

## Effective Surface Passivation of GaAs by Using Electrochemical Sulfurized Treatment

X.Y.Hou, Z.S.Li, W.Z.Cai, X.M.Ding and Xun Wang

Surface Physics Laboratory, Fudan University

Shanghai 200433, CHINA

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 photoluminescence spectrum of such anodic sulfurized GaAs surface shows big intensity enhancement as compared with that of as-etched GaAs sample, and no visual intensity decaying occurs under laser beam illumination. The structure and composition of the passivation layers are investigated by the X-ray photo-electron spectroscopy.

### 1. INTRODUCTION

One of the major challenges facing compound semiconductor technology is the absence of a truly passivating native oxide. Although many extrinsic passivation techniques have been proposed such as the deposition of AlGaAs, ZnSe, P etc., but none of them can be served as a successful practical device technology. Recently, a new attempt to passivate GaAs surface by using sulfur deposited from  $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$  or  $(\text{NH}_4)_2\text{S}$  solution has been attracted much attention.<sup>1-6</sup> Sandroff et al. first employed this method to passivate the periphery of a mesa type AlGaAs/GaAs heterojunction bipolar transistor and obtained an improvement of dc current gain up to a factor of sixty. The S treatment can reduce surface recombination velocities 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.<sup>6,7</sup> The sulfur passivation could be of practical importance if its effect is stable. However, it has been found that the low surface recombination is easily lost after one-half hour exposure to the atmosphere. Spindt and Spicer<sup>8</sup> has proposed that the structure of sulfur treated GaAs consists of two parts: a monolayer S bonded to Ga atoms to form a sulfide/GaAs interface and a "thick" layer of  $\text{As}_2\text{S}_3$  molecules sitting on top of the Ga-S termination. The thick layer is easy to sublime even at room

temperature. The oxidation of GaAs after atmospheric gasses penetrate the overlayer left by the sulfur treatment causes the failure of passivation. To improve the stability of sulfur treated GaAs surfaces, we developed an electrochemical sulfurized technique which could create a robust overlayer to prevent the sulfide/GaAs interface from being oxidized in atmosphere. PL study shows that the low surface recombination velocity could persist even under laser illumination.

### 2. EXPERIMENTAL

n-type Te-doped GaAs(100) single-crystal wafers with the doping concentration in the range of  $7 \times 10^{15} \text{ cm}^{-3}$  to  $8 \times 10^{18} \text{ cm}^{-3}$  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 75s, rinsed by deionized water and then fixed on a Teflon holder for passivation in  $(\text{NH}_4)_2\text{S}$  solution. A dc voltage applied between the backside of the wafer and a metal cathode placed in the solution would thus result in an anodic current, assisting the uptake of sulfur on the GaAs surface. After anodization, the sample was then loaded into the vacuum chamber of an electron spectrometer to carry out the X-ray photoelectron spectroscopy (XPS) measurements.

### 3. RESULTS AND DISCUSSIONS

#### 3.1 Strong Sulfurization Process

As pointed out by Spindt and Spicer, the interaction between S and GaAs is relatively mild as compared with that between oxygen and GaAs. It is the reason that the S-Ga bonds, which are not so strong, could easily be broken and replaced by O-Ga bonds. The electrochemical sulfurized treatment we employed could enhance the S interaction with GaAs. During the anodic process, the current density reached 100mA/cm<sup>2</sup> in the beginning, then decreased gradually and ultimately stabilized at several tenth of mA/cm<sup>2</sup>. The thickness of sulfurized layer estimated from the XPS measurements is about 2 nm, which is much thicker than one monolayer as obtained by ordinary sulfur treatment. This sulfurized method is denoted as strong sulfurization process as the reaction is quite intensive in comparison with the mild sulfurization process which will be described below.

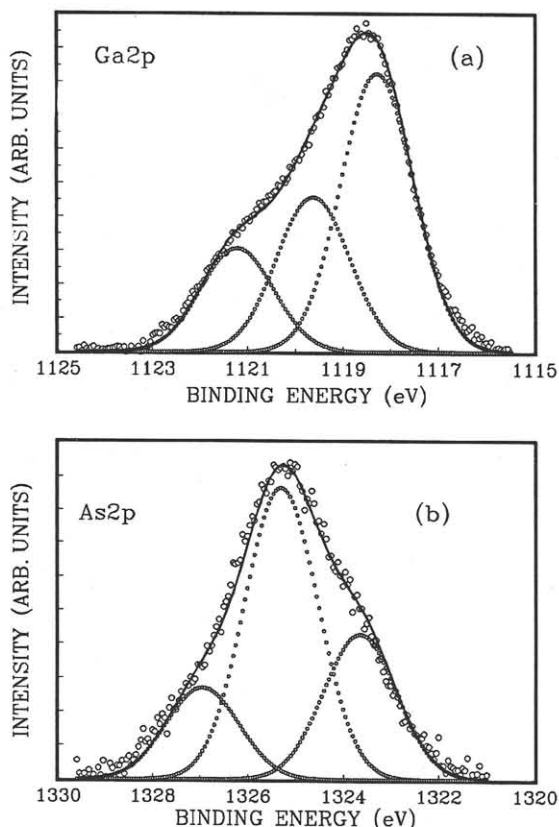


Fig.1 Ga2p and As2p core level spectra after anodic S passivation

Shown in Fig.1 are the Ga2p and As2p XPS peaks of an anodic sulfurized GaAs(100) surface. The curve fitting of Ga2p results in three overlapped peaks at the binding energies of 1118.25, 1119.60 and 1121.15 eV respectively. The peak of lowest binding

energy corresponds to the Ga atoms in GaAs. The two higher binding energy peaks are related with Ga2p in sulfurized states. The chemical shifts of these two states are 1.35 and 2.90 eV respectively, which are significantly larger than the chemical shift of Ga2p for those (NH<sub>4</sub>)<sub>2</sub>S dipped sample.

The similar situation happens for As2p peaks. The broad As2p peak could also be separated into three peaks with the two higher binding energy peaks shifted 1.6 eV and 3.3 eV respectively. The highest energy peak has never been found in Na<sub>2</sub>S·9H<sub>2</sub>O or (NH<sub>4</sub>)<sub>2</sub>S treated samples. It is believed that this peak is attributed to sulfurized As, possibly in the form of As<sub>2</sub>S<sub>5</sub>.

#### 3.2 Mild Sulfurization Process

The strong sulfurization process described above has the drawback that the severe corrosion reaction between electrochemical solution and substrate makes the sample surface fairly rough after treatment. For the mild sulfurization process, the initial anodic current was no larger than 1 mA/cm<sup>2</sup> and finally stabilized at 100 μA/cm<sup>2</sup>. The sample surface remains mirror-like even though the sulfurized passivation layer reaches very thick, say 100 to 200 nm.

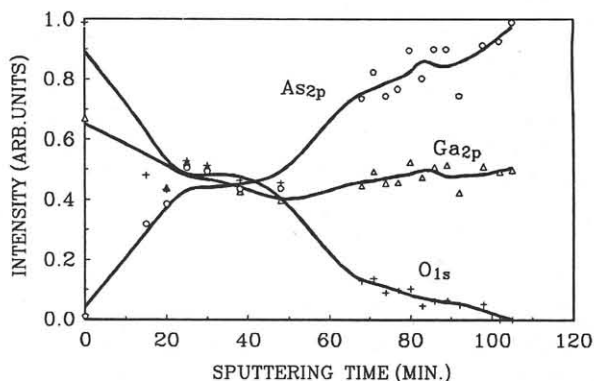


Fig.2 XPS depth profile of S-passivated layer

The composition of the passivated layer was investigated. Fig.2 shows the depth profiling of O1s, Ga2p and As2p intensities measured by XPS combined with Ar<sup>+</sup> ion sputtering. It can be seen that the oxygen concentration in the film is negligible at the film/substrate interface, while As is absent on the surface region of the passivation film. From the line shapes of Ga2p and As2p (not show here), it is illustrated that within the outer part of the anodic film, (about the thickness of 50 nm), the Ga2p peak could be separated into two components with the chemical shift of 1.5 and 2.5 eV respectively. They are

probably correspond to the Ga(OH) and Ga(OH)<sub>3</sub> states. While the As2p peak is composed of four components corresponding to different oxide states of As. No Ga2p and As2p peaks from Ga-As bonding state could be observed. In the inner part of the film, the peak shapes and positions of Ga2p and As2p are fully different from that of outer part. They are all shifted to lower binding energies. The curve fittings of Ga2p and As2p spectra all lead to four components, one from the Ga-As bonding states and other three peaks are related with different Ga-S and As-S bonding states. The composition of S in the film is not easy to determine since the S2p peak is always overlapped with a Ga core level peak or As core level peak under the excitation of either MgK<sub>α</sub> or AlK<sub>α</sub> X-ray source. By a very careful treatment of the differential spectrum between S-containing and S-free films, it could be verified that S does exist in the passivation layer with its concentration lower in the outer portion and higher in the inner portion of the film.

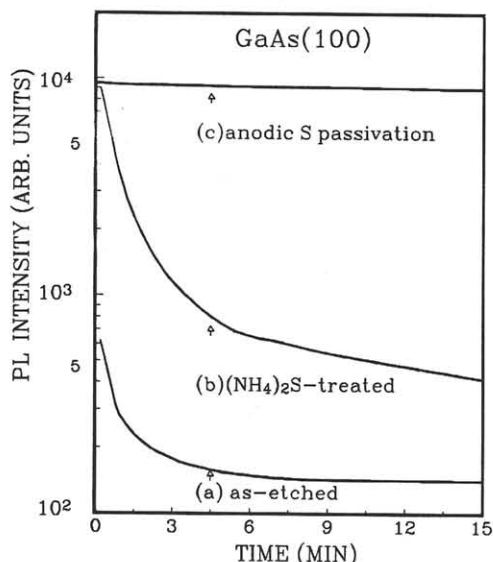


Fig.3 The PL spectra of GaAs(100) after different surface treatments

### 3.3 Photoluminescence

The passivation effect of the anodic sulfurized method has been verified by the photoluminescence measurements shown in Fig.3. The PL intensity not only increases by two orders of magnitude after anodic S-passivation as compared with the as-etched sample, but also remains unchanged under 1.1 kW/cm<sup>2</sup> Ar<sup>+</sup> laser illumination for 30 min. While a rapid decay of PL intensity under illumination was observed for (NH<sub>4</sub>)<sub>2</sub>S-treated sample. Our results thus show that the anodic sulfurized treatment results in

the formation of a very stable S passivation layer, which could resist the photo-assisted oxidation process.

### Acknowledgement

This work was partially supported by the National Natural Science Foundation of China.

### REFERENCES

- 1) C.J.Sandroff, R.N.Nottenberg, J.C.Bischoff and R.Bhat, *Appl.Phys.Lett.* **51**, (1987)33.
- 2) M. S. Carpenter, M. R. Melloch, and T. E. Dungan, *Appl. Phys. Lett.* **53**, (1988)66.
- 3) Jia-Fa Fan, Haruhiro Oigawa and Yasuo Nannichi, *Jpn. J. Appl. Phys.* **27**, (1988) L2125.
- 4) M.S.Carpenter, M.R.Melloch, B.A.Cowans, Z.Dardas and W.N.Delgass, *J.Vac.Sci. Technol.* **B7**; (1989)845.
- 5) M.S.Carpenter, M.R.Melloch and M.S. Lundstrom *Appl.Phys.Lett.* **52**, (1988)2157.
- 6) H.Oigawa, J.Fan, Y.Nannichi, K.Ando, K. Saiki, and A.Koma, in: *Extended Abstracts of the 20th International Conference on Solid State Devices and Materials (The Japan Society of Applied Physics, Tokyo, 1988)* p.263.
- 7) B.J.Skromme, C.J.Sandroff, E.Yablonovitch and T.Gmitter, *Appl. Phys. Lett.* **51**, (1987) 2022
- 8) C.J.Spindt and W.E.Spicer, *Proc. 12th State-of-the-art Program on compound semi-conductors*, Eds. D.C.D'Avanzo, R.E.Enstrom, A.T.Macrander and D.DeCoster, *The Electrochemical Society. INC.* (1990) p3.