

Electrochemical sulfur passivation of GaAs

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An anodic sulfurized treatment of GaAs has been developed to passivate its surfaces preventing oxidation. The photoemission core level spectra show that the surface Ga and As atoms are bonded to S atoms to form a thick sulfurized layer. No oxygen uptakes on the sulfurized GaAs surface as illustrated by the high resolution electron energy loss spectroscopy. The results of photoluminescence spectra verify that the passivated surface has low surface recombination velocity and can protect the photoassisted oxidation under laser illumination.

Sulfur treatment by $(\text{NH}_4)_2\text{S}_x$ or $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ solution of GaAs (100) surface has been proved to be an effective passivation technique.¹⁻⁶ The effect is particularly distinct with $(\text{NH}_4)_2\text{S}$ solution, which removes the native oxide, etches GaAs and covers the surface with sulfur atoms, it in turn suppresses the oxidation of the surface in air. The sulfur-passivated GaAs surface has lower surface density of states, which results in the reduction of surface recombination velocity, as verified by the room-temperature photoluminescence (PL) spectrum, where the intensity of light emission from interband transition increased almost two orders of magnitude for sulfur-treated GaAs as compared with as-etched surface.^{6,7} Sandroff *et al.* passivated the periphery of a mesa type AlGaAs/GaAs heterojunction bipolar transistor with $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ solution and obtained an improvement of dc current gain up to a factor of sixty.¹

Before sulfur treatment can be employed as a routine process in GaAs device technology, there remain some problems to be solved, especially the problem of aging. It has been shown that the sulfur passivated layer, which consists of only one monolayer of sulfur atoms, is not stable in the atmosphere. After a long time exposure to air, especially under the illumination, the sulfide layer will be replaced by oxide resulting in the rapid drop down of PL intensity.

In this work, we develop a new sulfur passivation method—the anodic sulfurized technique of GaAs. It can form a thick sulfide layer to prevent the GaAs surface from being oxidized in air. The PL spectra of sulfur passivated GaAs surfaces show big intensity enhancement without visual intensity decaying even under laser beam illumination.

n-type GaAs (100) single-crystal wafers with a typical doping concentration of $7\times 10^{15}\text{ cm}^{-3}$ were used in the experiments. The sample was ultrasonically cleaned in acetone and ethanol, etched by $\text{H}_2\text{SO}_4\text{:H}_2\text{O}_2\text{:H}_2\text{O}$ (5:1:1) solution for 75 s, rinsed by deionized water and then fixed on a Teflon holder for passivation in $(\text{NH}_4)_2\text{S}$ solution. The holder was so designed that when it was partly dipped into the passivation apparatus, only one face of the GaAs wafer would contact with the solution. A dc voltage applied between the backside of the wafer and a metal plate placed in the solution would thus result in an anodic current, assisting the uptake of sulfur on the GaAs surface. The anodic current density ranged from one to tens of mA/cm^2 de-

pending on the resistivity of samples. As the anodic process proceeded, the current density decreased and ultimately reached a stabilized value of several tenths of mA/cm^2 . The sample was then loaded into the vacuum chamber of an electron spectrometer to carry out the x-ray photoelectron spectroscopy (XPS) and high resolution electron energy loss spectroscopy (HREELS) measurements. The photoluminescence measurement was performed at room temperature with a Spex Raman spectrometer. The light source was an Ar^+ laser which incidented on the sample surface with a power density of 1.1 kW/cm^2 .

$\text{Ga}3d$, $\text{Ga}2p$, $\text{As}3d$, and $\text{As}2p$ core level peaks of anodic sulfurized GaAs (100) surface excited by $\text{AlK}\alpha$ x-ray source are shown in Figs. 1 and 2. The curve fitting of $\text{Ga}3d$ results in three overlapped peaks at the binding energies of 19.10, 20.75, and 22.35 eV, respectively. The peak of lowest binding energy corresponds to the Ga atoms in GaAs. The two higher binding energy peaks are related with $\text{Ga}3d$ in sulfurized states. The chemical shifts of these two states are 1.65 and 3.25 eV, respectively, which are significantly larger than the chemical shift of $\text{Ga}3d$ in Ga_2O_3 (1.1–1.4 eV).^{8,9} For $\text{Ga}2p$ peaks, it consists of three components as shown in Fig. 1(a). The components at the binding energies of 1119.60 and 1121.15 eV (with the chemical shifts of 1.35 and 2.90 eV) are also related to the Ga sulfurized states. The binding energies of these peaks are also larger than that of $\text{Ga}2p$ in oxidized state. McGuire *et al.* have measured the $\text{Ga}3p$ core levels in Ga_2O_3 and Ga_2S_3 , they found an upward shift of about 1 eV for $\text{Ga}3p$ binding energy in Ga_2S_3 with respect to that in Ga_2O_3 .¹⁰ It is certain that there exists some chemically stable gallium sulfide compositions (possibly Ga_2S_3) in the anodic sulfurized layer. If we assume that all the Ga atoms in this layer are bonded with sulfur atoms and the unshifted $\text{Ga}3d$ peak is contributed by the GaAs substrate, then the thickness, d , of the layer can be estimated from the relation $I=I_0\exp[-d/(\lambda\cos\theta)]$. Here I is the intensity of the unshifted (substrate) $\text{Ga}3d$ peak, I_0 the total intensity, λ the electron escape depth, and θ the angle of emission. The kinetic energy of $\text{Ga}3d$ photoelectrons excited by $\text{AlK}\alpha$ photons is about 1466 eV, and λ is about 30 Å correspondingly. θ is 42° in our experiments. I/I_0 is approximately 1/2, as one can see from Fig. 1(b). The thickness calculated using these parameters is 15 Å, which is much thicker than one monolayer as obtained by ordinary sulfur treatment, i.e., dipped in $(\text{NH}_4)_2\text{S}$ solution.

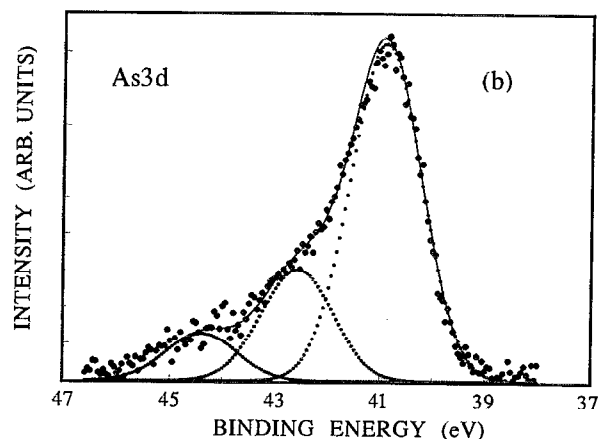
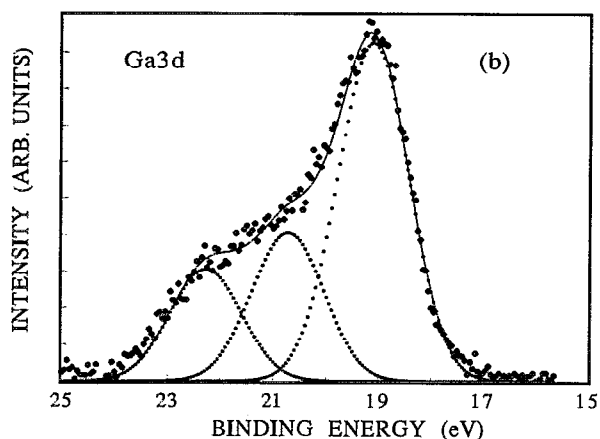
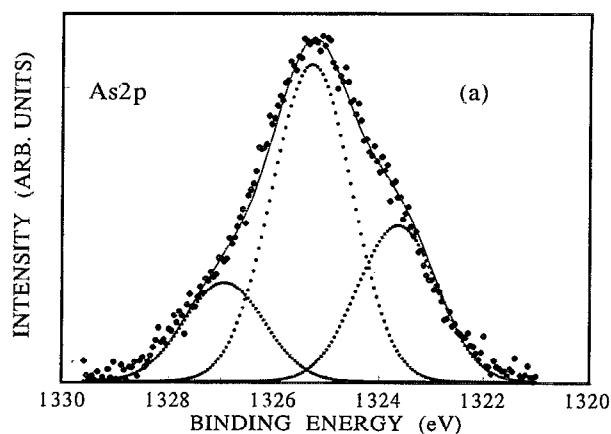
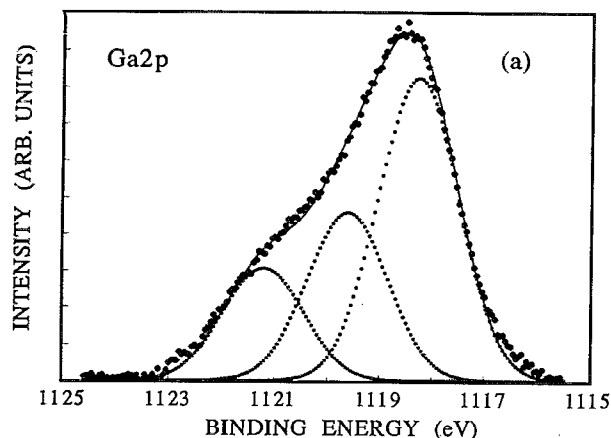


FIG. 1. Ga $2p$ and Ga $3d$ core level spectra after anodic S passivation.

FIG. 2. As $2p$ and As $3d$ core level spectra after anodic S passivation.

The GaAs surface treated by $(\text{NH}_4)_2\text{S}$ dipping didn't show the chemical shift of Ga $3d$ in ordinary XPS measurement.¹¹⁻¹⁶ By using synchrotron radiation to reach a very high energy resolution, a Ga $3d$ shifted peak corresponding to S bonded Ga atoms was distinguished, but the chemical shift is only about 0.6 eV,¹⁷ much smaller than that in the Ga $_2\text{S}_3$ compound.

In Fig. 2, the core level peaks of As $3d$ and As $2p$ also show very remarkable chemically shifted components. The curve fitting treatment separates the broad As $2p$ peak into three peaks at the binding energies of 1323.65, 1325.25, and 1326.95 eV, and As $3d$ into 40.90, 42.60, and 44.40 eV peaks, respectively. The low energy peaks (1323.65 eV for As $2p$ and 40.90 eV for As $3d$) originate from As in GaAs. The chemically shifted As $2p$ peak at 1325.25 eV is even stronger than the unshifted peak at 1323.65 eV. It also verifies that a thick S-passivated layer has been found. The highest energy peak with a shift of 3.3–3.5 eV has never been found in $(\text{NH}_4)_2\text{S}$ and $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ treated samples, where the peak positions of As $2p$ and As $3d$ contributed by S bonding state shifted only up to 1.8 eV.^{16,17} We are not sure whether this high energy component arises from oxidized As or sulfurized As. However, the chemical shift of As $2p$ in As $_2\text{S}_3$ is only 2.7–2.8 eV,¹⁸ therefore the formation of As $_2\text{S}_3$ is more likely if the 3.3–3.5 eV shifted peak is attributed to sulfurized As.

HREELS has been verified to be a sensitive technique to detect the existence of oxygen uptaken on GaAs surfaces.¹⁹ The appearance of a loss peak at the energy of 90 meV is indicative of the stretching vibration of Ga—O and As—O bonds. The energy loss spectra obtained on GaAs surfaces treated by chemical etching, $(\text{NH}_4)_2\text{S}$ and anodic sulfurized treatment are shown as curves (a), (b), and (c) in Fig. 3, respectively. The chemically etched surface shows significant oxidation. The loss peaks at the energies of 180 and 370 meV are related with the unavoidable carbon hydride contaminations in air. The absence of 90 meV loss peak in curves (b) and (c) verifies that on both samples the sulfur-passivated layers are actually formed, which prevented the uptake of oxygen on surfaces.

Oigawa *et al.*⁶ reported the enhancement of photoluminescence intensity of the GaAs sample after $(\text{NH}_4)_2\text{S}$ treatment. The PL intensity increased about two orders of magnitude as compared with the as-etched sample. The phenomenon could be explained as the reduction of the carrier recombination center at the GaAs surface by S passivation. However, under the illumination of Ar⁺ laser at the flux of 1.2 kW/cm², the PL intensities of both as-etched and $(\text{NH}_4)_2\text{S}$ passivated samples decayed rapidly. After 30 min illumination, there was actually no marked difference of PL intensities between these two samples. The above observation was repeated in our experiment as

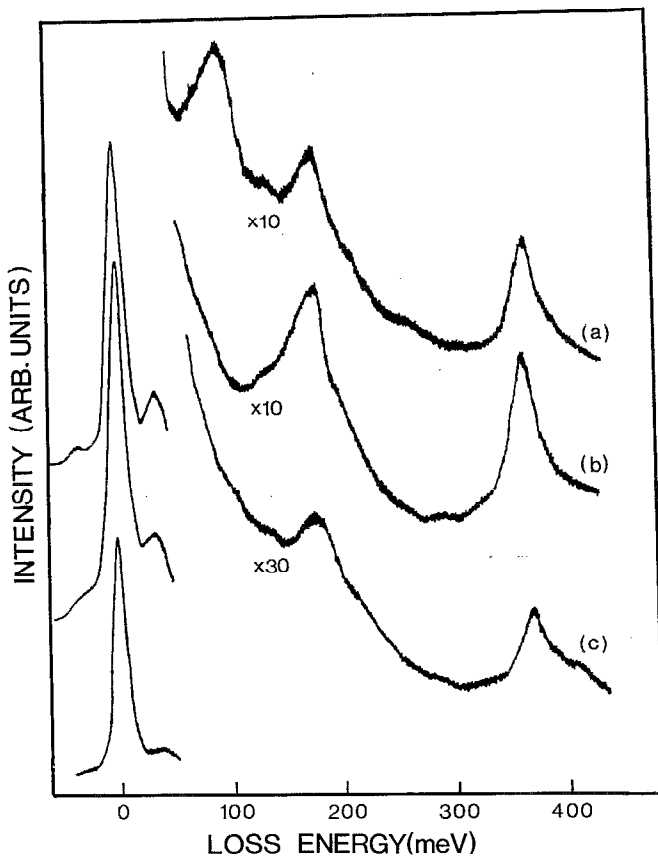


FIG. 3. The HREELS spectra of GaAs(100). (a) as-etched, (b) ordinary S passivation in $(\text{NH}_4)_2\text{S}$ solution, and (c) anodic S passivation in $(\text{NH}_4)_2\text{S}$ solution.

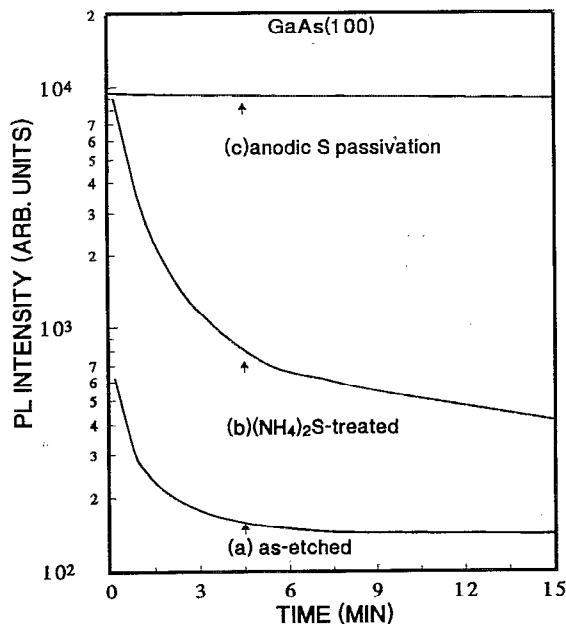


FIG. 4. The PL spectra of GaAs(100). (a) as-etched, (b) ordinary S passivation in $(\text{NH}_4)_2\text{S}$ solution, and (c) anodic S passivation in $(\text{NH}_4)_2\text{S}$ solution.

shown by curves (a) and (b) in Fig. 4. But in our anodic sulfurized GaAs sample, the deterioration effect by photon illumination is eliminated as shown by curve (c) in Fig. 4. The PL intensity not only increases by two orders of magnitude after S passivation as compared with the as-etched sample, but also remains unchanged under $1.1 \text{ kW/cm}^2 \text{ Ar}^+$ laser illumination for 30 min. The rapid decay of PL intensity under illumination was explained as the photon-assisted oxidation effect, i.e., the S atoms bonded with the GaAs surface are replaced by O atoms under illumination. Our result shows that after anodic sulfurized treatment, the S atoms are strongly bonded to the GaAs surface to form a very stable S passivation layer, which could resist the photoassisted oxidation process.

In conclusion, we have demonstrated that by using an anodic sulfurized method, the GaAs surface can be effectively passivated. The formation of a thick sulfurized layer with the thickness of about 15 \AA can greatly reduce the surface recombination velocity and keep the surface quite stable. The electrochemical sulfurized treatment seems to be a promising technique to solve the surface passivation problem of GaAs over the ordinary S treatment methods.

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