

A mild electrochemical sulfur passivation method for GaAs(100) surfaces

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We have developed a mild electrochemical sulfurization technique which can form a very thick sulfide layer on GaAs(100) surface. This sulfide layer is quite stable in air. The photoluminescence spectrum of such anodic sulfurized GaAs surface shows a large intensity enhancement as compared with that of as-etched GaAs samples. No visual intensity decay occurs under the laser beam illumination after the sample has been maintained in air for more than seven months. The structure and composition of the passivation layers are investigated by x-ray photoelectron spectroscopy and the mechanism of layer formation is discussed. © 1995 American Institute of Physics.

I. INTRODUCTION

The passivation of III-V compound semiconductor surfaces, especially GaAs, has long been a difficult task. Among the various passivation methods, the sulfur treatment by $(\text{NH}_4)_2\text{S}_x$ or $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ solution of GaAs(100) surface proposed first by Sandroff *et al.*¹ seems to be the most promising one and has been widely investigated.²⁻⁶ The great enhancement of the photo luminescence (PL) intensity and the improvement of dc current gain of a S-passivated mesa-type AlGaAs/GaAs heterostructure bipolar transistor verified that the treatment drastically reduces the surface recombination velocity. However, the ordinary S-passivation technique is unstable. The low surface recombination is easily lost after a period of exposure to the air. The failure of S passivation is caused by the structure of the passivation layer. It has been found⁷ that there is only about one monolayer of S atoms bonded to GaAs to form a sulfide/GaAs interface, and this thin layer can be oxidized in air, resulting in the failure of passivation. To overcome this problem, MacInnes *et al.*⁸ coated the GaAs surface with cubic GaS thin film by the metalorganic chemical vapor deposition (MOCVD) technique. In our earlier work, an electrochemical sulfurization method was suggested to improve the stability of the passivation effect.⁹ This technique is fairly simple and easy to handle compared to MOCVD. The result was quite encouraging. However, since the current density used was too high, the severe corrosion reaction between electrochemical solution and substrate made the sample surface fairly rough after the treatment. In this work, we develop a mild electrochemical sulfur passivation method and demonstrate its effect and mechanism of passivation.

II. EXPERIMENT

N-type Te-doped GaAs(100) single-crystal wafers with the doping concentration of $8 \times 10^{18} \text{ cm}^{-3}$ were used in the experiments. The sample was first 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 de-ionized water, and then fixed on a Teflon holder for passivation in $(\text{NH}_4)_2\text{S}$ solution. A dc voltage was applied between the backside of the wafer and a Ta cathode was placed in the solution. The current was less than 1 mA/cm^2 at the beginning and finally stabilized at about $100 \mu\text{A/cm}^2$. The sample surface could remain mirror-

like all the time, even when the sulfurized passivation layer becomes very thick. The typical thickness of the passivated layer was around 100–150 nm. After anodization, the sample was loaded into the vacuum chamber of an electron spectrometer to carry out the x-ray photoelectron spectroscopy (XPS) measurements. The PL measurement was performed at room temperature with a Raman spectrometer (JOBIN YVON U1000). The light source was an Ar^+ laser with a power density shining on the sample surface of 1.5 kW/cm^2 (150 mW in an area of 0.01 mm^2).

III. RESULTS AND DISCUSSION

The composition of the passivation layer was measured by XPS combined with Ar^+ ion sputtering. Figure 1 shows the depth profiles of O 1s, Ga 2p, and As 2p intensities. According to the composition, the film could be roughly divided into two parts. The outer part of the layer (with a thickness of about 50 nm) consists of Ga, As, and O, with the As concentration depleted at the outermost part. The inner part of the layer (the other 50 nm) consists of S, Ga, and As with only a small amount of O. At the film/substrate interface region, the oxygen concentration can actually be neglected. The concentration of S in the film is not easy to determine since the S 2p peak is always overlapped with the Ga or As core level peak under the excitation of either Mg K_α or Al K_α x-ray source. By a subtracting treatment of the spectra between the S-containing and S-free films, it could be veri-

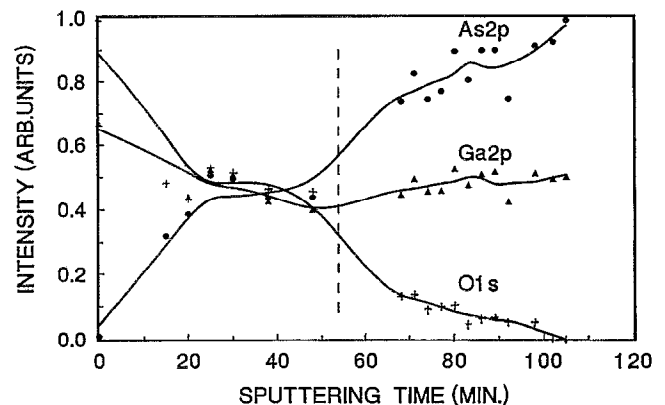


FIG. 1. XPS depth profile of S passivation layer.

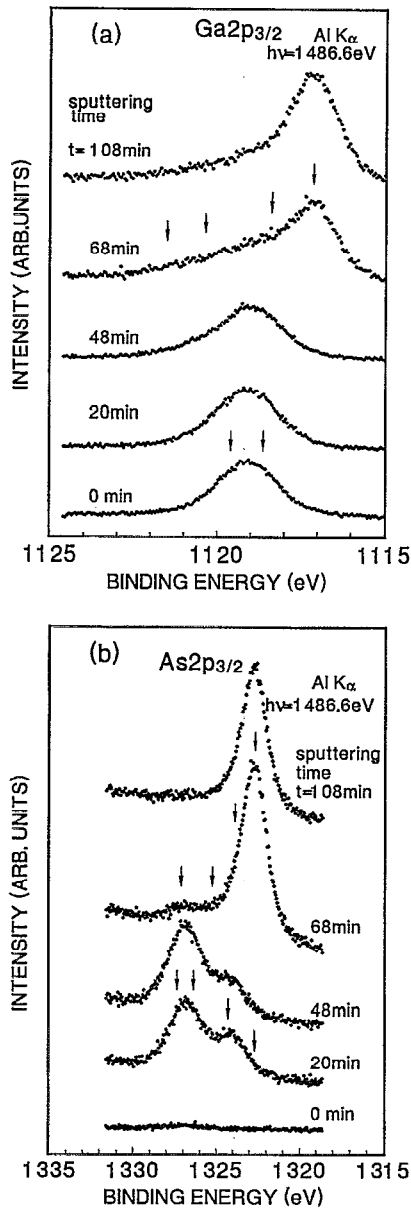


FIG. 2. The Ga 2p and As 2p XPS peaks of an anodic sulfurized GaAs(100) at different sputtering times.

fied that S does exist in the passivation layer with its concentration lower in the outer part and higher in the inner part of the film.

The line shapes of Ga 2p and As 2p peaks at different parts of the film were compared, as shown in Fig. 2. In the outer part of the film, i.e., below the sputtering time of 50 min the Ga 2p peak could be separated by the curve fitting into two components with the chemical shifts of 1.5 and 2.5 eV toward higher binding energies, respectively. The peak positions of these two components are shown as arrows in Fig. 2. These two chemically shifted peaks are most likely attributed to the oxides of Ga rather than sulfides. The same argument is applied to the As 2p peak, where three chemically shifted peaks (indicated by arrows) corresponding to different oxide states of As could be identified by curve fitting. No Ga 2p and As 2p peaks from Ga-As bonding state

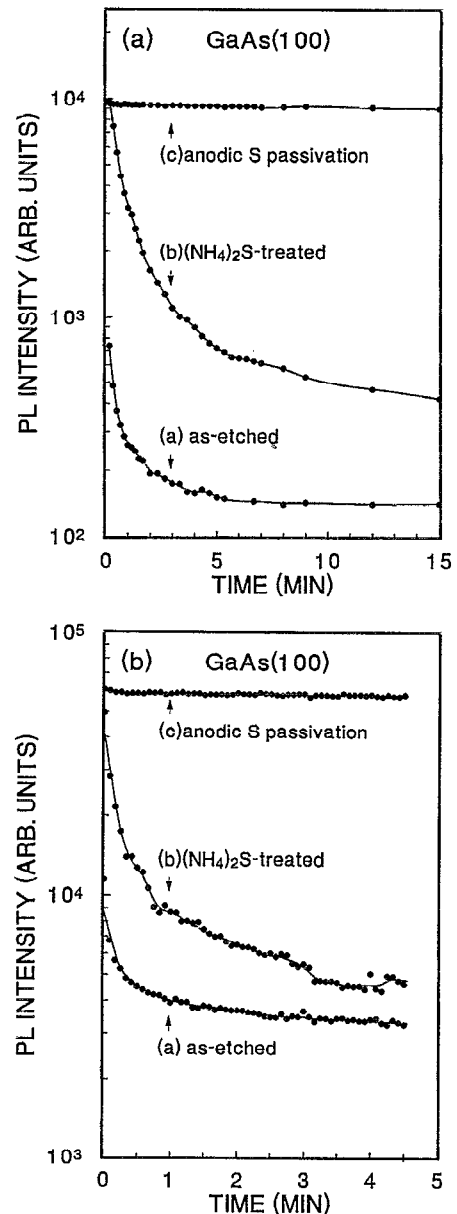


FIG. 3. The variation of PL intensity of GaAs(100) vs the laser illumination time for different samples, (a) as-prepared, (b) after seven months.

could be observed. In the inner part of the film (the sputtering time >60 min), the peak shapes and positions of Ga 2p and As 2p are completely different from those of the outer part. The curve fittings of Ga 2p and As 2p spectra all lead to four components, one from the Ga-As bonding state and the other three peaks related to different Ga-S and As-S bonding states. The largest chemical shift of these states is about 4.3–4.4 eV.

The passivation effect of the anodic sulfurization treatment was checked by the PL measurement. The PL intensity was recorded as a function of laser illumination time for different samples, as shown in Fig. 3(a). The PL intensity increases by one-and-a-half orders of magnitude after the anodic S passivation as compared to the as-etched surface. It also remains unchanged under the Ar⁺ laser illumination for

30 min. For the $(\text{NH}_4)_2\text{S}$ treated sample, a rapid decay of PL intensity under the same illumination condition is observed, although the initial PL intensity is enhanced.

The passivation effect could be maintained for quite a long period. After keeping in air for seven months, the sample still shows the improvement of PL intensity and its stability under laser illumination, as shown by Fig. 3(b). The composition of the film shown above is believed to be responsible for the stabilization. The sulfide/GaAs interface is protected by the thick oxide layer, which prevents the re-oxidation of the S-Ga bonds and stabilizes the passivation effect.

To explain the formation of a nonuniform passivation overlayer shown in Fig. 1, the following process is suggested. In the S containing solution, two competitive chemical reaction processes occur. The first one is the reaction of GaAs substrate with S^{2-} ions in the solution to form the sulfides, the other one is the reaction of the formed sulfides with H_2O , which etches the sulfides and converts them into oxides. In the ordinary $(\text{NH}_4)_2\text{S}_x$ dipping, the second reaction is markedly strong, so the sulfide layer formed is mostly converted into oxides, which are soluble in water. Therefore, only one monolayer of S atoms remains on the surface. In the case of electrochemical sulfurization, the action of a strong electric field attracts a larger amount of S^{2-} ions accumulated at the electrolyte/GaAs interface. The chemical reaction results in the formation of the sulfide layer. The reaction of OH^- ions from the solution with the substrate could be neglected due to the low concentration of OH^- at the interfacial region. The sulfide layer then could form with the thickness larger than one monolayer. As the thickness of the passivation layer increases, the S^{2-} ions could penetrate the film through very thin holes and accumulate on the GaAs substrate surface to make the sulfurization reaction continue. The voltage drop now is mainly across the interface. This

leads to the rapid decrease of S^{2-} concentration at the outer part of the film, where the reaction between the sulfides and H_2O will play the main role. Thus, the outer part of the passivation layer will be converted from sulfide into oxide.

IV. CONCLUSION

It is shown that the mild anodic sulfurization method can greatly improve the S passivation effect by creating a thick S-containing layer. The strong chemical bonds of Ga-S on the GaAs surface are isolated from the ambient. The re-oxidation of Ga-S bonds is thus prevented and the stabilization of passivation is expected.

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