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Structure of Se-adsorbed GaAs(111)*A*-($2\sqrt{3}\times2\sqrt{3}$)-*R*30° surface

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The adsorption of Se on the GaAs(111)*A* surface forms a well-ordered ($2\sqrt{3}\times2\sqrt{3}$)-*R*30° reconstruction. We have proposed a structure model for the GaAs(111)*A*-($2\sqrt{3}\times2\sqrt{3}$)-*R*30°-Se surface, which consists of two Se trimers located at a hollow site of the GaAs(111)*A* surface and three Ga vacancies per unit cell. The proposed structure model sufficiently explains experimental data from reflection high-energy electron diffraction, x-ray photoelectron spectroscopy, and scanning tunneling microscopy, and satisfies electron counting requirements. [S0163-1829(99)09311-X]

I. INTRODUCTION

Adsorption of foreign atoms on semiconductor surfaces often results in the reconstruction of the outermost surface layers. The induced surface reconstruction is generally accompanied by the modification of the surface electronic properties, which has attracted considerable attention. In particular, there is a growing interest in the adsorption of Se and S atoms on the surfaces of III-V compound semiconductors, because of their passivating properties.[1,2]

Numerous studies have shown that Se and S atoms are adsorbed on the polar (001) surface of GaAs forming a variety of reconstructions, (2×1),[3–8] (4×3),[4] (2×3),[4,8] and (2×6).[9,10] On the other hand, on another polar surface of {111}, only a (1×1) reconstruction has been observed.[5,11]

This paper reports that a reconstructed structure of ($2\sqrt{3}\times2\sqrt{3}$)-*R*30° is formed on the Se-adsorbed GaAs(111)*A* surface. In this study, we use three complementary experimental techniques, scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), and reflection high-energy electron diffraction (RHEED), the combination of which allows us to systematically study the atomic structure of the ($2\sqrt{3}\times2\sqrt{3}$) surface. On the basis of STM observations and XPS measurements, we have proposed a structure model consisting of two Se trimers and three Ga vacancies per unit cell. Atomic coordinates of the proposed structure model have been determined by using rocking-curve analysis of RHEED.

II. EXPERIMENT

The experiments were performed in a dual-chamber molecular-beam-epitaxy (MBE) system equipped with the RHEED, XPS, and STM apparatuses. Nondoped and Zn-doped ($P\approx1\sim4\times10^{19}\,\mathrm{cm}^{-3}$) on-axis GaAs(111)*A* substrates were employed for this study. A detailed description of the surface cleaning treatments for GaAs(111)*A* substrates used in this study has been given elsewhere.[12] After the growth of a few hundred layers of GaAs, the surface showed a sharp (2×2) RHEED pattern corresponding to a Ga-stabilized (2×2) surface.[13] The sample was then transferred via ultrahigh-vacuum transfer modules to another MBE chamber for the Se adsorption. The sample was exposed to a Se beam with a beam-equivalent pressure of 1.0×10^{-7} Torr at temperatures ranging from 250 to 450 °C.

RHEED-rocking curves were measured along the $[10\bar{1}]$ direction with an electron energy of 12 keV. Intensities of the five spots on the zeroth Laue zone, (0 0), ($0\ \pm\frac{1}{2}$), and ($0\ \pm1$), measured by a charge-coupled device camera with a microcomputer system, were used in a structure analysis.

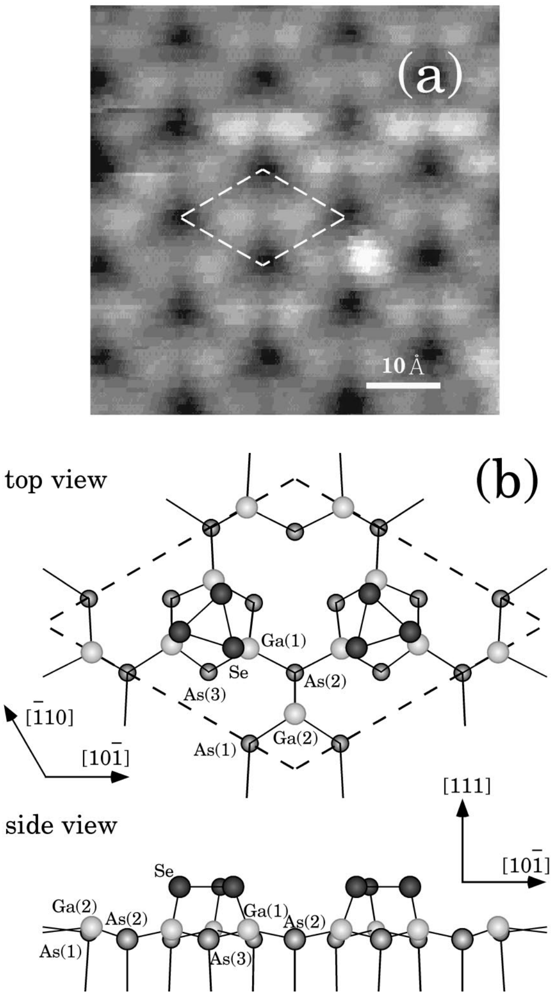

FIG. 1. GaAs(111)A-$(2\sqrt{3}\times2\sqrt{3})$-$R30°$-Se surface reconstruction. (a) A filled state STM image (60×60 Å^2) taken with a tunneling current of 0.9 nA and a sample bias of -2.55 V; (b) the proposed structure model. The $(2\sqrt{3}\times2\sqrt{3})$-$R30°$ unit cell is outlined with dashed lines.

The glancing angle of the incident electron beam was changed by using the extended beam rocking facility (Staib, EK-35-R and k-Space, kSA400) with intervals of ~0.04°. STM observations were performed at room temperature in the constant-current mode with a tunneling current of 0.9 nA and a sample voltage of -2.55 V. XPS measurements were carried out by using monochromatic Al $K\alpha$ radiation (1486.6 eV). Photoelectrons were detected at varied emission angles in the range of 10° to 60° from the surface.

III. RESULTS AND DISCUSSION

When the GaAs(111)A-(2×2) surface was exposed to the Se beam at temperatures ranging from 400 to 450 °C, the RHEED pattern immediately changed to (1×1). With increasing exposure time, reflections corresponding to a $(2\sqrt{3}\times2\sqrt{3})$-$R30°$ structure emerged (~30 s) and were most clearly observed in the range of 40 to 50 s. After a 60-s exposure, the $(2\sqrt{3}\times2\sqrt{3})$ reflections gradually decreased in intensity and completely disappeared at ~120 s, leaving the (1×1) reflections alone. On the other hand, during the Se exposure at temperatures below 400 °C, the sharp $(2\sqrt{3}\times2\sqrt{3})$ RHEED patterns were never observed. Thus, for the following STM, XPS, and RHEED analysis, the $(2\sqrt{3}\times2\sqrt{3})$ surface was prepared by exposing the GaAs(111)A surface to the Se beam at 425 °C for 45 s.

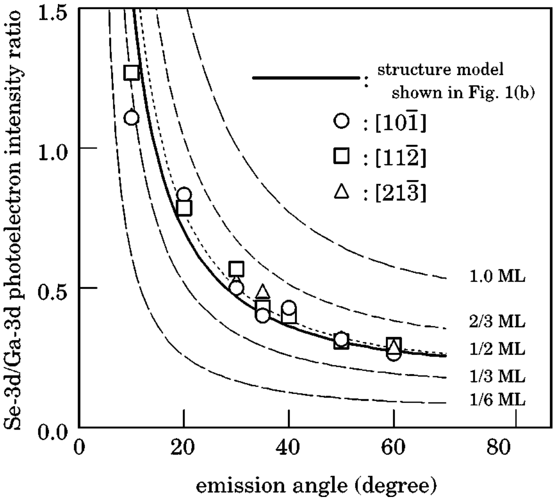

FIG. 2. Photoelectron intensity ratios of Se $3d$/Ga $3d$ plotted as a function of a photoelectron emission angle from the surface.

Figure 1(a) shows a typical filled state STM image of the GaAs(111)A-$(2\sqrt{3}\times2\sqrt{3})$-$R30°$-Se surface, where the unit cell is indicated by dashed white lines. In this image, hexagonal rings consisting of six protrusions are clearly resolved. The periodicity along the $[11\bar{2}]$ and equivalent directions is about 14 Å, being consistent with a $(2\sqrt{3}\times2\sqrt{3})$ reconstruction rotated by 30° with respect to the (1×1) surface unit cell. No (2×2) reconstructed areas corresponding to the cleaned GaAs(111)A surface were observed even in larger scale images. The peak-to-peak (black-to-white) corrugation was found to be ~2.0 Å, which is considerably larger than that (~0.1 Å) observed for the Ga-vacancy buckling structure of the GaAs(111)A-(2×2) surface.^{14} On the other hand, similar amplitude of corrugation has been observed for the As-trimer adatom structure of GaAs(111)B-(2×2).^{14} Thus, it is likely that the protrusion in Fig. 1(a) is responsible for an isolated adatom structure composed of some atoms. However, it remained unclear how many atoms each protrusion in the STM image consists of.

We have performed XPS measurements so as to estimate the coverage of Se on the $(2\sqrt{3}\times2\sqrt{3})$ surface. Figure 2 shows the photoelectron intensity ratio of Se $3d$/Ga $3d$ as a function of a photoelectron emission angle from the surface. The photoelectron intensities were measured by changing the detection angle along three directions of $[10\bar{1}]$, $[21\bar{3}]$, and $[11\bar{2}]$, in order to make sure that the photoelectron diffraction effects are negligible. Also shown in Fig. 2 are photoelectron intensity ratios calculated for various Se coverage as noted in the figure legend. In this calculation, which is based on an exponential adsorption law for electrons, numerical values for mean-free path of electrons and the cross section for Se $3d$ normalized to Ga $3d$ were taken to be 16 Å (Ref. 12) and 2.21,^{15} respectively. We assume that Se atoms are adsorbed at the on-top site of the bulk-terminated (unreconstructed) GaAs(111)A surface, the Se-Ga bond length being the same as the sum of covalent radii of the Se and Ga atoms (2.40 Å).^{16} A very good agreement between the measured

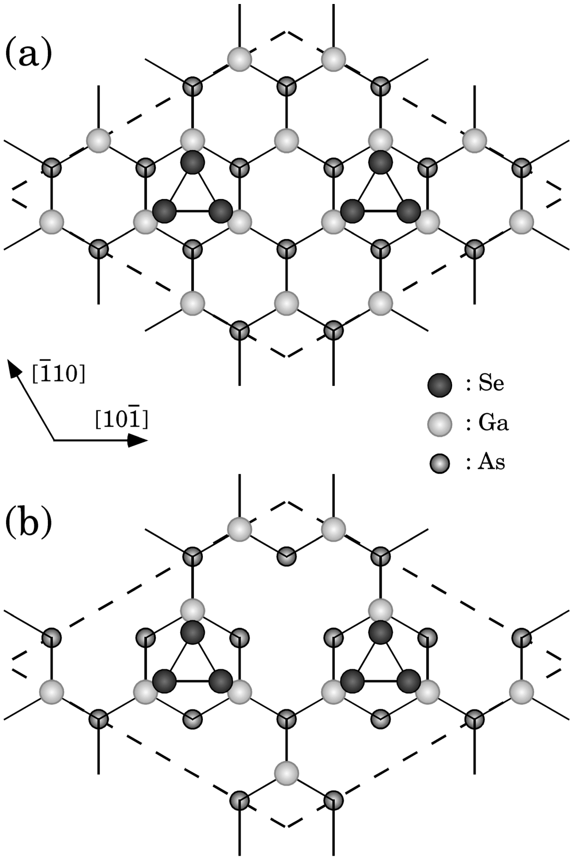

FIG. 3. Possible structure models for the GaAs(111)A-$(2\sqrt{3}\times2\sqrt{3})$-$R30°$-Se surface. (a) Trimer model; (b) trimer-vacancy model. In either model, the H_3 site has been assumed for the Se trimer.

and calculated intensity ratios is obtained at Se coverage of 0.5 monolayer (ML), which corresponds to six Se atoms per $(2\sqrt{3}\times2\sqrt{3})$ unit cell.[17] Here, 1 ML of Se is defined as 7.22×10^{14} atoms/cm^2, which is the site-number density of the unreconstructed GaAs(111)A surface. Since the unit cell of the $(2\sqrt{3}\times2\sqrt{3})$ surface has two protrusions in Fig. 1(a), we conclude that each protrusion consists of three Se atoms (a Se trimer).

Figure 3(a) shows a possible structure model for the $(2\sqrt{3}\times2\sqrt{3})$ surface, in which the Se trimer is located on the bulk-terminated (111)A surface. This model, however, does not satisfy electron counting requirements:[18] in addition to six partially filled dangling bonds of Ga atoms, the Se trimer would result in a $\frac{9}{4}$ electrons excess per trimer. Such an excess charge can be eliminated by removing three Ga atoms per unit cell [Fig. 3(b)]. The removal of three Ga atoms creates nine dangling bonds of As with a $\frac{5}{4}$ electron in the layer below, leaving three Ga dangling bonds ($3\times\frac{3}{4}=\frac{9}{4}$ electrons). Thus, charge transfer from Ga atoms ($\frac{9}{4}$ electrons) and Se trimers ($\frac{18}{4}$ electrons) to nine As atoms transforms the As- and Se-dangling bonds into fully occupied state and the Ga-dangling bonds into empty state. The resultant surface is electronically stabilized, not leaving any partially filled dangling bonds. We point out that the amount of the removed Ga atoms is the same as that of Ga vacancy for the Ga-vacancy buckling structure of the GaAs(111)A-(2×2) substrate.[13]

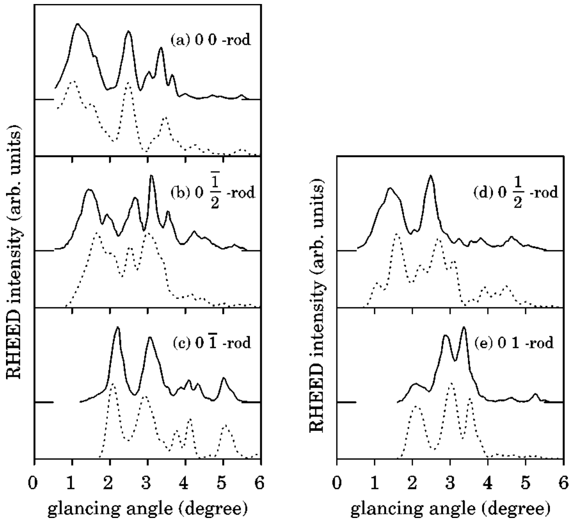

FIG. 4. Normalized experimental rocking curve (solid curve) of the (0 0), $(0\pm\frac{1}{2})$, and $(0\ \pm1)$ beams for the GaAs(111)A-$(2\sqrt{3}\times2\sqrt{3})$-$R30°$-Se surface. The dotted curves are calculated for the optimized structure model [Fig. 1(b)].

In order to determine the atomic coordinates of the proposed structure model [Fig. 3(b)], we performed RHEED analysis on the basis of the dynamical diffraction theory. In the present analysis, we assume that the surface relaxation extends no further than the first As layer. RHEED intensities were calculated by the multislice method proposed by Ichimiya.[19] In this calculation, 17 beams on the zeroth Laue zone with the incident electron beam along the $[10\bar{1}]$ direction were used: (0 0), $(0\ \pm\frac{1}{2}),\ldots,$ $(0\ \pm\frac{7}{2})$, and $(0\ \pm4)$. The Fourier components of the potential for elastic scattering was derived from the electron scattering factors for Ga, As, and Se tabulated by Doyle and Tuner.[20] We include a correction to the Fourier component of the potential so that the mean-inner potential is consistent with the value estimated from the present experiment, i.e., -13.6 eV. The imaginary part of the crystal potential for inelastic scattering is assumed to be 10% of its real part. The thickness of a slice, in which scattering potential was approximated to be constant toward the surface normal direction, was about 0.1 Å. In order to quantify the agreement between the calculated rocking curves and the experimental ones, the R factor defined as

$$R=\frac{1}{N}\sum_{g}\frac{\int[I_{go}(\theta)-c_gI_{gc}(\theta)]^2d\theta}{\int[I_{go}(\theta)]^2d\theta},\quad c_g=\frac{\int I_{go}(\theta)d\theta}{\int I_{gc}(\theta)d\theta}$$

was used.[21] Here, I_{go} and I_{gc} are the observed and the calculated intensities of beam g as a function of glancing angle θ, respectively, and N is the number of analyzed beams. The calculated rocking curves were convoluted with a Gaussian that has a full width at half maximum of 0.1°, corresponding to the experimental resolution.

Figures 4(a)–4(e) show the RHEED rocking curves measured from the GaAs(111)A-$(2\sqrt{3}\times2\sqrt{3})$-$R30°$ -Se surface, together with the calculated ones from the optimized structure model [Fig. 1(b)], in which the Se trimer is located at a hollow (H_3) site. The R factor of this structure is $R_{\min}=0.156$, showing a good agreement between the measured

TABLE I. The atomic coordinates for the optimized structure model for GaAs(111)A-($2\sqrt{3}\times2\sqrt{3}$)-$R30°$-Se. The atomic coordinates x and y are given as fractions of unit cell along the $[10\bar{1}]$ and $[\bar{1}10]$ directions in Fig. 1(b). The z coordinate refers to the [111] direction with magnitude equal to the bulk bilayer spacing of ~0.816 Å, the origin of which is at the outermost Ga layer of the bulk-terminated GaAs(111)A surface.

	Ideal			Reconstructed		
Atom	x	y	z	x	y	z
Se				0.103±0.03	1.677±0.03	2.081±0.08
Ga(1)	0.333	1.667	0.000	0.278±0.04	1.667±0.06	−0.270±0.06
Ga(2)	0.333	0.667	0.000	0.383±0.03	0.767±0.06	−0.417±0.18
As(1)	−0.333	0.333	−1.000	−0.358±0.04	0.358±0.04	−0.596±0.21
As(2)	0.667	1.333	−1.000	0.672±0.04	1.343±0.08	−0.988±0.10
As(3)	−0.333	1.333	−1.000	−0.358±0.06	1.343±0.06	−0.975±0.22

and the calculated rocking curves. On the other hand, a fourfold atop (T_4) site trimer model gives a large R factor of ~0.32, even after the structure optimization.

The structure parameters of the optimized structure [Fig. 1(b)] are listed in Table I with errors evaluated from the half width of the range where the R factor is smaller than $1.1\times R_{\mathrm{min}}$.[21] As can be seen in Fig. 2, the photoelectron intensity ratio calculated for these structure parameters (solid curve) agrees well with the experimental results. The Se-Se bond length in the trimer is 2.68 Å and is larger than that in bulk Se (about 2.32 Å).[22] On the other hand, we find that the Se-Ga bond length (2.05 Å) is significantly smaller than the sum of the atomic covalent radii (Se: 1.14 Å, Ga: 1.22 Å).[16] These results suggest that the Se-Se and Se-Ga bonds deviate to some extent from the covalent sp^3 character in the trimer configuration. Since the value of the Pauling electronegativity of Se (2.4) is larger than those of Ga (1.6) and As (2.0),[23] it appears likely that the Se-Se bond contains excess electrons, which weaken and expand the bond by occupying an antibonding state. This seems to be consistent with the experimental fact that the ($2\sqrt{3}\times2\sqrt{3}$) reconstruction is unstable against the formation of the (1×1) structure with increasing Se coverage, as mentioned earlier.

Another noteworthy finding is that all Ga atoms at the first Ga layer recede towards the bulk. In particular, Ga(2) atoms are displaced downward by a larger amount of 0.34 Å to form sp^2-type bonding configuration with their As nearest neighbors. This means that the dangling bond of Ga(2) becomes p_z-type empty state by transferring the charge from Ga to As, as we have expected. Indeed, As(3) atoms are pushed sideways, producing p^3-type bonds instead of sp^3 type, although these atoms are displaced towards the Ga-vacancy site. This is probably due to a larger displacement of Ga(2) than that of As(1): since Ga(1) atoms beneath the Se atoms laterally move towards the center of the Se trimer, As(2) and Ga(2) are also displaced so as to maintain their bond lengths.

IV. CONCLUSIONS

In conclusion, we have determined the structure model for the GaAs(111)A-($2\sqrt{3}\times2\sqrt{3}$)-$R30°$-Se surface using RHEED, XPS, and STM. The proposed model consists of two Se trimers and three surface-Ga vacancies per unit cell: the trimer has a Se-Se bond length of 2.68 Å and is adsorbed at the H_3 site of the vertically compressed GaAs surface bilayer.

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