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Chemical-state-resolved x-ray standing-wave analysis using chemical shift in photoelectron spectra

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A chemical-state-resolved x-ray standing-wave analysis using the chemical shift in photoelectron spectra was performed for a GaAs(001) surface treated with a $(NH_4)_2S_x$ solution. The sulfur atoms in the S-Ga chemical state on the surface are at the bridge site but are not highly ordered. The degree of ordering of the sulfur atoms in the S-Ga chemical state is improved, and randomly distributed sulfur atoms in the S-As and S-S chemical states disappear as a result of post annealing.

Structural analysis of same-element atoms in multiple chemical states near a surface can provide greater insight into chemical and physical phenomena at the surface. As a chemical-state-resolved surface-structure-analysis technique, chemical-shift photoelectron diffraction and holography by surface core-level photoemission have only been demonstrated for the reconstructed clean surface[1] and for the molecule adsorbed surface.[2]

The x-ray standing-wave (XSW) technique is capable of locating the position of particular atomic species at a crystal surface or interface.[3] With an incident beam of soft x rays, the technique is suitable for investigating the position of light-element atoms. Therefore, we have performed such an analysis by collecting fluorescent x rays as secondary emissions for structure analysis of the S/GaAs system.[4–6] We recently demonstrated the near-edge x-ray standing-wave (NEXSW) technique as a chemical-state-resolved surface- and interface-structure-analysis technique.[5] This was an extension of the soft XSW technique that used the chemical sensitivity of the fluorescent x-ray yield near the absorption edge of a target element. The advantage of the NEXSW technique is that the positional information of specific chemical-state atoms buried under the overlayer can be obtained by the detection of fluorescent x rays that have a long escape length. However, a slight difference in chemical states cannot be resolved by this technique.

Collection of Auger electrons or photoelectrons, which are surface sensitive, has already been accomplished with this technique.[7–11] Woicik *et al.* reported that surface reconstructed atoms can be discriminated from bulk atoms by collecting low-energy highly surface-sensitive Auger peaks in XSW analysis.[9] On the other hand, collecting photoelectrons in XSW experiments is also considered to be advantageous because of the chemical sensitivity. However, we are unaware of chemical shifts in core-level photoelectrons previously being used to discriminate for a specific chemical state in XSW analysis. We report here a chemical-state-resolved structure-analysis technique that combines x-ray photoelectron spectroscopy and XSW. This photoelectron-spectroscopy x-ray standing-wave (PSXSW) technique allows us to investigate the distribution of a specific chemical state of a given element adsorbed on a crystal surface.

The development of electronic GaAs devices has been hindered by difficulties in reducing the surface-state density and controlling the Fermi-level position. One promising technique to passivate the GaAs surface is the $(NH_4)_2S_x$ treatment reported by Nannichi *et al.*:[12] a GaAs wafer is dipped into an $(NH_4)_2S_x$ solution that removes the natural oxide, 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. Photoemission spectroscopy studies[13] showed S-Ga, S-As, and S-S bonds on the $(NH_4)_2S_x$-treated GaAs surface. The S-As and S-S bonds disappeared after annealing above 250 °C in vacuum, changing the reflection high-energy electron-diffraction pattern to 2×1 for the S/GaAs(001) surface. The atomic configuration of the 2×1 reconstructed surface, which was obtained by annealing in a vacuum after being dipped in an $(NH_4)_2S_x$ solution, has already been investigated by soft XSW.[6] However, we are unaware of any quantitative structural investigation of the $(NH_4)_2S_x$-treated GaAs(001) surface before annealing. This is because an average structure can only be obtained with the usual structure-analysis technique for such multiple-chemical-state systems. It should be noted that sulfur atoms in the S-As and S-S chemical states do not disappear without any thermal treatment for this $(NH_4)_2S_x$-treated GaAs(001) surface. This indicates that chemical-state-resolved structure analysis is required to investigate the ordering degree and positional information of sulfur atoms in S-Ga chemical state for this surface. Therefore, the first PSXSW investigation was performed for the $(NH_4)_2S_x$-treated GaAs(001) surface structure, and the feasibility of this technique was demonstrated.

An *n*-type GaAs(001) wafer was dipped into an $(NH_4)_2S_x$ solution for 1 h at 60 °C. It was then placed in an ultrahigh vacuum chamber for 5 days to release most of the amorphous sulfur by sublimation. This left a surface covered with very thin layers of sulfur atoms. The PSXSW experiments were carried out at NTT beamline 1A of the Photon Factory at the National Laboratory for High Energy Physics[14] using an ultrahigh vacuum three-axis goniometer system. Both the $(1\bar{1}1)$ and (111) diffraction planes of (001) substrate were inclined about 54° to the (001) surface. To determine the three-dimensional position of the sulfur atoms,

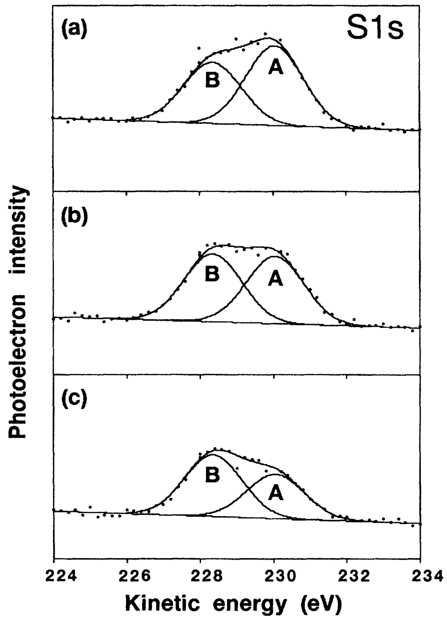

FIG. 1. Sulfur 1*s* photoelectron spectra excited by 2.7-keV soft x rays near the (1$\bar{1}$1) Bragg condition shown as (a), (b), (c) in Fig. 2.

noncentrosymmetric (1$\bar{1}$1) and (111) reflection experiments were performed. The (111) reflection experiment can be set up by rotating the ϕ axis 90° after the (1$\bar{1}$1) reflection experiment.[6] Sulfur 1*s* photoelectrons excited by soft x rays of 2.7 keV were collected with the electron energy analyzer.

In our XSW analysis, the anomalous atomic scattering factors reported by Henke *et al.*[15] and the room-temperature Debye-Waller factors for the Ga and As atoms calculated from $B = 0.91$ Å^2 (Ref.16) are used. The theoretical intrinsic curves were convoluted by the instrumental resolution.[6] Two parameters *P* and *F*, which are determined in the XSW analysis, are called the coherent position and the coherent fraction, respectively. *P* gives the position of the target atoms with respect to the specific bulk-extrapolated reflection planes. In our case, *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. *F* generally includes both the Debye-Waller factor and the fraction of the atoms at the actual lattice sites defined by *P*.

Figure 1 shows the sulfur 1*s* photoelectron spectra excited by 2.7-keV incident soft x rays under various conditions around the (1$\bar{1}$1) Bragg condition. Strictly speaking, these spectra should be separated into three components: S-Ga, S-As, and S-S.[17] However, the difference between the S-As and S-S chemical components is smaller than the resolution of the incident beam and they are hard to separate quantitatively. Therefore, we separated the spectra into only two chemical components: peak *A* (S-Ga chemical component) and peak *B* (S-As and S-S chemical components). In the peak separation, a Gaussian function whose full width at half maximum of 1.85 eV was used for both peaks, and the chemical shift between peaks *A* and *B* was fixed at 1.70 eV. As shown in Fig. 1, the angular-dependent changes of the photoelectron intensity seem to be different between peaks *A* and *B*. The PSXSW results of peak *A* (S-Ga chemical state component) and peak *B* (S-As and S-S chemical state component) are shown in Fig. 2. The scattering of the data points was mainly caused by errors in the peak separation.

P and *F* of peak *A* and *B* were determined from least-square fits to the theoretical profiles. The (1$\bar{1}$1) and (111) results for peaks *A* and *B* are listed in Table I, together with the previous results for an annealed sample.[6] The *P* and *F* values are quite different between peaks *A* and *B*. It should be noted that those for peak *A* + *B*, which are the same as the conventional soft-XSW results, are also different from those for both peaks *A* and *B*. The *F* values for peak *A* indicate that the sulfur atoms in the S-Ga chemical state order, though the values are slightly smaller than those after annealing. Furthermore, the *P* values of peak *A* are close to those of the annealed sample. On the other hand, the *F* values for peak *B* of almost 0 indicate a random distribution of sulfur atoms in S-As and S-S chemical states. The *P* values for peak *B* were not identified and have no meaning because the *F* values were 0. Therefore, analytical error bars of *P* values for peak *B* were very large. This random distribution explains why the *P* values of peak *A* are close to those of peak *A* + *B*, while the *F* values of peak *A* + *B* are less than half those of peak *A*. The random distribution of sulfur atoms in S-As and S-S chemical state suggests that they may form a cluster on the surface.

The total-energy calculation of Ohno[18] revealed that the most stable site is a bridge site and the second most stable site is an on-top site. Figure 3 shows the bridge site and the on-top site with respect to the Ga-terminated GaAs(001) sur-

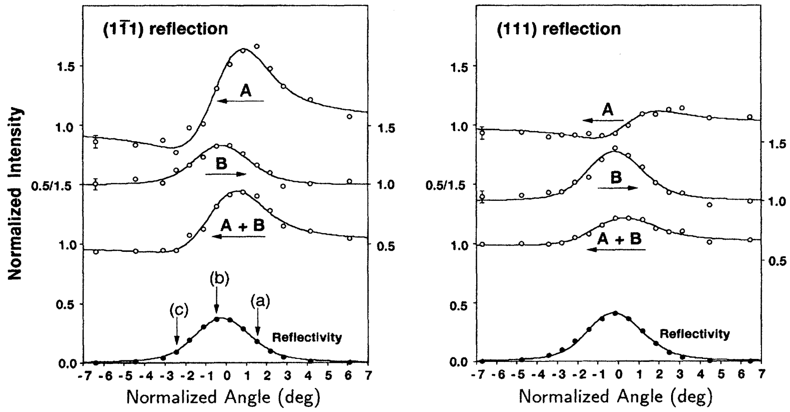

FIG. 2. PSXSW results of (1$\bar{1}$1) and (111) reflections. The solid circles are the rocking-curve data points, and the open circles are the sulfur 1*s* photoelectron intensities of different chemical states. Typical error bars are indicated for the left side data points. Curves are theoretical fits to the data. (a), (b), (c) in the left figure correspond to the angular positions where photoelectron spectra in Fig. 1 were obtained.

TABLE I. Coherent position P and coherent fraction F for $(NH_4)_2S_x$-treated GaAs(001) before and after annealing.

	Before annealing (this study)			After annealing (Ref. 6)
	Peak A	Peak B	$A+B$	Fluorescent x-ray yield
$P_{1\bar{1}1}$	0.06±0.01	0.8±0.1	0.05±0.01	0.073±0.004
P_{111}	0.85±0.01	0.1±0.4	0.85±0.01	0.822±0.002
$F_{1\bar{1}1}$	0.70±0.05	0.04±0.03	0.34±0.02	0.81±0.01
F_{111}	0.56±0.02	0.01±0.03	0.26±0.01	0.79±0.01

face. Considering the crystal symmetry of this system, $P_{1\bar{1}1}$ and P_{111} should be equal to $P_{\bar{1}11}$ and $P_{\bar{1}\bar{1}1}$, respectively. Therefore, the position of the sulfur atoms projected in the (110) plane (side view 1) 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) can be obtained from P_{111}. The S-Ga bond length obtained by the total-energy calculation is 2.27 Å for the bridge site and 2.03 Å for the on-top site.[18] In these models, the coherent positions for the bridge site $P_{1\bar{1}1_B}$ and P_{111_B} are 0.065 and 0.815, respectively, and those for the on-top site $P_{1\bar{1}1_O}$ and P_{111_O} are 0.484 and 0.234, respectively. The experimental F and P values for peak A suggest that the sulfur atoms in the S-Ga chemical state occupy the bridge site due to the $(NH_4)_2S_x$ solution treatment while they are not highly ordered. The PSXSW can be used for assigning the chemical-shifted peaks in the core-level spectra, so the origin of the chemical shifts can be determined definitely. It is verified that peak A in the sulfur 1s core-level spectra originated from the S-Ga chemical state.

It is found that there is a significant difference between the $F_{1\bar{1}1}$ of 0.70 and the F_{111} of 0.56 for peak A. This difference may be explained by either the coexistence of multiple sites of sulfur atoms (the bridge site and the on-top site) or the anisotropical distribution of disordered sulfur atoms. Although there should be chemical shift between sulfur atoms in the bridge site and those in the on-top site, the difference might be too small to separate the peak A into different chemical components. Therefore, in order to judge the coexistence of the multiple sites or the anisotropical distribution of disordered sulfur atoms, F and P values for the coexistence of the multiple sites should be estimated by using Ohno's models. The F_{111}, which gives a distribution in the [111] direction (side view 2), is more strongly affected by the difference between these two sites than the $F_{1\bar{1}1}$, which gives a one-dimensional distribution of sulfur atoms in the $[1\bar{1}1]$ direction (side view 1). If there are several atomic positions, the resulting coherent fraction F and coherent position P are given by the following equation:[19]

$$F\exp(2\pi Pi)=\sum_j \{r_jF_j\exp(2\pi P_ji)\}, \tag{1}$$

with $\Sigma_j r_j=1$, where r_j is the probability of the jth atomic site, F_j the discriminated coherent fraction ranging between 0 and 1, and P_j the discriminated coherent position. The discriminated coherent fractions for both the bridge site and the on-top site might be assumed to be about 0.8 as obtained for ordered sulfur at the bridge site.[7] If the probability of the bridge site r_B and that of the on-top site r_O are assumed to be 0.8 and 0.2, respectively, the $F_{1\bar{1}1}$ and F_{111} calculated by using Eq. (1) are 0.73 and 0.58, respectively, and the $P_{1\bar{1}1}$ and P_{111} calculated by using Eq. (1) are 0.096 and 0.776, respectively. Although these F values agree well with the experimental F values, these P values do not agree well with the experimental P values. This suggests that the amount of unstable on-top sulfur atoms should be less than 20%. Therefore, most sulfur atoms in the S-Ga chemical state occupy the bridge site while they are not highly ordered, and this anisotropical disordering is improved by the thermal treatment.

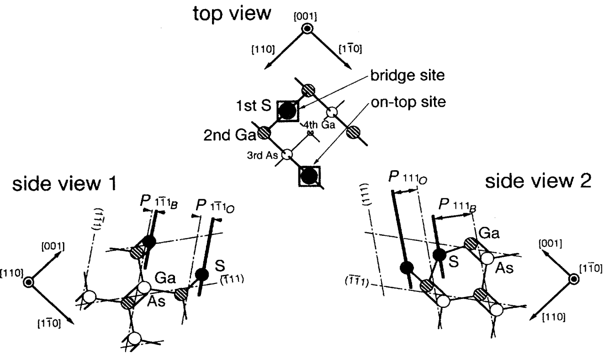

FIG. 3. Schematic top view and side views of GaAs(001) surface. Most stable and second most stable adsorption sites on the Ga-terminated GaAs(001) surface are referred to as the bridge site and the on-top site, respectively. Most of the sulfur atoms in the S-Ga state occupy the bridge site for $(NH_4)_2S_x$-treated GaAs(001) surface.

The XSW results give the position of target atoms with respect to the bulk-extrapolated reflection planes. This indicates that the results of the adsorbed layer do not include any information about the substrate relaxation. Recently Lessmann, Drube, and Materlik[11] observed the Ge (001) substrate relaxation induced by the Sb adsorption by collecting Ge LMM Auger electron yields. Although there may also be such a relaxation of the top GaAs layer in this system, such a surface-sensitive XSW result of the Ga and As emission was not measured in this study.

In conclusion, we have developed the PSXSW technique. To demonstrate the feasibility of this technique, the $(NH_4)_2S_x$-treated GaAs(001) surface structure was investigated in this study. The highest binding-energy chemical component in sulfur 1s core-level spectra (peak A) originates from ordered sulfur atoms that bond with Ga atoms. The sulfur atoms in the S-Ga chemical state on $(NH_4)_2S_x$-treated GaAs(001) surface are at the bridge site while they are not highly ordered. By the post annealing, the ordering degree of the sulfur atoms in the S-Ga chemical state are improved and randomly distributed sulfur atoms in S-As and S-S chemical states disappear.

The resolution of incident soft x rays is wider than that of ultraviolet x rays. If a much narrower energy resolution is obtained for the soft x-ray region, a slight chemical shift will be resolvable. Then, the PSXSW technique will be applied to various clean surface reconstructions that have slightly shifted surface components in the core levels.

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