Investigation of neutralized $(NH_4)_2S$ solution passivation of GaAs (100) surfaces

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Synchrotron radiation photoelectron spectroscopy combined with scanning electron microscopy (SEM) and gravimetry has been used to study GaAs (100) surfaces treated with a neutralized $(NH_4)_2S$ solution. Compared to the conventional basic $(NH_4)_2S$ solution treatment, a thick Ga sulfide layer and strong Ga–S bond were formed on the GaAs surface after dipping GaAs wafers in a neutralized $(NH_4)_2S$ solution. Gravimetric data show that the etching rate of GaAs in the neutralized $(NH_4)_2S$ solution is about 15% slower than that in the conventional $(NH_4)_2S$ solution. From SEM observation, fewer etching pits with smaller sizes were found on the neutralized $(NH_4)_2S$-treated GaAs surface. © *1997 American Institute of Physics.* [S0003-6951(97)01247-3]

Since Sandroff *et al.*[1] reported that dipping in a sulfide solution could significantly improve the characteristics of GaAs-based devices, $(NH_4)_2S$ has attracted much attention and been used frequently for passivating GaAs surfaces.[2–10] The passivation has proved effective in that, upon dipping, the surface oxide layer can be thoroughly removed and surface Ga and/or As bonds can be saturated by sulfur atoms, as photoemission data show.[2–10] It is also found that satisfactory passivation may be achieved by using a less basic $(NH_4)_2S_x$ rather than the stoichiometric $(NH_4)_2S$ solution.[6,8] The basicity of the solution may play some role in the surface sulfuration process. In this letter, we report the passivation of the GaAs (100) surface using a neutralized $(NH_4)_2S$ solution instead of the basic one. The experimental results obtained show that, compared to the basic one, the neutralized $(NH_4)_2S$ solution is a moderate etchant to GaAs and that dipping in such a solution may lead to the formation of a thick passivation layer in which S bonds to Ga strongly.

The major experimental technique used in the present work is synchrotron radiation photoemission spectroscopy (SRPES), which reveals the presence of more chemically shifted Ga $3d$ and As $3d$ components than those observed previously.[4] In addition, scanning electron microscopy (SEM) and gravimetry were used to monitor variations in surface morphology and weight of the sample, respectively.

SRPES measurements were carried out at the National Synchrotron Radiation Laboratory, Hefei. Semi-insulating GaAs (100) single-crystal wafers used in the experiments were ultrasonically cleaned in trichloroethylene, acetone, and ethanol in sequence, etched by $5H_2SO_4+1H_2O_2+1H_2O$ solution for 2 min, and then dipped in fresh-prepared neutralized $(NH_4)_2S$ solution for about 4 h at room temperature. The neutralized $(NH_4)_2S$ solution was prepared by dropping dilute HCl (about 10% v/v) in conventional $(NH_4)_2S$ solution ($p\mathrm{H}\cong 11.5$) until the pH value reached 7. After being rinsed with deionized water and dried by flowing nitrogen, the samples were transferred into the SRPES chamber with a base pressure of 2×10^{-8} Pa. A photon energy of 90 eV was used in the measurements of the Ga $3d$ and As $3d$ core levels.

SEM images for neutralized and basic $(NH_4)_2S$-treated GaAs (100) surfaces were observed with a JSM-T200 (JEOL) microscope. The gravimetric measurements were carried out using an electronic balance of type MA260S with a precision of 10^{-4} g.

The SRPES spectra for Ga $3d$ and As $3d$ of the neutralized $(NH_4)_2S$-treated and subsequently annealed (in UHV) surfaces are shown in Figs. 1 and 2, respectively. All peaks are curve fitted with fixed spin-orbit splitting shifts and $3d_{5/2}/3d_{3/2}$ branching ratios. They are 0.43 eV and 1.5 for Ga

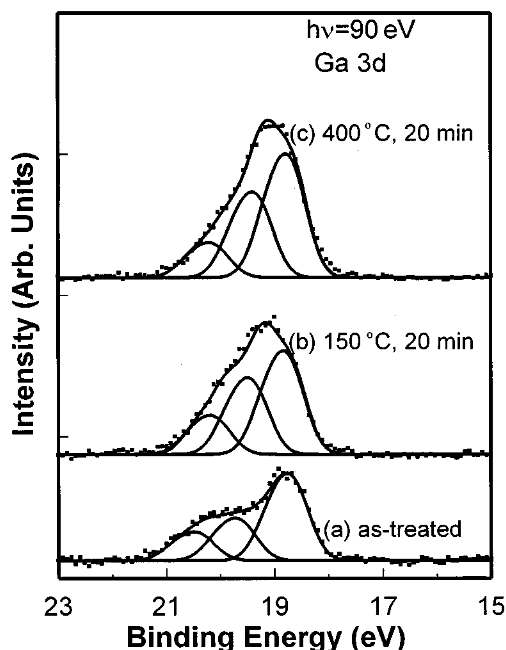

FIG. 1. SRPES spectra for Ga $3d$ of neutralized $(NH_4)_2S$-treated and post-annealed (in UHV) GaAs (100) surfaces.

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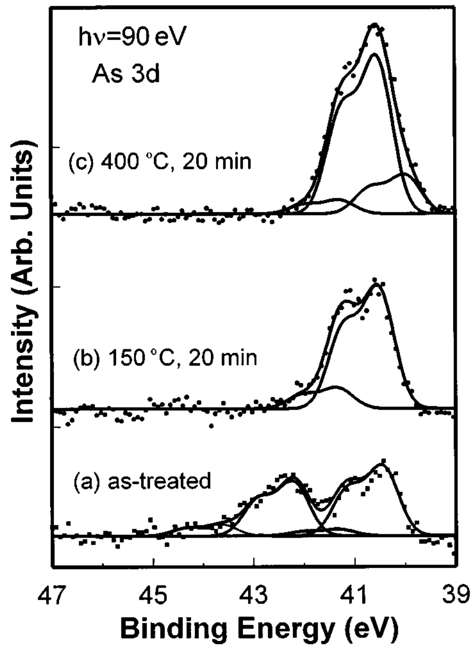

FIG. 2. SRPES spectra for As $3d$ of neutralized $(NH_4)_2S$-treated and postannealed (in UHV) GaAs (100) surfaces.

$3d$, and 0.69 eV and 1.42 for As $3d$, respectively. The binding energies referred to below are the values of the $3d_{5/2}$ levels with respect to the valence-band maximum of the clean GaAs (100) surface.

Figure 1(a) shows the Ga $3d$ peak of the as-treated GaAs surface, which can be fitted by three overlapped components at binding energies of 18.86, 19.83, and 20.60 eV, respectively. The component with the lowest binding energy corresponds to the Ga atom in GaAs. The other two components with chemical shifts of 1.74 and 0.97 eV, respectively, should be related to Ga $3d$ in sulfurized states, as no Cl signals could be detected. Since previous SRPES results showed that only the 0.55 eV shifted Ga $3d$ component could be found at the basic $(NH_4)_2S$-treated GaAs surface,[4] the present data mean that the neutralized $(NH_4)_2S$ passivation can form stronger Ga–S bonds on the treated GaAs surface.

The Ga $3d$ peaks of the surfaces postannealed at 150 and 400 °C for 20 min are shown in Figs. 1(b) and 1(c), respectively, along with the fitted results. There remains the overall three-component structure, but the chemical shifts are reduced to 1.39 and 0.64 eV, respectively. The reason for the reduction of the chemical shifts of the sulfurized states is probably that annealing leads to a conversion of the sulfurized Ga states from polysulfide to monosulfide. Up to now, the reported Ga $3d$ shifts related to Ga–S states are 3.25,[7] 1.70,[6] 1.65,[7] 1.3,[11] and 0.55 eV,[4] depending upon the treatment methods used. Although the intensities of the sulfurized Ga $3d$ peaks did not change proportionally after annealing, the total intensity of the two Ga–S states was almost constant relative to that of the GaAs bulk states. In other words, high-temperature annealing could not result in a further increase of the amount of Ga sulfides, though the ratio of different Ga sulfide species might change.

If we assume that the Ga sulfide layer is uniformly covered on the as-dipped GaAs surface, the relationship between the integrated intensity of the Ga sulfides states, I_s, and that of the GaAs states, I_b, can be represented as,[12]

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

where λ and θ are the mean-free path ($\sim$0.5 nm) and takeoff angle ($\sim 0°$) of the photoelectron, and d is the thickness of the Ga sulfide layer. If the density of the sulfide layer is 3.8×10^{22} cm^{-3},[8] the calculated Ga sulfide coverage is about 2 ML on the neutralized $(NH_4)_2S$-treated GaAs (100) surface. Cowans *et al.*[2] produced a slightly Ga-enriched surface where the sulfur coverage was only 0.6 ML after dipping in basic $(NH_4)_2S$ solution. This suggests that a thicker sulfide layer can be formed on the neutralized $(NH_4)_2S$-treated GaAs surface.

In Fig. 2(a), the As $3d$ peak of the as-treated GaAs (100) surface is shown. As result of curve fitting, there appear four overlapped components. The two dominant components are from the GaAs state with a binding energy of 40.91 eV and the As–S state with a chemical shift of 1.75 eV, and the intensities of the other two components are weak and their chemical shifts are 0.86 and 3.16 eV with respect to the GaAs state, respectively. The 0.86 eV shifted As $3d$ component might be attributed to the S adsorption state on the As bridge site,[4,13] while the 3.16 eV shifted one is probably associated with the high-valence state of As sulfide or As oxide that cannot be identified from the given photoelectron spectra. In previous work,[4,6] the poor stability of As sulfides was confirmed by photoelectron spectroscopy. The 1.75 eV shifted As $3d$ state associated with As sulfide was completely desorbed after annealing at above 360 °C.[4,6] In the present case, the 3.16 and 1.75 eV shifted As $3d$ states are completely desorbed from the neutralized $(NH_4)_2S$-treated GaAs (100) surface after annealing at 150 °C, as shown in Fig. 2(b). This indicates that the As sulfides are weakly bound on the GaAs surface and can easily be desorbed or decomposed after annealing at lower temperature. Annealing at 400 °C results in the appearance of a new shifted As $3d$ component, located at a binding energy 0.55 eV lower than the bulk component. This may be attributed to the existence of an As dimer due to breaking of As–S bonds, as Paget *et al.* suggested.[9] These kinds of As $3d$ shifts to lower binding energies were also observed by Larive *et al.* recently.[10]

SRPES data show that a thicker Ga sulfide layer with chemical shifts in the range of 1.3–1.8 eV can be formed on the neutralized $(NH_4)_2S$-treated GaAs (100) surface. Recently, Paget *et al.*[9] also observed a 1.28 eV shifted Ga $3d$ peak on the basic $(NH_4)_2S$-treated GaAs surface, but its intensity is about 30 times smaller than that of the bulk component. This indicates that the stronger Ga–S bonds are not formed on the basic $(NH_4)_2S$-treated GaAs surface. The difference between the results obtained by the two methods can be explained in terms of the passivating mechanism of GaAs in $(NH_4)_2S$ solution. The conventional wet sulfur passivation of GaAs in a basic S-containing solution is actually an etching process, during which the chemical reaction and dissolution take place alternately. The native oxide layer on the GaAs surface is first removed when the GaAs wafer is dipped in the $(NH_4)_2S$ solution. Then the S^{--} ions in the solution bond to the Ga and As atoms on the GaAs surface and produce Ga and As sulfides. Because these sulfides are

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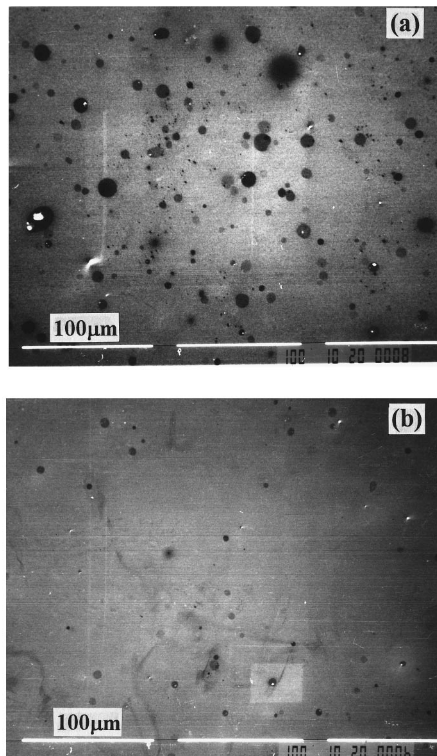

FIG. 3. SEM images for basic (a) and neutralized (b) $(NH_4)_2S$-treated GaAs (100) surfaces.

soluble in a basic $(NH_4)_2S$ solution,[14] the coexistence of reaction and dissolution results in only a very thin sulfide layer on the treated GaAs surfaces. The reduction of the solution pH value (basicity) appears to repress the solubility of the Ga and As sulfides in the solution and results in a thicker Ga sulfide layer with stronger Ga–S bonds on the neutralized $(NH_4)_2S$-treated GaAs surface.

The etching rates of GaAs in the basic and neutralized $(NH_4)_2S$ solution have been measured to be 0.363 and 0.325 nm/h at 15 °C, 0.284 and 0.244 nm/h at 4 °C using the gravimetric method, respectively. The etching rate of GaAs in the neutralized $(NH_4)_2S$ solution is 15% slower. It seems that the solubility of Ga sulfides in the $(NH_4)_2S_x$ solution formed by adding elemental S to the $(NH_4)_2S$ solution decreases also, because Sugahara *et al.*[16] found a large-shifted (1.7 eV) Ga $3d$ peak on the $(NH_4)_2S_x$-treated GaAs surface. Overall, the reduction of sulfide solubility in the $(NH_4)_2S$ solution is the key to forming the thicker Ga sulfide layer on the treated GaAs surface. In addition, the morphology of the neutralized $(NH_4)_2S$-treated GaAs surface is greatly improved. SEM morphologic images of basic and neutralized $(NH_4)_2S$-treated GaAs surfaces are shown in Figs. 3(a) and 3(b), respectively. The round etching pits are observed on the GaAs surfaces treated by both methods. More etching pits with larger sizes are distributed on the basic $(NH_4)_2S$-treated GaAs surface, with the maximum diameter of the etching pits being about 16 μm. Contrarily, fewer etching pits with smaller sizes can be found on the neutralized $(NH_4)_2S$-treated GaAs surface, where the maximum diameter of the etching pits is about 8 μm. At the bottom of the etching pits, there is a smooth surface as compared to the basic solution-treated GaAs surface. With further development, it is possible that the neutralized $(NH_4)_2S$ treatment could be developed as a chemical pretreating method in GaAs molecular beam epitaxy growth.

In conclusion, it is easy to form a thicker Ga sulfide layer and stronger Ga–S bonds with a slower etching rate of GaAs and slower dissolution of Ga and As sulfides in the neutralized $(NH_4)_2S$ solution. Fewer etching pits with smaller sizes can be found on the neutralized $(NH_4)_2S$-treated GaAs surface.

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