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First-order surface-structure transition on the (001) InAs surface studied with improved high-energy electron reflectivity measurements

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The electron-beam specular reflectivity of an InAs(001) surface was quantitatively measured as current through an electrode at several substrate temperatures. The reflectivity changes discontinuously at the reconstruction transition from As-stable (2×4) to In-stable (4×2) with hysteresis cycle as a function of the substrate temperature, indicating a first-order transition. The reflectivity change during As desorption shows that the desorption rate has a local minimum at the transition because of the existence of a metastable state due to the first-order transition.

The surface of III-V compound semiconductors has many interesting features with regard to the surface physics as well as in the application to electric and optoelectronic devices. There are many kinds of reconstructions observed on the surface.[1-3] It is well known that various reconstructions are due to different surface stoichiometries. However, elementary surface processes that determine surface reconstruction have not been well studied. The surface-reconstruction transition is one of the most interesting phase transitions in two-dimensional systems and provides important information on the chemical kinetics related to the phase transitions. The authors previously reported the relation between surface-reconstruction transition and the process of As desorption from a (001) GaAs surface.[4] In this report, the difference in the surface-structure transition between InAs and GaAs(001) surfaces is made clear and the As desorption process related to the structure transition for an InAs(001) surface is investigated by improved reflection high-energy electron-diffraction (RHEED) observation. The results clearly show that the As desorption rate strongly depends on the surface structure, and its behavior at the structure transition is different for different surface-structure transition.

In this improved RHEED method, the reflected electron-beam intensity is obtained as a current through a small electrode placed in front of the fluorescence screen. This improves the linearity and signal-to-noise ratio and allows a more quantitative RHEED observation. The details of the experimental setup are explained elsewhere.[5] Undoped semi-insulating GaAs and undoped *n*-type InAs were used for the substrates. They were etched in H_2SO_4:H_2O_2:H_2O solution (5:1:1 for GaAs and 20:1:1 for InAs). In the molecular-beam-epitaxy (MBE) chamber, surface oxide was removed by thermal annealing in an As_4 flux prior to the experiment. The annealing temperature and As_4 flux were 630 °C and 5×10^{-6} Torr for GaAs, and 500 °C and 1×10^{-5} Torr for InAs. A 200-nm-thick buffer layer was grown at 580 °C for GaAs and 470 °C for InAs before the RHEED observation. The RHEED acceleration voltage was 20 kV. The incident azimuth was [110] and the glancing angle was 0.9°. The substrate temperature was measured by infrared pyrometer.

Electron-beam specular reflectivity of GaAs and InAs(001) surfaces was measured under an As pressure of about 2.5×10^{-6} Torr (Fig. 1). We first increased the substrate temperature and then decreased it. Since the rate of temperature change was about 1 °C/min, thermal equilibrium was established for each observation. For both InAs and GaAs, a twofold pattern, which corresponds to an As-stable (2×4) surface, was observed at low substrate temperatures, and a fourfold pattern, which corresponds to a metal-stable (4×*x*) (*x* = 2,6,8) surface, was observed at high substrate temperatures. There is a large difference in the transition region.

With InAs, the electron reflectivity changed discontinuously as a function of the temperature, with a 10 °C-wide

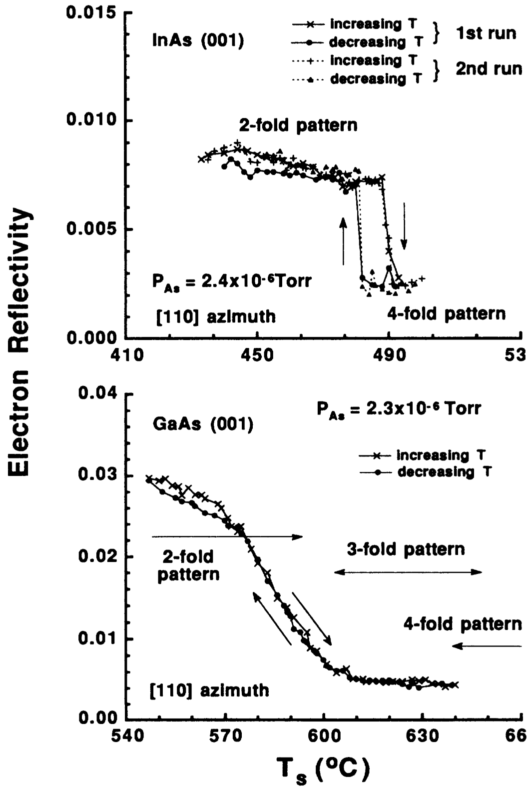

FIG. 1. Specular reflectivity vs substrate temperatures for (001) InAs and GaAs surfaces.

hysteresis cycle. This result was obtained reproducibly. The reflectivity changes in two different runs coincide perfectly (see Fig. 1). This result suggests that the surface-structure transition from As-stable (2×4) to In-stable (4×2) is a first-order one and that the surface that has an intermediate As coverage between these two surfaces is not stable for an InAs(001) surface. It was reported by Moison, Guille, and Bensoussan[6] that the reconstruction transition for InAs(001) has a hysteresis cycle. Our results clearly show that a physical parameter, i.e., the electron reflectivity or probably the As coverage itself, has a discontinuous dependence on substrate temperature due to a first-order surface-structure transition. On the other hand, with GaAs, the reflectivity changed gradually as a function of the temperature, passing through an intermediate (3×1) surface without hysteresis. The transition is higher order for GaAs(001) and a mixed (3×1) surface can exist for any degree of As coverage.

The influence of this structure transition on the As desorption process was then examined in detail. Figure 2 shows the change in specular beam reflectivity and the transition point of the surface structure when the As supply to the InAs(001) surface was terminated for several substrate temperatures. The electron specular reflectivity decreased due to the As desorption from the surface. It is clearly observed that the slope of this decrease has a minimum value in the neighborhood of the transition and increases after this transition; especially, the reflectivity reached a stable value without a transition to an In-stable surface at temperatures lower than 430 °C. The reflectivity is not a simple smooth function of As surface coverage, but depends on the reconstruction and surface roughness; even the diffraction condition (in-phase or out-of-phase, for example) is different for different surface reconstructions.[7] However, since similar phenomena were observed at different azimuths and incident angles, the As desorption rate probably takes a minimum value in the neighborhood of the transition. These results suggest that, for an InAs(001) surface, the existence of a metastable state resulting from the first-order transition slows the rate of As desorption in the neighborhood of the transition.

The reflectivity change during a twofold reconstruction can be fitted by an exponential function, and the Arrhenius plot of the decay constant gives an activation energy of 1.65 eV. This value is close to the value obtained from the temperature dependence of the III-to-V ratio with which the transition was observed during the growth.[8] The reflectivity change during a fourfold pattern was better fitted with an exponential curve when a [010] azimuth was used than a [110] azimuth. The activation energy of an As desorption process during a fourfold pattern, 4.2 eV, was evaluated from the reflectivity change at this azimuth. The activation energy differs for different reconstructions.

Figure 3 shows the result of similar observations with a GaAs(001) surface. As mentioned before,[4] the decay rate changes discontinuously due to the reconstruction transition but the slope of this decrease has no minimum value at the transition.

Next, we confirm the existence of a metastable state by another experiment. A small amount [0.1 monolayer (ML)] of In atoms was deposited on an InAs(001) surface at 430 °C when the reflectivity almost reached the stable value after the As shutter was closed (Fig. 4). Since just 0.1 ML of In atoms made the reconstruction transition, the surface just before the deposition is metastable and As desorption is suppressed at the transition. In addition, the slope of the reflectivity change after the deposition is steeper than with no deposition. This suggests that the As desorption, which was suppressed until

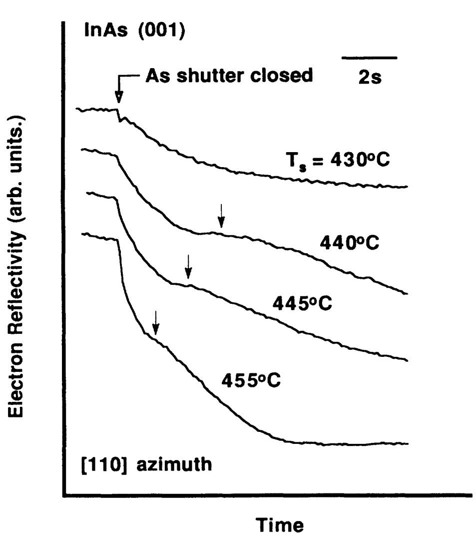

FIG. 2. Change in RHEED specular beam reflectivity when As$_4$ supply to the surface was terminated for an InAs(001) surface at various substrate temperatures. The RHEED pattern changed at the arrow from twofold to fourfold.

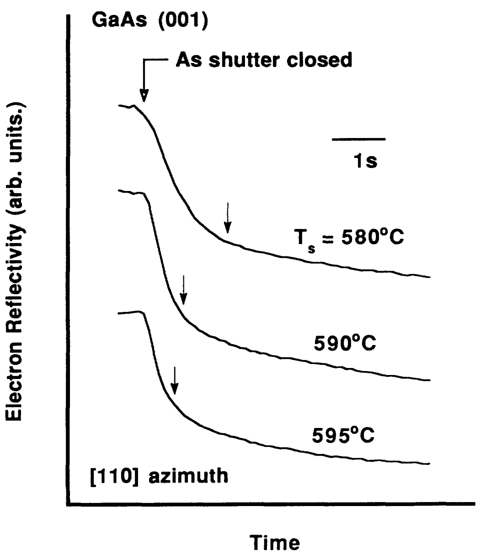

FIG. 3. Change in RHEED specular beam reflectivity when As$_4$ supply to the surface was terminated for a GaAs(001) surface at various substrate temperatures. The RHEED pattern changed at the arrow from twofold to threefold.

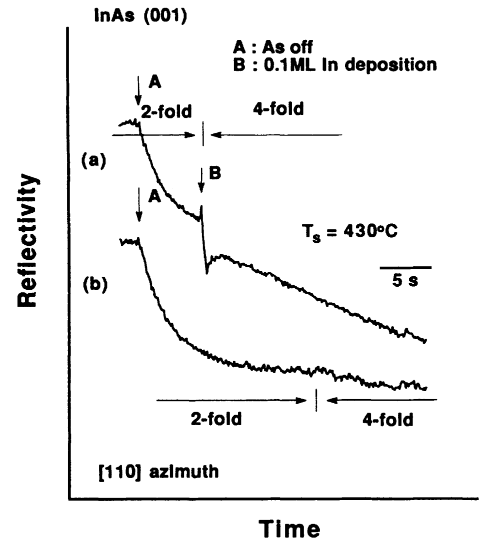

FIG. 4. Electron-beam specular reflectivity changes were plotted when As_4 supply was terminated at *A* and when (a) 0.1 ML of In atoms were supplied at *B* and (b) no In atom was supplied.

the reconstruction transition, was enhanced when a small amount of In was deposited on the surface. This can be interpreted as the In deposition breaking the metastable state and enhancing the As desorption from the surface. On an InAs(001) surface, the surface which has an intermediate As coverage between As-stable (2×4) and (4×2) may not be thermodynamically stable. On the other hand, the intermediate surface can exist as (3×1) on a GaAs(001) surface. This difference may be caused by the difference in bond strength between GaAs and InAs.

In summary, we explored the As desorption from an InAs(001) surface as revealed by an improved RHEED analysis, which allows accurate *in situ* determination of electron-beam reflectivity by measuring the reflected electron-beam current. The electron reflectivity under As pressure changes discontinuously as a function of the temperature with a hysteresis cycle, indicating first-order surface-structure transition. The As desorption is suppressed near the structure transition, since the metastable state exists due to the first-order transition.

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