

## Oxidation of Sulfur-Treated GaAs Surfaces Studied by Photoluminescence and Photoelectron Spectroscopy

M. Oshima, T. Scimeca, Y. Watanabe, H. Oigawa \* and Y. Nannichi \*

NTT Interdisciplinary Research Laboratories, Musashino-shi, TOKYO 180, JAPAN

\* University of Tsukuba, Tsukuba-shi, Ibaraki 305, JAPAN

The initial oxidation features of  $(\text{NH}_4)_2\text{S}_x$ -treated GaAs surfaces has been investigated by photoelectron spectroscopy in order to correlate the photoluminescence (PL) degradation caused by oxidation with band bending and surface chemical bonding changes. Direct correlation between the drastical upward band bending caused by oxidation and PL degradation is observed. It is also found that the S-passivated surface inhibits oxidation reaction, and that the underlying GaAs is oxidized leaving the surface Ga-S layer unoxidized.

### 1. Introduction

Treating the GaAs surface with  $(\text{NH}_4)_2\text{S}_x$  treatment has been shown to be effective in reducing the GaAs surface state density and unpinning the surface Fermi level<sup>1)</sup>. However, it is found that the passivation effect, as revealed by photoluminescence(PL) measurements, degrades quickly when the sample is placed in atmosphere. Although Sandroff et al<sup>2)</sup> studied the oxidation of sulfur-treated GaAs by X-ray photoelectron spectroscopy(XPS), no direct correlation between oxidation and PL degradation has been reported.

In this study, the degradation effect of a well-defined sulfur-passivated GaAs surface<sup>3)</sup> during oxidation is investigated using PL and surface-sensitive synchrotron radiation photoelectron spectroscopy(SRPES).

### 2. Experimental

Experiments were performed on Beamline 1A at the Photon Factory located in the National Laboratory for High Energy Physics. The photon energy was set at about 80 eV for Ga3d and As3d and at about 210 eV for S2p to obtain surface sensitive information. The photon energy was determined by measuring the Fermi edge from a fresh Au sample. The energy resolution for the SRPES measurements was determined to be 0.26eV from the Fermi edge shape of a clean Au sample.

The samples were n-type GaAs wafers with a

carrier density of  $1 \times 10^{18} \text{ cm}^{-3}$ . The GaAs samples with orientations (111)B, (100) and (111)A were treated with a  $(\text{NH}_4)_2\text{S}_x$  solution for 1 hour at 60 °C, and introduced into the analysis chamber. The samples were annealed at 480°C for 10 min. Oxidation was performed by exposing the sample to dry oxygen gas for  $10^3$  and  $10^6$  L exposures and to air for 1 min ( $10^{10}$  L) and 20 min( $2 \times 10^{11}$ L). Furthermore, heavy oxidation was induced by exposing the sample in atmosphere with UV light from a low pressure Hg lamp.

PL measurements were performed at room temperature with 514.5nm Ar laser excitation at about  $1 \text{ kW/cm}^2$ . Samples were n-type GaAs wafers( $7 \times 10^{17} \text{ cm}^{-3}$ ).

### 3. Results and discussion

#### 3.1 Photoluminescence measurements

Figure 1 shows the photoluminescence intensity of  $(\text{NH}_4)_2\text{S}_x$ -treated GaAs and 480 °C annealed GaAs as a function of atmospheric exposure time. The PL intensity of the S-treated and annealed GaAs drastically decreases immediately after exposing the sample to atmosphere and saturates to an intensity of about one-20th of the initial intensity. This degradation is believed to be due to surface oxidation which results in surface defects and band bending. It should be noted that the 480 °C annealed surface after sulfur treatment shows higher PL intensity than the as-treated

surface. This can be attributed to the formation of a thermodynamically more stable Ga-S layer passivating the GaAs surface than the As-S layer formed on the as-treated surface. Based on the ab initio calculations<sup>4)</sup>, Ga-S bond formation is effective in drastically eliminating surface states. Therefore, it is thought that oxidation may disrupt the stable Ga-S bonds and form surface defects.

In order to eliminate the possibility that PL degradation may be due to laser irradiation, the PL intensity was also measured in vacuum. However no PL intensity changes were observed even for after irradiating the sample for more than 60 minutes, indicating that the PL degradation is caused by oxidation.

### 3.2 Photoelectron spectroscopy

Sandroff et al<sup>2)</sup> reported from XPS results with an AlK  $\alpha$  X-ray source that  $(\text{NH}_4)_2\text{S}_x$ -treated GaAs surface exposed to 200 torr  $\text{O}_2$  for 40 min shows almost no oxidation. However, since XPS is not surface sensitive, a possibility that the PL degradation is attributed to a slight oxidation which results in band bending and defect formation cannot be ruled out.

In order to correlate the PL degradation features with band bending caused by oxidation, the valence band was directly measured by surface sensitive SRPES. Figure 2 shows the valence band spectra from the GaAs(111)B surface under various conditions. It is found from the valence band spectra that  $E_F$ -VBM varies from 1.2 eV for the S-passivated GaAs with S-Ga bonds to 0.8 eV for the 20 min air-exposed surface. This value of 0.8 eV corresponds to  $\phi_{bi}$ =0.6 eV, which is almost equal to the value predicted by the Advanced Unified Defect Model(AUDM)<sup>5)</sup>. In this case, a band bending of 0.6 eV corresponds to the formation of a depletion region of about 350 Å, which is much smaller than the PL probing depth of about 2,000 Å. Therefore, the PL degradation is not attributed mainly to an extended depletion region, but to surface defects which act as surface recombination centers.

It is found that GaAs(111)A exhibits the most band bending with  $10^6\text{L O}_2$  exposure, while GaAs(100) represents an intermediate case. The GaAs(111)B exhibits the least amount of band bending. However, by exposing to air for 20 min, all surfaces show nearly the same degree of band bending.

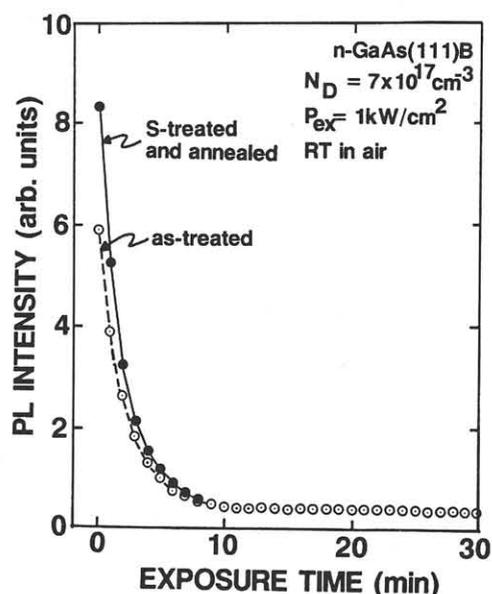


Fig. 1 Photoluminescence intensity change with exposure time to air. The excitation source was an Ar laser with 1 kW/cm<sup>2</sup>.

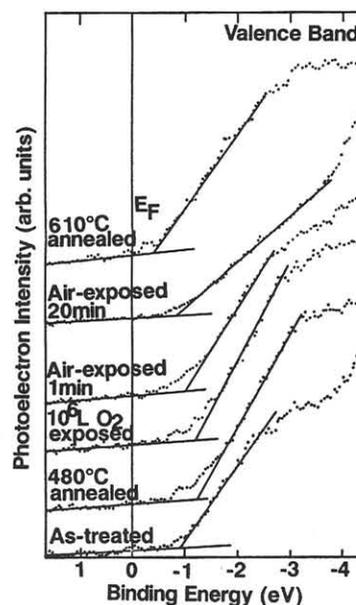


Fig. 2 Valence band spectra of  $(\text{NH}_4)_2\text{S}_x$ -treated and 480 °C annealed GaAs(111)B surfaces exposed to dry oxygen and air. The photon energy was 80.3 eV.

In Fig. 3, the As3d photoelectron spectra from  $(\text{NH}_4)_2\text{S}_x$ -treated GaAs and 480 °C annealed GaAs surfaces which are exposed to dry oxygen gas and atmosphere are plotted. It is found that the S-passivated GaAs surface shows almost no oxidation by dry oxygen, and that exposure to atmosphere for 1 min induces upward band bending although As atoms are not oxidized at all. A small shoulder in the Ga3d spectra indicates Ga is slightly oxidized, resulting in

surface band bending. However, a 0.7 Å thick As<sub>2</sub>O<sub>3</sub> layer is formed, when the sample is exposed for 20 minutes to atmosphere. Furthermore, exposure to atmosphere and UV light heavily oxidizes As at the S/GaAs surface to As<sub>2</sub>O<sub>5</sub>.

For comparison, MBE-grown GaAs(111)B surface was also exposed to air. It should be noted that the S-passivated GaAs surface shows much slower oxidation than the As-terminated surface, indicating the usefulness of the S overlayer in preventing oxidation. Furthermore, the oxidation rate strongly depends on surface orientation. The (100) surface shows the fastest oxidation rate, resulting in the oxide layer of 2.1 Å. This difference in oxidation is too large to be explained by the bonding energies of S-Ga, which are 6.1 eV for (111)B and 5.7 eV for (100). Therefore, there is a possibility that the oxidation is not initiated by Ga-S bond breaking.

From the Ga3d photoelectron spectra exposed for 20 min in air from the S/GaAs surfaces, all surfaces have a GaS<sub>x</sub> component as well as a Ga<sub>2</sub>O<sub>3</sub> component, based on peak deconvolution procedures. The S2p photoelectron spectra were also measured from the same samples using a photon energy of about 210 eV. As shown in Fig. 4, surface S atoms on GaAs(111)B which are strongly bonded to Ga atoms are not oxidized at all even after a 20 min air exposure. The same results were obtained also for the GaAs(111)A and (100) surfaces. These results suggest an oxidation mechanism in which oxygen atoms penetrate through the surface Ga-S layer which acts as a protective layer against oxidation, oxidizing the underlying GaAs layer, while leaving the Ga-S layer unoxidized.

The resistance of the Ga-S layer to oxidation is verified by the fact that surface S is oxidized only by irradiating UV light from a low pressure Hg lamp in atmosphere. An almost identical SO<sub>x</sub>/S-Ga component ratio was observed for the GaAs(111)A and (100) surfaces as well. These results suggest that forming two or three Ga-S layers on top of GaAs surfaces may result in a passivated GaAs surface more resistant to oxidation.

#### 4. Conclusions

The S-passivated GaAs surfaces show the effect of protecting the oxidation reaction. However, oxidation causes a drastic upward band

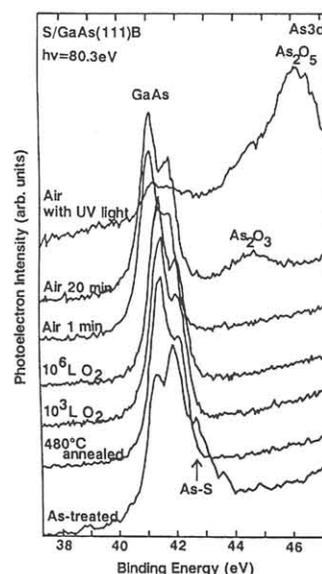


Fig. 3 As3d SRPES spectra of (NH<sub>4</sub>)<sub>2</sub>S<sub>x</sub>-treated and 480 °C annealed GaAs(111)B surfaces exposed to dry oxygen and air. The photon energy was 80.3 eV.

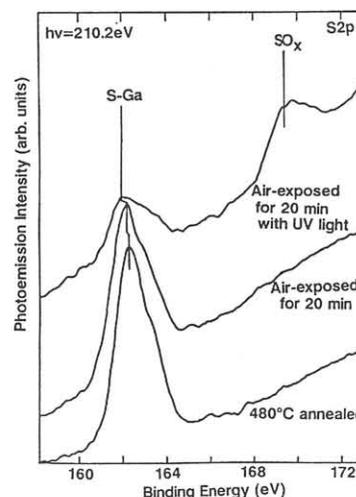


Fig. 4 S2p SRPES spectra of the air-exposed GaAs(111)B, (100) and (111)A surfaces for 20 min after the sulfur treatment and 480°C annealing in vacuum. The photon energy was 210.2eV.

bending of 0.6eV, which is in good agreement with the photoluminescence degradation features. Although the underlying GaAs below the surface is oxidized, the surface S is not oxidized, implying a thicker Ga-S layer may be effective in reducing PL degradation of the S-treated GaAs surface.

#### References

- 1) J. Fan et al., J. J. A. P. 27(1988)L2125.
- 2) C.J. Sandroff et al., J. V. S. T. B7(1989)841.
- 3) H. Sugahara et al., Surf. Sci. 242(1991)335.
- 4) T. Ohno et al., Phys. Rev. B42 (1990) 11194.
- 5) W.E. Spicer et al, J. V. S. T. B6(1988) 1245.