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Transition with a hysteresis cycle in surface reconstruction on GaAs(001) observed by optical reflectance spectroscopy

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Transitions in GaAs(001) surface reconstruction have been studied by using reflectance anisotropy spectroscopy. The transition between $c(4\times4)$ and (2×4) exhibits a 20 °C wide hysteresis cycle under As_4 flux of 2×10^{-7} Torr beam equivalent pressure. The width of the hysteresis becomes smaller under higher As_4 pressure, i.e., at higher temperature and at higher speed of the temperature change. On increasing the temperature, the $c(4\times4)$ surface changes slowly into (2×4) in about 2 h. The transition is a reversible reaction with different activation energies.

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The GaAs(001) surface has attracted much attention during the past few decades for both technological and scientific reasons.[1–13] GaAs(001) exhibits a sequence of reconstruction depending on the substrate temperature and surface stoichiometry ranging from As-rich $c(4\times4)$ structure to a Ga-rich (4×2) one. Recent growth techniques such as molecular-beam epitaxy (MBE) and metal organic vapor phase epitaxy (MOVPE) make it possible to prepare a variety of reconstructed surfaces of GaAs(001),[14] which can also be examined *in situ* to evaluate their composition and crystallographic and electronic structures. In particular, As-rich (2×4) and $c(4\times4)$ surfaces are of greatest technological interest because of their applications to atomically controlled epitaxial growth and self-assembled dot growth.[15–20] Numerous studies on $c(4\times4)$ and (2×4) surfaces have been intensively performed by both experimental[1–9] and theoretical[6,10–13] approches. Furthermore, the surface-phase transition between them has been studied by many research groups.[7,21–24] From recent scanning-tunneling microscopy (STM) observations, surface diffusion of Ga and Ga adatoms on $c(4\times4)$ surface are considered to play a key role in the structural change of $c(4\times4)$.[7,22] They have suggested a model for the surface-phase transition. However, there is no report about the difference between the heating process and the cooling process in the transition. In this paper we focus our attention on the reconstruction transition between $c(4\times4)$ and (2×4) surfaces and report on a distinct hysteresis cycle, i.e., a reversible reaction with different activation energies. Our finding enables us to obtain consistent model explaining the transition process with the hysteresis cycle.

We performed reflectance anisotropy spectroscopy (RAS) on clean, singular (misorientation of ±0.3 °C) oriented GaAs(001) substrate during the phase transition and simultaneously characterized the change by high energy electron diffraction (RHEED) under As_4 flux of about 2×10^{-7} and 5×10^{-6} Torr beam equivalent pressures. The sample temperature was measured by a pyrometer. Before the measurements, an undoped 120-nm GaAs was grown at 530 °C on the GaAs(001) substrate. RAS signal was measured between the complex near-normal-incidence reflectances of light linearly polarized along two principle axes [110] and [110], which can be expressed in terms of the surface dielectric anisotropy.[14,19,25–28] The two-prism photoelastic-modulator configuration allowed us to measure both relative amplitude $\Delta r/r$, i.e., $(r_{\bar{1}10}-r_{110})/(r_{\bar{1}10}+r_{110})$, and phase $\Delta\theta$ of the anisotropy of the complex reflectance.

RAS spectra measured under As_4 flux of 2×10^{-7} Torr beam equivalent pressure as a function of the temperature are shown in Fig. 1. Horizontal dotted lines indicate the zero levels for each spectrum. We increased the sample temperature in a range from 414 to 464 °C. RAS spectrum was recorded after keeping the surface in 10 min at every temperature. Measurement time for one spectrum was about 15 min. Here, we focus on the signal at ~2.6 eV. The initial surface structure at 414 °C is $c(4\times4)$, which shows the negative RAS structure at ~2.6 eV related to the top-layer [110] dimmer. A remarkable change observed near 440 °C in Fig. 1

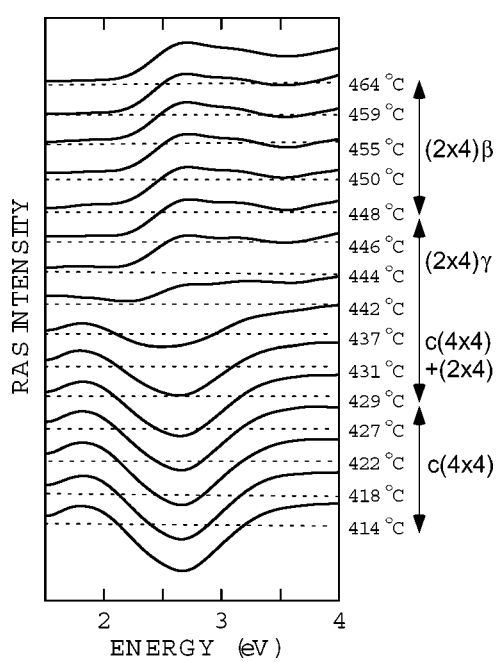

FIG. 1. RAS spectra as a function of substrate temperature for an singular oriented GaAs(001) surface with As pressure of 2×10^{-7} Torr. The temperature was changed from 414 to 464 °C.

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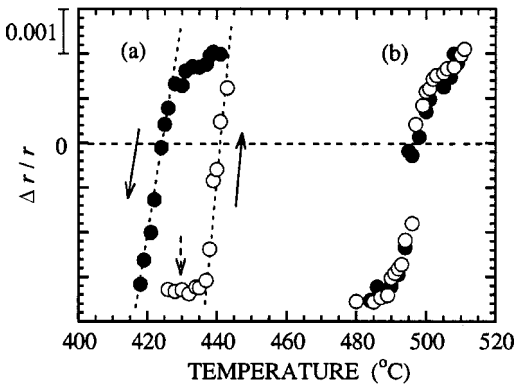

FIG. 2. RAS signal intensity at 2.6 eV as a function of substrate temperature for an exactly oriented GaAs(001) surface with As pressures of (a) 2×10^{-7} and (b) 5×10^{-6} Torr. We first increase the sample temperature and then decreased it. Open and closed circles indicate data recorded on increasing and decreasing the temperature, respectively.

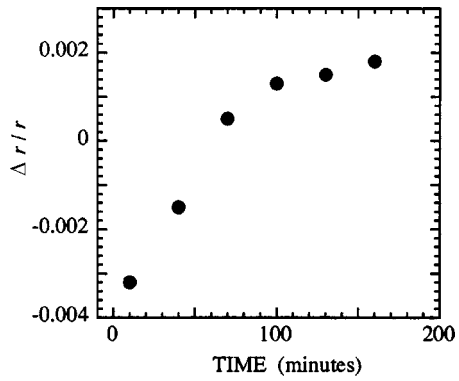

FIG. 3. RAS signal intensity at 2.6 eV as a function of annealing time. The annealing was performed at 430 °C under As_4 flux of 2×10^{-7} Torr. A dashed arrow in Fig. 2 indicates the temperature noticed here. The start surface shows $c(4\times4)$.

corresponds to the transition from $c(4\times4)$ to $(2\times4)\beta2$. The (2×4) surfaces show the positive structure which is considered to be associated with the [110]-As dimmer[14,25,26] or a surface-perturbed bulk E_1 critical point.[28] Therefore, the sign inversion is observed. During this transition, the RHEED shows patterns for $c(4\times4)$ mixed with (2×4). After that, the pattern changes into $(2\times4)\gamma$ and then becomes clear $(2\times4)\beta2$ at about 450 °C. The $(2\times4)\beta2$ phase appears up to 470 °C.

Figure 2 plots the temperature dependence of the RAS signal intensity at 2.6 eV measured under (a) 2×10^{-7} and (b) 5×10^{-6} Torr. We first increased and then decreased the sample temperature. Here, RAS spectrum was recorded after keeping the surface in 10 min at every temperature, and measurement time for one spectrum was about 15 min. The RAS signal intensity is the amplitude at 2.6 eV. Open and closed circles indicate data recorded on increasing and decreasing the temperature, respectively. Under As_4 flux of 2×10^{-7} Torr, the RAS signal changes remarkably as a function of the temperature, exhibiting a 20 °C wide hysteresis cycle. This result was obtained reproducibly, when we recorded data under the same conditions such as the time interval between the measurements. As traced by dotted lines in Fig. 2(a), the slope of the RAS-signal change is slightly different in the heating process and the cooling process. The change in the heating process is steeper. The width of the hysteresis is smaller under higher As_4 pressure, i.e., at higher temperature [Fig. 2(b)]. A similar hysteresis cycle observed in the RHEED specular beam intensity was reported for the surface-phase transition between As-stable (2×4) and In-stable (4×2) structures of InAs(001), in which the surface structure transition is a first-order phase transition.[29–31] However, the hysteresis width observed for the $c(4\times4)$-(2×4) transition on the GaAs(001) *depends* on the annealing time after the temperature is kept constant. This property is substantially different than that for the InAs case. The annealing-time dependence of the 2.6-eV signal is shown in Fig. 3. The measurement was performed under As_4 flux of 2×10^{-7} Torr. At first the temperature was set at less than 400 °C, then we increased the sample temperature and kept it, i.e., annealed, at 430 °C. A dashed arrow in Fig. 2 indicates the temperature noticed here. The start surface shows $c(4\times4)$. The $c(4\times4)$ surface changes slowly into $(2\times4)\beta2$, and the intensity converges to a constant positive level for the $(2\times4)\beta2$ in about 2 h.

The observed results indicate that the hysteresis is caused by the fact that the change from $c(4\times4)$ to (2×4) progresses slowly. Figure 4(a) shows the well-known atomic structure involving three top-layer As dimmers for $c(4\times4)$.[3] We consider a step structure consisting of $c(4\times4)$ domains. It is known that the completed $c(4\times4)$ surface shows many large islands with $c(4\times4)$ reconstruction.[3,22] During the phase change, a (2×4)-RHEED pattern is superimposed on the $c(4\times4)$ pattern. Recent detailed STM observations[7,22] and theoretical calculations[24] revealed a $c(4\times4)$ surface lying lower than the (2×4) surface. Since the number of Ga atoms on the surface is constant during the phase change under our experimental condition, the total number of Ga atoms is conserved. We note the arrangement of Ga atoms; $(2\times4)\beta2$ has a missing Ga row in the second layer exposing As dimmers in the third layer [Fig. 4(c)], though the third layer of $c(4\times4)$ is fully covered by Ga. Therefore, Ga atoms have to move at the transition. Based on a widely accepted atomic structure involving three top-layer As dimmers for $c(4\times4)$, Ga atoms are supplied from the step edge of the upper terrace to the lower $c(4\times4)$ surface to form (2×4) unit cells on the lower $c(4\times4)$. This step is

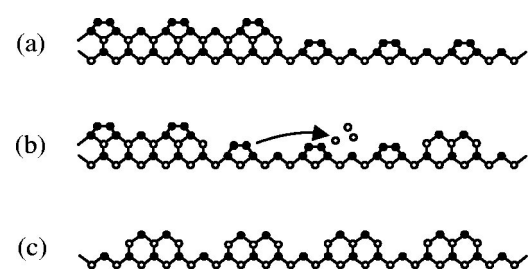

FIG. 4. Surface cross sections of the reconstruction transition from (a) $c(4\times4)$ to (c) $(2\times4)\beta2$. Open and closed circles indicate Ga and As atoms, respectively.

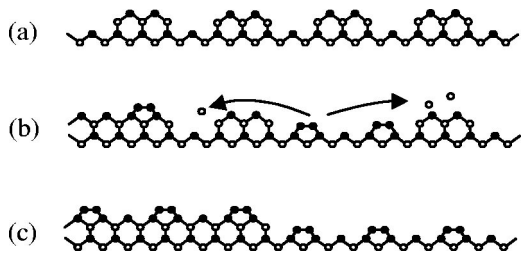

FIG. 5. Surface cross sections of the reconstruction transition from (a) $(2\times4)\beta2$ to (c) $c(4\times4)$. Open and closed circles indicate Ga and As atoms, respectively.

drawn in Fig. 4(b). Even if $c(4\times4)$ has Ga and As species intermixing layers as pointed out by Bell *et al.*,[7] some of the Ga must be supplied from the step edge. In contrast to the abovementioned transition from $c(4\times4)$ to $(2\times4)\beta2$, in the transition from $(2\times4)\beta2$ to $c(4\times4)$, on the other hand, some Ga may migrate to step edges after local melting of the 2×4 structure.[7,22] Bell[7]and Kanisawa[22] concluded that the amount of Ga that can be accommodated in this way depends on the migration length of Ga atoms during the annealing process, which may be enhanced during the phase transition. This step is drawn in Fig. 5(b).

Based on the models shown in Figs. 4 and 5, we discuss the main factor in the transition between reconstructions. The density of local melting site in the transition from $(2\times4)\beta2$ to $c(4\times4)$ is much higher than the step edge density of the $c(4\times4)$ domains that supply Ga atoms in the transition from $c(4\times4)$ to $(2\times4)\beta2$. This explains why the change from $c(4\times4)$ to $(2\times4)\beta2$ progresses slowly. Next we focus on the process shown in Fig. 4(b), where Ga atoms can not migrate, i.e., the Ga-As bond does not break, without breaking the excess As dimmers. This is a characteristic process in the transition from $c(4\times4)$ to $(2\times4)\beta2$ and does not appear in the reverse process. Therefore, excess thermal energy is necessary to break excess As dimmers in the transition from $c(4\times4)$ to $(2\times4)\beta2$, which is considered to be the main factor of this transition. On the other hand, it is impossible to transform (2×4) into $c(4\times4)$ without decomposing Ga-As units and supplying extra As. The quick response of this transformation indicates that its activation energy is small. Although there has not yet been reported an activation energy barrier height for As-adatom migration on an As-rich GaAs(001) surface, the As diffusion might be enhanced at the substrate temperature at which the transition begins, and incorporation of As atoms occurs quickly. Thus, the rate-limiting step in the transition from $(2\times4)\beta2$ to $c(4\times4)$ is the local melting of Ga-As units which supply the mobile Ga atoms.

The relatively steep slope of the RAS-intensity change that was observed on increasing the temperature as shown in Fig. 2(a) indicates that (2×4) unit cells are formed at once after the excess As dimmers are broken. Under As_4 flux of 5×10^{-6} Torr, the transition occurs at high temperature ($\sim495\,^{\circ}$C), and the width of the hysteresis is smaller. This result means that the temperature ($\sim495\,^{\circ}$C) is high enough to break the excess As dimmers.

In summary, we studied surface phase transitions on GaAs(001) using RAS. The RAS signal shows sign inversion upon the surface reconsruction transition between $c(4\times4)$ and (2×4). The RAS signal observed under As_4 flux of 2×10^{-7} Torr changes remarkably as a function of the temperature, exhibiting a $20\,^{\circ}$C wide hysteresis at the transition between $c(4\times4)$ and (2×4). The width of the hysteresis becomes smaller under higher As_4 pressure, i.e., at higher temperature, and at higher speed of the temperature change. On increasing the temperature, the $c(4\times4)$ surface changes slowly into (2×4) in about 2 h. The transition is a reversible reaction with different activation energies. Our finding enables us to obtain a consistent model explaining the transition process with the hysteresis cycle.

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