which corresponds to the average number of As atoms in a row along the misorientation direction for the 2° misoriented surface, was used for this simulation. The calculated hysteresis widths for the exactly oriented surface, A surface, and B surface were 8.7, 4.9, and 0.6 °C. Although these values do not exactly reproduce the experimental widths, the tendency is qualitatively consistent with the experimental results and suggests that the As-As interaction along the $[1\bar{1}0]$ direction is stronger than that along the [110] direction.

In conclusion, the first-order surface stoichiometry transition on an InAs(001) surface was studied by reflection high-energy electron diffraction. The hysteresis width observed for a surface misoriented toward the $[1\bar{1}0]$ direction is smaller than that for an exactly oriented surface showing reduced metastability. This phenomenon was not significant for the surface misoriented toward the [110] direction. A Monte Carlo simulation with a two-dimensional anisotropic Ising model shows that this phenomenon is explained by a finite size effect on the first-order phase transition caused by the periodic monomolecular steps on the surface and suggests that the interaction between two As units along the surface has a large anisotropy caused by the anisotropic surface structure.

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