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Structure of the sulfur-passivated GaAs(001) surface

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The adsorption position of sulfur atoms in the sulfur-passivated GaAs(001) surface is investigated by soft-x-ray standing-wave triangulation using two types of noncentrosymmetric $(1\bar{1}1)$ and (111) diffraction planes inclined by 54° to the (001) surface. The sulfur atoms are at the bridge site on the Ga-terminated GaAs(001) surface, forming bonds with the underlying Ga atoms. The sulfur atomic layer is approximately 1.1 Å above the underlying Ga atomic layer. The existence of symmetric sulfur-sulfur dimers lining up in the $[1\bar{1}0]$ direction is not confirmed for the 2×1 reconstructed S/GaAs(001) surface.

The development of GaAs electronic devices has been hindered by difficulties in reducing the surface-state density and controlling the Fermi-level position. Since the Na_2S chemical treatment was reported by Sandroff *et al.*,[1] a number of other attempts to passivate GaAs surfaces by using sulfide treatments[2–9] have been made. One promising technique is the $(NH_4)_2S_x$ treatment reported by Nannichi *et al.*:[5] a GaAs wafer is dipped into an $(NH_4)_2S_x$ solution that removes the natural oxides, etches the GaAs, and covers the surface with sulfur atoms. The wafer is then put into a vacuum chamber, where most of the amorphous sulfur is released by sublimation, leaving the surface covered with very thin layers of sulfur atoms. According to photoemission spectroscopy studies,[10,11] while there are both S-Ga and S-As bonds on the as-treated surface, the S-As bonds disappear, and the reflection high-energy-electron-diffraction (RHEED) pattern changes to 2×1 for S/GaAs(001) after annealing above 250 °C in a vacuum.[5,7,11] Furthermore, Ohno[12] calculated total energies for four possible adsorption sites, such as the bridge, on-top, hollow, and antibridge sites, on the Ga-terminated GaAs (001) surface, and concluded that sulfur atoms are at the bridge position and are twofold coordinated. On the other hand, Lu and co-workers[13,14] reported that the x-ray absorption near-edge structure and x-ray photoelectron diffraction results of a 1×1-S/GaAs(001) surface, which was obtained by dipping a GaAs wafer in an $(NH_4)_2S$ solution and then rinsing with water, are consistent with the theoretical prediction. Quantitative evaluations of the position of sulfur atoms on a sulfur-passivated GaAs(001) surface, however, have not been done. Furthermore, the atomic configuration of the 2×1 reconstructed S/GaAs(001) surface, obtained by annealing in a vacuum after being dipped in an $(NH_4)_2S_x$ solution, has not yet been studied.

The x-ray standing-wave (XSW) technique is capable of locating the position of particular atomic species at a crystal surface.[15] In the XSW analysis of adsorbates on III-V compound semiconductor surfaces, we can distinguish between the group-III atomic site and the group-V atomic site by using noncentrosymmetric (111) reflection.[16] On the other hand, in order to investigate the position of light-element atoms, the XSW experiment should be performed by using soft x rays. This is because the large cross sections of soft x rays for light-element atoms ensure high emission intensity of the monolayer-order light-element atoms. For analyzing the structure of the S/GaAs system, the (111) back reflection soft-x-ray standing-wave experiment by scanning the photon energy is not suitable. This is because the 1.9-keV photon energy for the normal-incidence GaAs(111) reflection is lower than the energy of the sulfur K absorption edge (2.47 keV) and those photons cannot excite the sulfur $K\alpha$ fluorescent x rays (2.307 keV). Therefore, the angle-scan soft-x-ray standing-wave technique is used for structure analysis of the S/GaAs system,[17–21] and is also very effective for analyzing the structure of buried interfaces such as those in metal/S/GaAs and insulator/S/GaAs systems.[18–20] Recently, we proposed and confirmed the validity of using soft-x-ray standing waves to determine the three-dimensional structure of S/GaAs(111)*A* and (111)*B* surfaces.[21] However, it is difficult to use this technique for structure analysis of sulfur-passivated GaAs(001) surface. Symmetric reflections of the GaAs(001) substrate, such as (002) and (004), are difficult to be used in the soft-XSW analysis, because the (002) reflection is too weak [the structure factor of GaAs(002) reflection is very small] and the (004) reflection cannot be obtained by soft x rays of about 2.5 keV which is just above the sulfur K absorption edge. Although the (004) reflection XSW experiment may be possible by using the brilliant undulator hard x rays of more than 4.4 keV, which has smaller cross section for sulfur 1*s*, for the sulfur-passivated GaAs(001) system, the centrosymmetric (004) XSW results cannot distinguish the group-III atomic position from the group-V atomic position. Noncentrosymmetric reflections, such as (111) and (113), should be used to determine the atomic site of the adsorbate on the III-V compound semiconductor in the XSW analysis. In this study, we use two different types of asymmetric (111) and $(1\bar{1}1)$ reflections of a GaAs(001) substrate to determine the structure of the sulfur-passivated GaAs(001) surface. This technique can be applied to surface structure analysis of adsorbates on a III-V compound semiconductor (001) substrate.

An *n*-type GaAs(001) wafer was dipped into an $(NH_4)_2S_x$ solution for 1 h at 60 °C. It was then annealed in a vacuum for 10 min at about 500 °C. The 1×1 RHEED pattern of the sample at room temperature changed to 2×1 with the annealing.[11] After cooling down to room temperature, it was transferred to an

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analysis chamber without being exposed to air.

The soft-x-ray standing-wave experiments were carried out at the NTT beamline 1*A* of the Photon Factory at the National Laboratory for High Energy Physics.[22] We developed an ultrahigh-vacuum three-axis goniometer system to perform the angle-scan soft-x-ray standing-wave experiment. For the GaAs(001) substrate, both the $(1\bar{1}1)$ and (111) diffraction planes were inclined about 54° to the (001) surface. In order to determine the three-dimensional position of the sulfur atoms by angle-scan soft-x-ray standing-wave triangulation using noncentrosymmetric $(1\bar{1}1)$ and (111) diffraction planes, the (111) experiment can be setup by rotating the ϕ axis 90° after the $(1\bar{1}1)$ reflection experiment. Therefore, these two types of reflection experiments can be performed using the same arrangement (Fig. 1). Sulfur Kα fluorescent x rays were collected by a highly pure Si detector with a 50-μm-thick Be window. When a fluorescent x-ray detector is located at a glancing angle with respect to the sample surface, the detector's dead time caused by substrate fluorescent x ray signals can be eliminated. In the experimental arrangement shown in Fig. 1, however, the detector in the polarized direction is not located at a glancing angle with respect to the sample surface. Figure 2 shows fluorescent x-ray spectra collected by the highly pure Si detector with and without the Be window. Without the Be window, fluorescent x rays of substrate elements such as Ga L and As L are very strong. In this case, therefore, the detector's dead time cannot be suppressed if the detector is not located far away from the sample. In contrast, by using a 50-μm-thick Be window, the background of the fluorescent x-ray spectra can be eliminated and weak sulfur signals can be collected more precisely.[23] The signal intensity (about 20 counts/sec at off Bragg condition) and the signal-to-background ratio are high enough to be quantitatively analyzed.

The angular dependent fluorescent x-ray yield, $Y(\theta)$, is given by

$$Y(\theta)=1+R(\theta)+2F\sqrt{R(\theta)}\cos[2\pi P-\delta(\theta)]\ , \qquad (1)$$

where $R(\theta)$ is the intrinsic reflectivity and $\delta(\theta)$ the phase between the two plane waves which form the interference field. Here, $R(\theta)$ and $\delta(\theta)$ can be computed as a function of incident angle θ for GaAs(111) reflection. We used the anomalous atomic scattering factors reported by Henke *et al.*[24] and the room-temperature Debye-Waller factors of the Ga and As atoms calculated from $B=0.91$ Å^2.[25,26] The theoretical intrinsic curves were convoluted by the instrumental resolution.[21] The two parameters *P* and *F* in Eq. (1), which are determined in the XSW analysis, are called the coherent position and the coherent fraction, respectively. These parameters contain structural information on target atoms. The coherent position *P* gives the position of the target atoms with respect to the specific bulk-extrapolated reflection planes. In our case, the coherent position *P* is defined as the normal distance in units of the GaAs(111) *d* spacing from the (111) net planes, which lie at the midpoint of the Ga-As double layers.[16] The coherent fraction *F* includes both the Debye-Waller factor and the fraction of the atoms at the actual lattice sites defined by the coherent position *P*. In other words, the coherent fraction *F* acts as a measure of the degree of ordering. Sometimes, multiple position systems can be studied by analyzing the coherent fraction *F*.

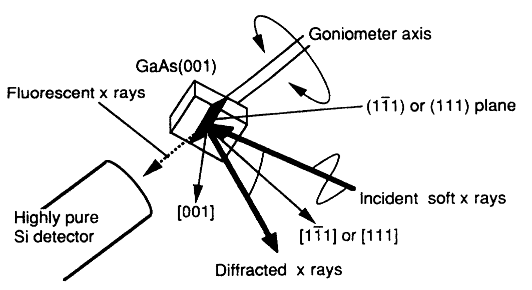

FIG. 1. The arrangement of the $(1\bar{1}1)$ and (111) reflection in the angle-scan mode soft-x-ray-standing-wave experiment for sulfur-passivated GaAs (001). A highly pure Si detector is in the polarized direction of the incident soft x rays.

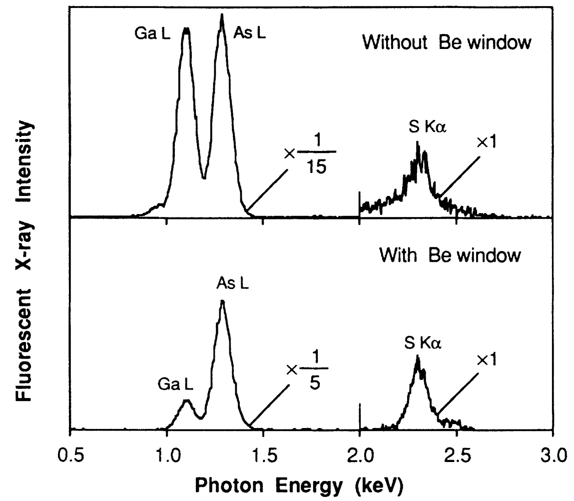

FIG. 2. Sulfur-passivated GaAs(001) fluorescent x-ray spectra collected by the highly pure Si detector. Fluorescent x rays were excited by 2.47-keV photons.

Figure 3 shows two types of soft-x-ray standing-wave results for the 2×1 reconstructed S/GaAs(001) surface. The coherent position *P* and the coherent fraction *F* are determined from least-square fits to the theoretical

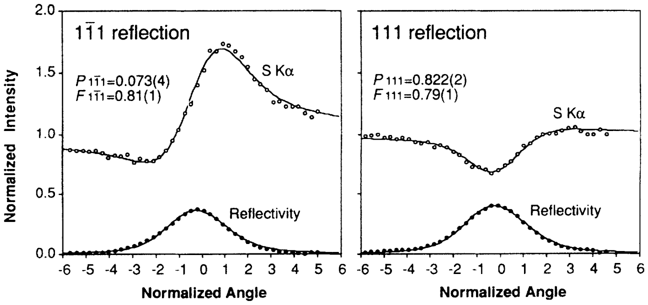

FIG. 3. Soft-x-ray standing-wave results of two types of experiments: (a) $(1\bar{1}1)$ and (b) (111) reflection. The horizontal axis is the normalized angle. The solid circles are the rocking-curve data points. The open circles are the sulfur Kα fluorescent x-ray yield data points. Curves are theoretical fits to the data.

profiles convoluted by the instrumental resolution. The $(1\bar{1}1)$ results yielded a $P_{1\bar{1}1}$ of 0.073(4) and an $F_{1\bar{1}1}$ of 0.81(1), whereas the (111) results yielded a P_{111} of 0.822(2) and an F_{111} of 0.79(1). Figure 4 shows possible adsorption sites, such as the bridge, on-top, hollow, and antibridge sites, with respect to the Ga-terminated GaAs(001) surface. Considering the crystal symmetry of this system, the $P_{1\bar{1}1}$ and P_{111} should be equal to the $P_{\bar{1}11}$ and $P_{\bar{1}\bar{1}1}$, respectively. Therefore the position of sulfur atoms projected in the (110) plane (side view 1 in Fig. 4) can be obtained only from $P_{1\bar{1}1}$, and the position of sulfur atoms projected in the $(1\bar{1}0)$ plane (side view 2 in Fig. 4) can be obtained only from P_{111}. According to the obtained coherent positions, $P_{1\bar{1}1}$ of 0.073(4) and P_{111} of 0.822(2), an antibridge site (AA' and A') and a bridge site (B and B') are possible. Without any assumptions, these two positions can not be distinguished only by these P values, because the difference between these sites is just one unit. However, because the distance between sulfur atoms at the antibridge site AA' and second layer Ga atoms becomes too great to form S-Ga bonds at the surface, only the bridge site BB' can be considered in the following discussion. This simple 1×1 bridge configuration also agrees with the most stable model derived from the total energy calculation.[12] The surface normal distance, $\mathcal{D}_{\text{S-Ga}}$, between the position of sulfur atoms at the bridge site and the position of the underlying Ga atoms, can be determined from either $P_{1\bar{1}1}$ or P_{111} and is given by

$$\mathcal{D}_{\text{S-Ga}}=d_{111}\sqrt{3}(P_{111}-\tfrac{5}{8})=d_{111}\sqrt{3}(P_{1\bar{1}1}+\tfrac{1}{8})\ , \qquad (2)$$

where d_{111} is the d spacing of the GaAs(111) net plane (3.264 Å). The distance can be independently obtained by using P_{111} or $P_{1\bar{1}1}$. $\mathcal{D}_{\text{S-Ga}}$ determined from $P_{1\bar{1}1}$ and P_{111} are 1.12(2) Å and 1.11 Å, respectively. This good agreement indicates that these two soft XSW results are consistent. The S-Ga bond length is about 2.3 Å, which is very close to the 2.27 Å derived from the total-energy calculation[12] and the 2.33 Å in a GaS bulk crystal.[27]

The surface has a 2×1 reconstruction according to the RHEED pattern. One possible origin of this reconstruction is the symmetric sulfur-sulfur dimers lining up in the $[1\bar{1}0]$ direction. This dimer model is also supported by a theoretical calculation: reducing the sulfur-sulfur bond length of 16% (0.64 Å) minimizes the total energy.[12] Here, $F_{1\bar{1}1}$ gives a one-dimensional distribution of sulfur atoms in the $[1\bar{1}1]$ direction (side view 1 of Fig. 4) that depends on the dimer formation. On the other hand, F_{111} gives a distribution in the [111] direction (side view 2 of Fig. 4) that is independent of the dimer formation. If all the sulfur atoms on the surface formed such sulfur-sulfur dimers, the ideal value of $F_{1\bar{1}1}/F_{111}$ would be 0.88. However, the experimental values of $F_{1\bar{1}1}$ and F_{111} are almost the same, and thus a significant difference cannot be recognized. Therefore, even if there are dimerized sulfur atoms on the surface, they are only a small amount of the total sulfur atoms and are formed only on the local area of the surface.[28] The lack of significant difference between the experimental values of F_{111} and $F_{1\bar{1}1}$ indicates that sulfur atoms seem to be isotropically distributed. About 0.8 of the F_{111} and $F_{1\bar{1}1}$ values, which is less than unity, may be caused by the thermal vibration of each sulfur atom and the existence of excess sulfur atoms in the substitutional As site.

In conclusion, a three-dimensional adsorption site of sulfur atoms on the GaAs(001) surface was studied by the soft-x-ray standing-wave analysis of two different types of asymmetric (111) and $(1\bar{1}1)$ reflections. The sulfur atoms were at the bridge site, forming bonds with the two underlying Ga atoms. The first-layer sulfur atomic plane is

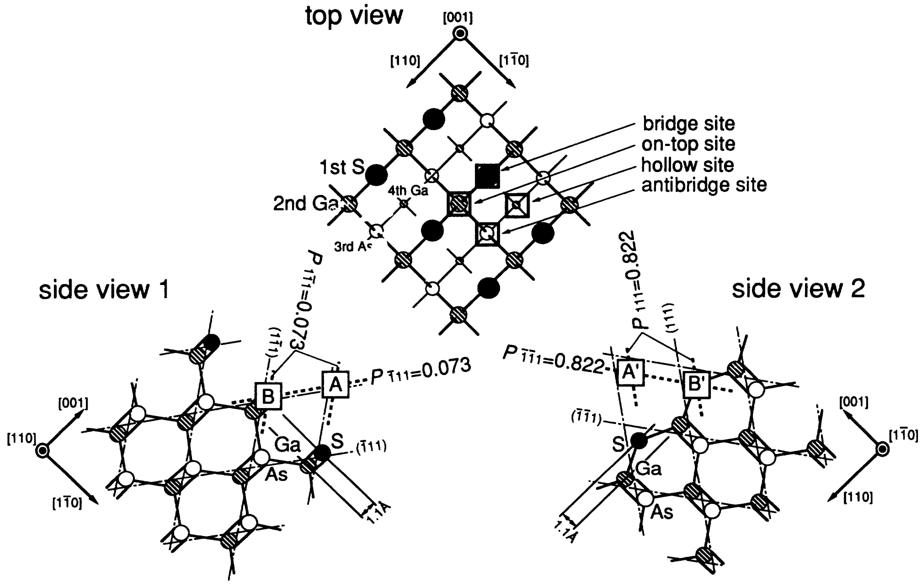

FIG. 4. Schematic top view and side views showing the position of the sulfur atoms with respect to the GaAs(001) substrate. Possible adsorption sites (squares) are referred to as the bridge site, on-top site, hollow site, and antibridge site. The position of sulfur atoms (solid circles) on the Ga-termined GaAs(001) surface is the bridge site defined as B and B' in the side views.

approximately 1.1 Å above the second-layer Ga atomic plane and the S-Ga bond length is about 2.3 Å. On the other hand, the existence of the symmetric sulfur-sulfur dimers lining up in the $[1\bar{1}0]$ direction was not confirmed by the experimental values of the coherent fractions.

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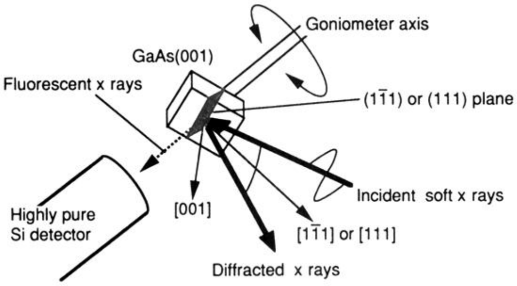

FIG. 1. The arrangement of the (1$\bar{1}$1) and (111) reflection in the angle-scan mode soft-x-ray-standing-wave experiment for sulfur-passivated GaAs (001). A highly pure Si detector is in the polarized direction of the incident soft x rays.