

Neutralized $(\text{NH}_4)_2\text{S}$ solution passivation of III–V phosphide surfaces

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Synchrotron radiation photoelectron spectroscopy has been used to investigate III–V phosphide GaP and InP (100) surfaces treated with a neutralized $(\text{NH}_4)_2\text{S}$ solution. Compared to the conventional basic $(\text{NH}_4)_2\text{S}$ solution treatment, a thick sulfide layer with P–S bond and strong Ga–S (In–S) bond of high thermal stability is formed on the neutralized $(\text{NH}_4)_2\text{S}$ -treated GaP (InP) (100) surfaces. The possible passivation mechanisms of the two $(\text{NH}_4)_2\text{S}$ solutions to III–V phosphide surfaces are also discussed. © 1998 American Institute of Physics. [S0003-6951(98)02946-5]

Surface and interface characteristics of semiconductors play a decisive role in many device technologies. Compared with others, III–V semiconductors are notoriously sensitive to surface/interface effects and the existence of midgap states which result in high surface recombination velocities and Fermi level pinning. Since Sandroff *et al.* reported that dipping in a sulfide solution could significantly improve the characteristics of GaAs-based devices,¹ $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{S}_x$ has attracted much attention and been used frequently for passivating surfaces of GaAs,^{1–4} and other III–V semiconductors such as InP (Refs. 5–17) and GaP.^{17–19} The method has proved to be effective in that, upon dipping, the surface oxide layer can be thoroughly removed and surface III and/or V atom bonds can be saturated by sulfur atoms, as shown by photoemission^{2–4,6–12,18,19} and Auger electron spectroscopies (AES).^{14,15,17} For InP in particular, it has been reported that improved electric properties¹⁶ and photoluminescence intensity¹⁰ could be observed on the S-passivated InP surfaces. It was also found that enhanced passivation could be achieved by using a less basic $(\text{NH}_4)_2\text{S}_x$ solution rather than the stoichiometric $(\text{NH}_4)_2\text{S}$ solution.^{2,3,6,7,16} This suggests that the basicity of the solution may play some roles in the surface sulfuration process. In this letter, we report application of a neutralized $(\text{NH}_4)_2\text{S}$ solution instead of commonly used basic solution to the passivation of InP (100) and GaP (100) surfaces. The experimental results obtained show that, dipping in the neutralized $(\text{NH}_4)_2\text{S}$ solution may lead to the formation of a passivation layer with thickness of 2 monolayers (MLs), in which S firmly bonds to In, Ga, and P with high thermal stability.

Synchrotron radiation photoemission spectroscopy (SRPES) used in the present work was performed at the National Synchrotron Radiation Laboratory, Hefei. Samples used in the experiment were mainly *n*-type (carrier density $2 \times 10^{18} \text{ cm}^{-3}$) InP and *n*-type (carrier density $5 \times 10^{17} \text{ cm}^{-3}$) GaP (100) wafers. They were ultrasonically cleaned in trichloroethylene, acetone, and ethanol in sequence for about 5 min each, etched in dilute HCl solution (about 5% v/v) for about 2 min, and then dipped in freshly prepared neutralized $(\text{NH}_4)_2\text{S}$ solution at room temperature for about

10 h. The preparation method of the neutralized $(\text{NH}_4)_2\text{S}$ solution was described previously.⁴ After being rinsed with deionized water and dried by flowing nitrogen, the samples with mirror-like surfaces were transferred into the SRPES chamber. Base pressure of chamber was better than $2 \times 10^{-8} \text{ Pa}$. The photon energies of 90 and 190 eV were used in the measurements of the Ga 3*d* (In 4*d*), and P 2*p* core levels, respectively.

SRPES spectra of In 4*d*, Ga 3*d* and P 2*p* core levels for the neutralized $(\text{NH}_4)_2\text{S}$ -treated and subsequently annealed [in ultrahigh vacuum (UHV)] InP and GaP surfaces are shown in Figs. 1–3, respectively. All peaks were curve fitted with fixed spin–orbit splitting shifts and $d_{5/2}/d_{3/2}$, $p_{3/2}/p_{1/2}$ branching ratios. They are, respectively, 0.85 eV and 1.5 for In 4*d*, 0.86 eV and 2 for P 2*p*, and 0.43 eV and 1.5 for Ga

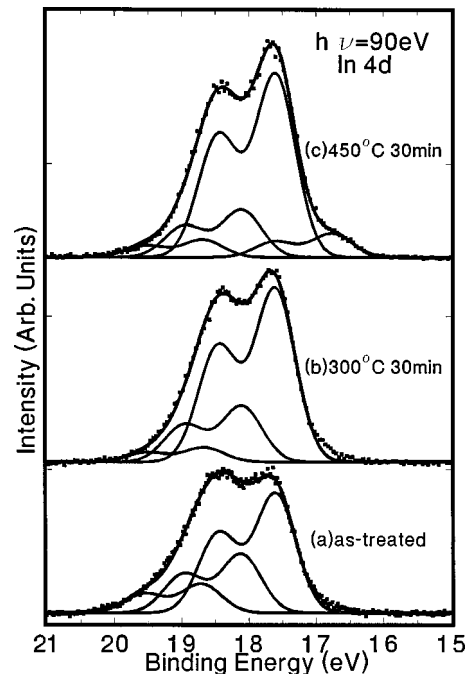


FIG. 1. SRPES spectra for In 4*d* of neutralized $(\text{NH}_4)_2\text{S}$ -treated and post annealed (in UHV) InP (100) surfaces.

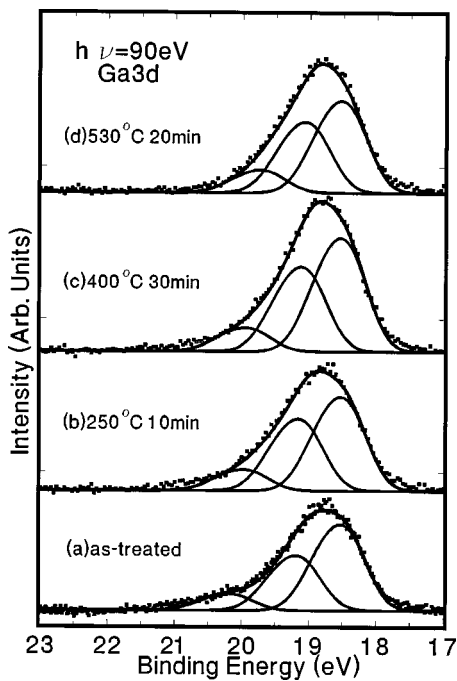


FIG. 2. SRPES spectra for Ga $3d$ of neutralized $(\text{NH}_4)_2\text{S}$ -treated and postannealed (in UHV) GaP (100) surfaces.

$3d$. The binding energies referred to below are the values of the $d_{5/2}$ and $p_{3/2}$ levels with respect to the valence-band maximum of the clean InP and GaP surfaces, respectively.

Figure 1(a) shows an In $4d$ spectrum of the as-treated InP (100) surface, in which the peak can be fitted by three overlapped components at binding energies of 17.60, 18.11, and 18.70 eV, respectively. The component with the lowest binding energy corresponds to the In atom in the InP bulk state. The other two components with chemical shifts of 1.10 and 0.50 eV, respectively, should be indium sulfide associated, as no Cl signal could be detected. Since previous

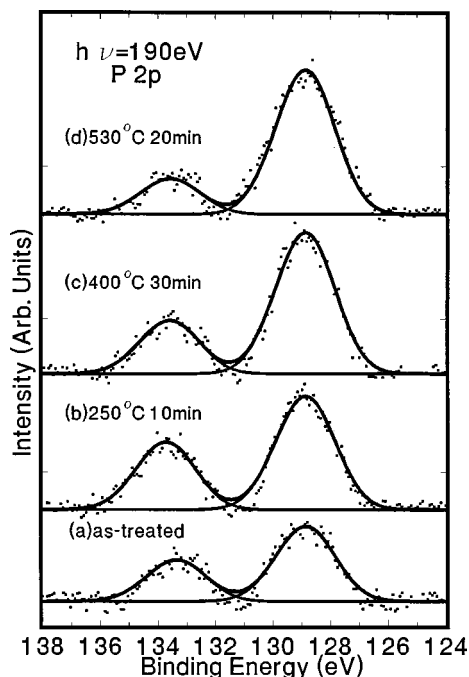


FIG. 3. SRPES spectra for P $2p$ of neutralized $(\text{NH}_4)_2\text{S}$ -treated and postannealed (in UHV) GaP (100) surfaces.

SRPES and high-resolution x-ray photoelectron spectroscopy (XPS) results showed that only indium sulfide states with small chemical shifts of 0.6,⁶ 0.5,⁷ and 0.4 eV (Ref. 8) could be found at the basic $(\text{NH}_4)_2\text{S}_x$ or $(\text{NH}_4)_2\text{S}$ -treated InP surfaces, the present data suggest that the neutralized $(\text{NH}_4)_2\text{S}$ passivation can result in the formation of stronger In-S bonds on the InP surfaces.

In $4d$ spectra of the samples postannealed at 300 and 450 °C for 30 min are shown in Figs. 1(b) and 1(c), respectively. The chemical shifts of the sulfide components remain constant during the annealing process, while their intensities decrease with the annealing temperature relative to that of InP bulk. The component with chemical shift of -0.85 eV in Fig. 1(c) is related to the metallic In state, whose intensity would further increase at elevated annealing temperature. Despite that, the sulfide states still existed on the annealed surfaces and a mirror-like surface could also be observed with naked eyes. This indicates a high stability of the sulfide states formed on the as-treated surfaces, consistent with the observation of Anderson *et al.*¹⁵

In Fig. 2(a), a Ga $3d$ core level spectrum of the as-treated GaP (100) surface is shown, and three overlapped components appear at binding energies of 18.40, 19.16, and 20.07 eV, respectively. The peak with the lowest binding energy was assigned to the GaP bulk, and the other two peaks with chemical shifts of 0.76 and 1.67 eV were attributed to Ga sulfide states. However, previous XPS results show that only a 0.58 eV shifted Ga $3d$ component could be detected at the basic $(\text{NH}_4)_2\text{S}$ -treated GaP surface.¹⁸ It is then obvious that the neutralized $(\text{NH}_4)_2\text{S}$ treatment can indeed form strong Ga-S bonds as we have previously observed in GaAs.⁴

Ga $3d$ spectra of the surface postannealed at 250, 400, and 530 °C are shown in Figs. 2(b)–2(d), respectively. Up to the highest temperature, there remains the overall three-component structure, with the intensity ratios of shifted to bulk components kept almost constant. These results are very similar to those previously observed from the neutralized $(\text{NH}_4)_2\text{S}$ -treated GaAs surface.⁴ Upon further annealing at higher temperature, the intensity of Ga-S related components decreased and a peak with chemical shift of -0.60 eV appeared (not shown here), this component is surely related to the metallic Ga state. So at least up to 530 °C, the Ga sulfides formed are quite stable.

Another effect of neutralized $(\text{NH}_4)_2\text{S}$ treatment on InP and GaP surfaces, is that stable P-S bonds can also form on the as-treated surfaces. No such species have been found on the basic $(\text{NH}_4)_2\text{S}$ -treated surfaces.^{5,8,14,18} P $2p$ core level spectra of as-treated and postannealed GaP (100) surfaces are shown in Figs. 3(a)–3(d). A component with chemical shift of 4.60 eV can be observed in all of these spectra, though its intensity decreases with increasing temperature. Obviously, the stability of this component is much higher than that of As-S bond which was completely desorbed at about 200 °C.⁴ Similarly, shifted P $2p$ component appears in the spectrum of the neutralized $(\text{NH}_4)_2\text{S}$ -treated InP (100) surfaces (not shown here), with a fair thermal stability. Although P-O bonds and P-S bonds have very similar binding energies (P $2p$ spectra of GaP and InP surfaces with native oxides not shown here),^{10,20,21} the present peak with chemi-

cal shift of 4.60 eV can be attributed to P–S bonds because only a trace amount of oxygen was detected, as in our previous observation.²² Furthermore, this component is very similar to that of sulfide-vapor-treated InP surfaces,^{20,21} and does not appear on the basic (NH₄)₂S-treated GaP (InP) surfaces.^{7–9,18} The observation that stable P–S bonding can exist at as-treated III–V phosphide surfaces is consistent with the results of recent theoretical studies.^{11–13}

Based on the above photoemission data, we can estimate the thickness of the sulfide layer formed on the as-treated surfaces. If we assume that the sulfide layer covers the as-dipped surfaces uniformly, the relationship between the integrated intensity of the sulfide state, I_s , and that of the bulk state, I_b , can be represented as

$$I_s/I_b = [1 - \exp(-d/\lambda \cos \theta)] / \exp(-d/\lambda \cos \theta), \quad (1)$$

where λ and θ are the mean-free path (~ 0.5 nm) and takeoff angle ($\sim 0^\circ$) of the photoelectrons, and d is the thickness of the sulfide layer. The calculated sulfide coverage is about 2 MLs on the neutralized (NH₄)₂S-treated InP or GaP surfaces. Previously reported sulfide coverages were less than 1 ML for basic (NH₄)₂S or (NH₄)₂S_x-treated InP surfaces^{7–9} and at most 1 ML for (NH₄)₂S-treated GaP surfaces.¹⁸ This means that a thicker sulfide layer can be formed on the neutralized (NH₄)₂S-treated GaP and InP surfaces.

The SRPES data presented show that a thicker sulfide layer with P sulfide in it and with chemical shift in the range of 1.3–1.7 eV for Ga sulfide and 0.9–1.1 eV for In sulfide can be formed on neutralized (NH₄)₂S-treated GaP and InP surfaces. The stability of P sulfide formed is much higher than that of As sulfide. Han *et al.* recently reported that InP surface covered with a thick sulfide layer was more resistant to oxidation or less influenced by a long time exposure to a moderate vacuum.¹⁰ The behavior of the Ga sulfide in the present case is very similar to that on the neutralized (NH₄)₂S-treated GaAs surfaces.⁴ Considering the fact that P sulfide and the stronger Ga–S (In–S) bonds are not formed on the basic (NH₄)₂S-treated GaP (InP) surfaces, the present data further confirm the passivation mechanisms in the two (NH₄)₂S solutions we suggested previously.⁴ When dipped in a (NH₄)₂S solution, the native oxide layers on the GaP or InP surfaces are effectively removed first, as AES measurements indicate,²² then the S²⁻ ions in the solution bond to the Ga (In) and P atoms on the GaP (InP) surface and form Ga (In) and P sulfides. As P sulfides are highly soluble in the basic solution,²³ the coexistence of reaction and dissolution results in only a very thin sulfide layer on the basic (NH₄)₂S-treated

GaP (InP) surface. Reduction of the solution pH value (basicity) to neutralization reduces the solubility of the Ga (In) and P sulfides in the solution. As a result, the sulfide formed can stick well on the surface and further deep sulfuration can occur.

In conclusion, the present SRPES data show that a thicker and thermally stable sulfide layer with P–S bonds and strong Ga–S (In–S) bonds is formed on the neutralized (NH₄)₂S-treated GaP (InP) surfaces.

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