$(NH_4)_2S_x$-treated InAs(001) surface studied by x-ray photoelectron spectroscopy and low-energy electron diffraction

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The chemical state of sulfur on $(NH_4)_2S_x$-treated InAs(001) and thermal stability of the surface have been studied by high-resolution x-ray photoelectron spectroscopy and low-energy electron diffraction. We find sulfur bonded to In and As atoms but no elemental sulfur for the as-treated surface. The binding energies of S $2p$ for sulfur bonded to In and As are very close. Only one chemical state in sulfur bonded to In is found, in contrast with treated GaAs(001), GaP(001), and InP(001) with two. The sulfur bonded to As atoms is desorbed upon annealing the sample at 300 °C in a vacuum. A diffuse (1×1) surface observed on the as-treated sample is reconstructed to a (2×1) structure upon annealing at 350 °C, which is different from a (1×2) structure for GaP(001) and InP(001). [S0163-1829(97)00727-3]

III-V compound semiconductors are important materials with potential applications for optoelectronic devices. In spite of their potential, however, these devices suffer because of surface instability in their characteristics.

Passivation of the surfaces by a solution containing sulfur has received much attention in the past 10 years because it tremendously improves the semiconductor surface's electronic properties.[1] Many studies, not only on the electronic properties but also on the surface chemistry, have been reported for the surfaces. Several chemical states of sulfur adsorbed on the surfaces were found using x-ray photoelectron spectroscopy (XPS): sulfur bonded to gallium, arsenic, and sulfur for GaAs,[2,3] and that to cations and sulfur for GaP (Refs. 4 and 5) and InP.[6–10] Two kinds of chemical states in the sulfur bonded to cations were distinguished for GaAs, GaP, and InP.

The surface structure of InAs(001) was extensively studied using reflection high-energy electron diffraction (RHEED),[11] scanning tunneling microscopy,[12] and ion scattering.[13] Only a few studies on the sulfur-treated InAs(001) surface were reported[14–16] but chemistry of the surface is not known. In this paper, we report the result on the passivated surface and the stability of it upon annealing studied by XPS and low-energy electron diffraction (LEED).

An n-type InAs (carrier density: $2 \times 10^{16}/cm^3$) sample was used for this experiment. It was degreased by acetone and ethanol for 15 min, rinsed by deionized (DI) water, and etched by a solution $(H_2SO_4:H_2O_2:H_2O=30:1:1)$ for 1 min at RT. This sample was dipped into an $(NH_4)_2S_x$ solution for 75 min at RT, then rinsed in running DI water, and finally dried in a flux of dry nitrogen. The sample was heated at 300 °C in an ultrahigh vacuum chamber by infrared light focused through a quartz window.

XPS measurements were carried out using a high-resolution spectrometer with a monochromatized Al $K\alpha$ source (SIENTA ESCA-200). The measurements were performed at 80° and 0° off the normal to the surface [take off angle (TOA): 10° and 90°, respectively]. The total resolution was about 0.4 eV. The binding energy was referred to 84.0 eV of the Au $4f_{7/2}$. We found that nitrogen was not left on the surface through all the experiments.

The surface structure and thermal stability of the treated sample annealed at 350 and 400 °C in a vacuum were examined using LEED and Auger electron spectroscopy (AES).

XPS spectra of In $3d_{5/2}$ and As $3d$ for etched (before sulfurization) InAs(001) are displayed in Fig. 1. Figure 2 shows XPS spectra of In $3d_{5/2}$, As $3d$, and S $2p$ measured at the TOA of 10° and 90° for $(NH_4)_2S_x$-treated InA(001) at RT. The spectral features in Figs. 2(a) and 2(c) are different from those in Figs. 2(b) and 2(d). Since this implies that some components on the surface are enhanced at TOA = 10°, the curve fitting using the nonlinear least-squares method was employed to decompose the components. The fitting parameters are the following: (i) For In bonded to As (S)—the binding energy (BE), 444.5 (445.0) eV and the full
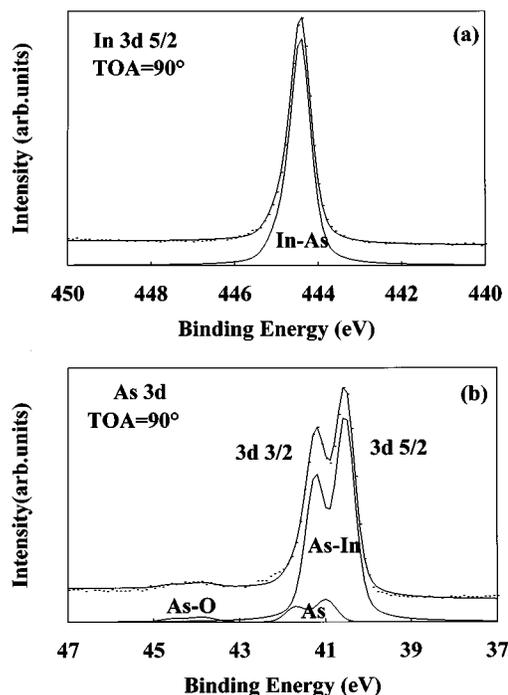

FIG. 1. XPS spectra of (a) In $3d_{5/2}$ and (b) As $3d$ for the etched InAs(001) surface. They were measured at TOA: 90°.
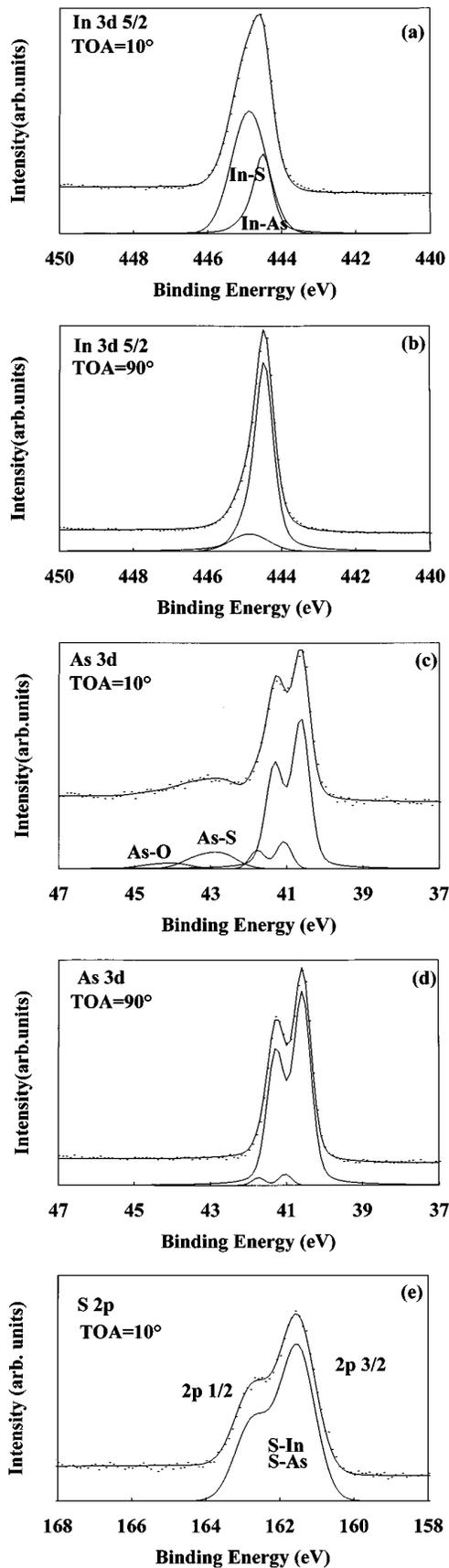
FIG. 2. XPS spectra of In $3d_{5/2}$ at (a) TOA: 10° and (b) 90°, As $3d$ at (c) 10° and (d) 90°, and S $2p$ at (e) 10° for the $(NH_4)_2S_x$-treated InAs(001) surface.

width at half maximum (FWHM), 0.6 (1.2) eV; (ii) For As $3d$—the spin-orbit splitting energy, 0.70 eV, the intensity ratio (3/2:5/2), 0.69, and the FWHM, 0.45 eV (0.90 eV for the oxide and sulfide); (iii) For S $2p$—the splitting energy, 1.08 eV, the ratio (1/2:3/2), 0.51 and the FWHM, 1.11 eV. Since the lifetime broadening is small for As $3d$ (0.06 eV) (Ref. 17) and S $2p$ (0.05 eV),[18] their peaks are fitted by the Gaussian. For In $3d_{5/2}$ with the large lifetime broadening (0.50 eV),[17] 40 (for In bonded to As) and 92% (for In bonded to S) Lorentzian are superimposed on the Gaussian peaks. Some parameters, the BE and FWHM for In $3d_{5/2}$ and As $3d$, were obtained by the present measurement on the etched surface (Fig. 1). The results obtained by the above procedure are also shown in the figure.

For Fig. 1, we find no other component except for In bonded to As (at 444.5 eV), which implies that there would exist a very small amount of the oxide on the etched surface if it does. Since the main As-$3d$ spectrum can not be fitted by one component, it is decomposed into two sets of the $3d$ spin-orbit couple lines at 40.6 and 41.0 eV for As $3d_{5/2}$. The latter component was reported in Ref. 3. A weak peak for the oxide is also found at about 44.1 eV.

We find a component at 445.0 eV in Figs. 2(a) and 2(b) except the main peak at 444.5 eV that is attributed to In $3d_{5/2}$ of In bonded to As from Fig. 1(a). The component at 445.0 eV corresponds to In bonded to sulfur on the surface because the BE is close to the previous result[9] and it is enhanced at the TOA, 10°. For the As $3d$ spectrum in Fig. 2(c), a component at 41.0 eV and two broad $3d$ peaks, where the spin-orbit splitting is not separated because of the broad FWHM, are decomposed at about 42.7 and 43.9 eV. The peaks at 41.0, 42.7, and 43.9 eV can be ascribed to amorphous elemental As, As bonded to sulfur, and arsenic oxide, respectively, from analogy in the result of sulfur-treated GaAs.[3,19] The result of Fig. 2(c) and 2(d) indicates that the oxide and sulfide exist on the surface but the elemental arsenic would be in the bulk.

We find the S $2p_{3/2}$ line at 161.6 eV. Since the binding energies of most sulfur atoms bonded to metals are between 160 and 162 eV,[19] and the peak intensities of In and As bonded to S are strong and weak for the former and the latter, respectively, the S-$2p$ spectrum consists of mainly sulfur bonded to In on the surface. The FWHM for S $2p_{3/2}$ (1.11 eV) in Fig. 2 is a little broader than that for sulfurized InP (Ref. 9) in which it was 0.98 eV measured at the 0.3 eV resolution. For the S $2p$ spectrum in sulfurized InP with a (1×1) structure, where the sulfur coverage was reported to be one, it was about 1.3 eV, obtained at the better resolution than 0.4 eV,[6] which is close to the resolution in this paper. We suggest from the above discussion that the S $2p$ spectrum consists of one chemical state except for S bonded to As. The BE of sulfur bonded to As will be discussed later.

This result is completely different from those in GaAs,[3] GaP,[5] and InP:[9] two kinds of chemical states in sulfur bonded to cations at about 161 and 162 eV for the $(NH_4)_2S_x$-treated samples were found. The two states were suggested to be sulfur on and under the surface.[3,5,9] It was reported that the etching rate for InAs(001) with the $(NH_4)_2S_x$ solution is faster by a factor of one or two orders of magnitude than that for GaAs(001) and InP(001).[14] If the rate is faster than the diffusion rate of sulfur into the bulk,
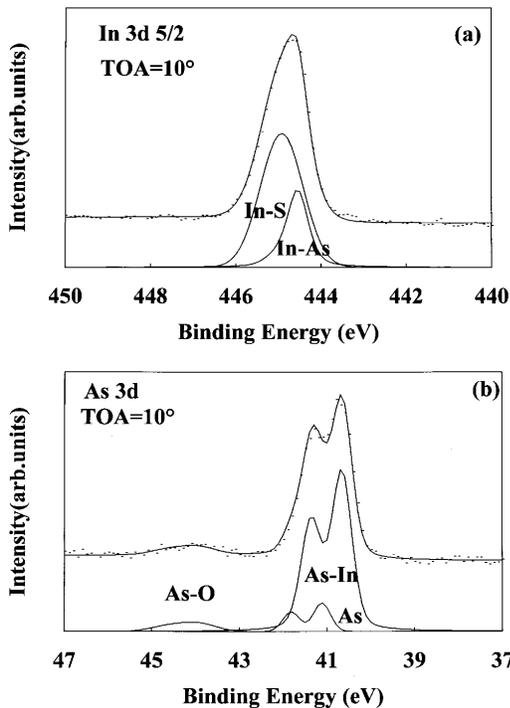
FIG. 3. XPS spectra of (a) In $3d_{5/2}$, and (b) As $3d$ measured at TOA: 10° for the sample annealed at 300 °C in the vacuum.

sulfur would exist only on the surface. We speculate that this is the reason why sulfur is bonded to In only on the InAs(001) surface but not in the bulk.

We measured the binding energies of As $3d$ and S $2p$ for As_2S_3 in order to determine the BE of As $3d$ and S $2p$. Since a charge up was occurring during the measurement, the BE could not be determined. Therefore, assuming that the BE of As $3d$ measured here is 42.7 eV, obtained in Fig. 2(c), that of S $2p$ is 161.7 eV, which is in good agreement with the result in Fig. 2(e). This implies that the BE's of S $2p$ for sulfur bonded to In and As are very close, resulting in one look alike component of S $2p$ in Fig. 2(e).

Figure 3 shows XPS spectra of In $3d_{5/2}$ and As $3d$ for the

treated surface annealed at 300 °C measured at TOA, 10°, where the spectra were fitted by using the same parameters employed in Fig. 2. We find that the 42.7 eV peak disappears upon annealing at 300 °C and two peaks at 41.0 and 43.9 remain, which suggests that sulfur bonded to arsenic was desorbed. The spectral features of In $3d_{5/2}$ and S $2p$ (not shown here) are not so much changed although their intensities were slightly decreased.

We estimate that the S coverage is about one monolayer. Assuming the mean-free path λ of In $3d_{5/2}$ electrons, about 20 Å, the total (observed) intensity of In $3d_{5/2}$, I, is expressed as[6]

$$I = I_0 \sum_{n=0}^{\infty} \exp(-nd/\lambda \sin\theta),$$

where I_0, n, d, and θ denote the intensity originating from the first In atom plane, the number of the plane, the distance between the planes (3 Å for InAs), and the take-off angle (10° in this paper), respectively. We obtain $I = 1.74I_0$, which implies that the intensity for InS is about 57%. This is a little less than that (76%) obtained in this paper. However, the coverage of sulfur is not far from one monolayer, taking account of the single component in the S $2p$ spectrum and the deviation in the assumptions in the above calculation.

We studied the surface structure and thermal stability of the $(NH_4)_2S_x$-treated InAs(001) using LEED and AES. We find a diffuse (1×1), clear (2×1), and (4×2) patterns for the as-treated and annealed samples in vacuum at 350 and 400 °C, respectively. These are in good agreement with the result obtained by RHEED.[14] The (2×1) structure is different from the previous results, a (1×2) structure, for treated GaP(001) (Ref. 4) and InP(001) (Ref. 18) surfaces. Taking account of the result that the sulfur atoms are bonded to In and the sulfur coverage is almost one monolayer, we speculate the (2×1) model that sulfur dimers bonded to the In atoms are aligned in the [110] direction with one missing row.

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