Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 739-741

Dry Sulfur Passivation of GaAs Surface Using ArF Excimer Laser with H_2S

M.Totsuka, N.Yoshida, S.Chichibu, T.Akane, H.Uji, H.Higuchi*, and S.Matsumoto
Department of Electrical Engineering, Faculty of Science and Technology, Keio University, 3-14-1, Hiyoshi, Yokohama 223, Japan
*Bentec Corporation, Tachihi No.30, 6-1 Sakae, Tachikawa, Tokyo 190, Japan

A new dry surface passivation using ArF excimer laser with H_2S gas was examined on GaAs(001). Native oxides at the surface were etched away by first laser irradiation in vacuum. By subsequent laser irradiation in H_2S gas ambient, GaAs surface was covered with sulfur atoms. This dry passivation technique is superior to the wet passivation process using $P_2S_5/(NH_4)_2S$-treatment in terms of the reduction of oxygen and the sulfur coverage ratio.

I. INTRODUCTION

A high density of surface states on the GaAs surface tends to fix the surface Fermi level. To reduce this surface states, sulfur passivation using inorganic compounds such as Na_2S, $(NH_4)_2S_x$, and $P_2S_5/(NH_4)_2S$ have been investigated[1)-6)]. Such aqueous sulfur treatments, however, have serious problems such as poor reproducibility and contamination of heavy metals. If surface passivation process is carried out in vacuum, these problems will be overcome. Therefore, dry passivation is much of interest.

We use ArF excimer laser to clean and passivate GaAs surface in H_2S gas ambient. The new dry passivation technique was compared with the wet $P_2S_5/(NH_4)_2S$-treatment and its chemical passivation mechanism was discussed.

II. EXPERIMENTAL

The samples were Si-doped n-GaAs(001). After etching samples in $H_2SO_4:H_2O_2:H_2O=3:1:1$ solution, they were placed into the chamber. An ArF excimer laser (λ=193 nm) with a full width at half-maximum (FWHM) of 17 ns was used for surface passivation. Passivation process using ArF excimer laser consists of the following two steps: (i) Surface cleaning process was carried out by the ArF excimer laser irradiation on the GaAs substrate perpendicularly in vacuum under conditions of energy density of 53 mJ/cm^2, repetition frequency of 100 Hz, and irradiation time of 15 to 300 sec. (ii) Sulfur-treatment was carried out by laser irradiation in H_2S gas ambient with partial pressure of 5 Torr immediately after the first step. 10.4% H_2S diluted with H_2 was used. The number of irradiated laser pulses was set at 1 with energy density of 53 mJ/cm^2.

Surface analyses by Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) were performed before and after the $P_2S_5/(NH_4)_2S$ or H_2S treatment.

III. RESULTS AND DISCUSSION

Figure 1 shows the dependence of the relative Auger peak-to-peak height (APPH) of Ga/Ga, As/Ga, O/Ga, and C/Ga upon surface cleaning time. When the number of irradiated laser pulses is 1, C/Ga considerably decreases, but O/Ga decrases insufficiently. By the irradiation of 15s at 100 Hz, O/Ga decreases sufficiently and saturates after 15s. On the other hand, while As/Ga increases after 1 pulse and 15s irradiations, it also decreases to the level similar to that of $P_2S_5/(NH_4)_2S$-treatment and saturates after 30s irradiation. Therefore after surface cleaning for 30s at 100 Hz, surface becomes clean and stoichiometric. $P_2S_5/(NH_4)_2S$-treatment data are also shown in Fig.1 and surface cleaning data are comparable to them. From these results, surface cleaning with ArF excimer

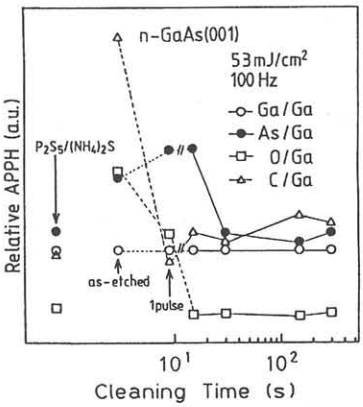

Fig.1. A dependence of the relative Auger peak-to-peak height of Ga/Ga, As/Ga, O/Ga, and C/Ga upon surface cleaning time.

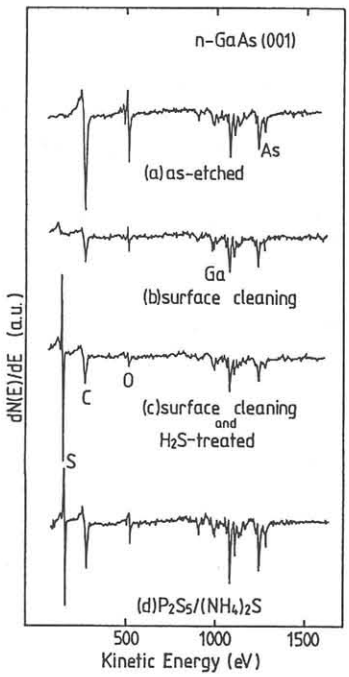

Fig.2. AES spectra from GaAs surface prepared by (a) as-etched, (b) surface cleaning, (c) surface cleaning and H_2S-treatment, and (d) $P_2S_5/(NH_4)_2S$-treatment.

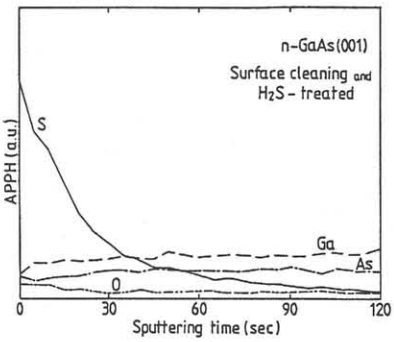

Fig.3. AES depth profiles of Ga, As, O and S in surface cleaning and H_2S-treated sample.

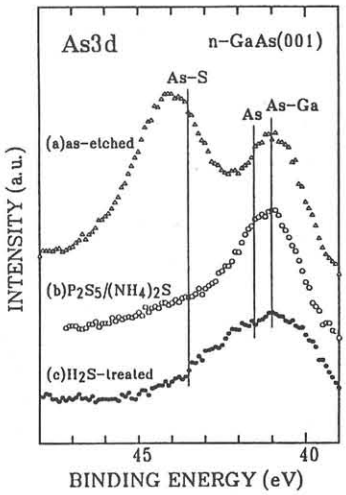

Fig.4. Angle-resolved XPS spectra of the As 3d core levels from GaAs surface prepared by (a) as-etched, (b) $P_2S_5/(NH_4)_2S$-treatment, and (c) H_2S-treatment.

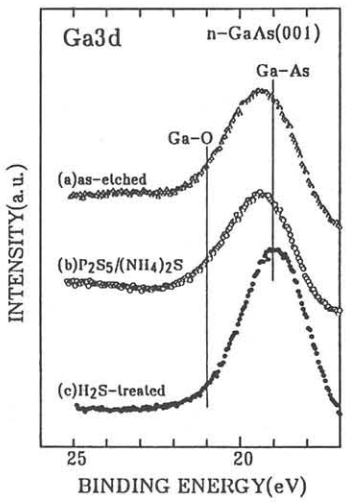

Fig.5. Angle-resolved XPS spectra of the Ga 3d core levels from GaAs surface prepared by (a) as-etched, (b) $P_2S_5/(NH_4)_2S$-treatment, and (c) H_2S-treatment.

laser irradiation is found to be effective to the same as $P_2S_5/(NH_4)_2S$-treatment in terms of carbon and oxygen reductions.

Figure 2 shows the AES spectra from GaAs surfaces. As shown in Fig.2(a), as-etched sample is covered with carbon and oxygen. These carbon and oxygen, however, are removed sufficiently by surface cleaning shown in Fig.2(b). Furthermore, after the H_2S-treatment, shown in Fig.2(c), the surface is covered with sulfur keeping C and O signals low. The S coverage and O reduction by the surface cleaning and H_2S-treatment are superior to those by $P_2S_5/(NH_4)_2S$-treatment(Fig.2(d)).

Figure 3 shows the AES depth profiles of Ga, As, O, and S in surface cleaning and H_2S-treated sample. The results confirm that there is less oxygen on the surface of GaAs substrate by both surface cleaning and H_2S-treatment. We should expect that the sulfur layers protects GaAs surface from absorption of oxygen.

Figure 4 shows angle-resolved XPS spectra ($\theta = 20°$) of the As 3d core level on the GaAs surface. As 3d reference energy of 41.0 eV for GaAs, 41.5 eV for elemental arsenic, and 43.5 eV for As_2S_3 are indicated by vertical lines. As-etched spectrum exhibits two peaks at binding energies of 41.0 eV and 44.1 eV. The former peak results from the GaAs, and the latter peak is assigned to a signal from oxidized arsenic. A signal from As_2O_3 is known to be observed at a binding energy of 44.9 eV, which is somewhat higher than the peak energy position 44.1 eV observed here. This result suggests the existence of suboxides, for example, AsO (43.0 eV) and As_2O (43.9 eV). In

both (b) $P_2S_5/(NH_4)_2S$- and (c) H_2S- treatment samples, however, the latter peaks (44.1 eV) vanish and the small shoulder peaks appear nearly at the As_2S_3 reference energy (43.5eV). In addition, the shoulder of H_2S-treatment is higher, so the sulfur atoms bonded to As exist more than $P_2S_5/(NH_4)_2S$-treatment.

Figure 5 shows the XPS spectra for the Ga 3d core level. Ga 3d reference energy of 19.0 eV for GaAs and 21.0 for Ga_2O_3 are shown by vertical lines. For the as-etched surface, Ga 3d peaks has a small shoulder, which is observed nearly at the Ga_2O_3 reference energy. By the (b) $P_2S_5/(NH_4)_2S$-treatment, this small shoulder almost vanishes. Also by the (c) H_2S-treatment, its shoulder vanishes and moreover Ga 3d peak becomes narrow and shifts to the energy position of the GaAs standard.

Results of Figs.4 and 5 indicate that the sulfur atoms on the H_2S-treated sample have S-As bond superior to $P_2S_5/(NH_4)_2S$-treatment shown in Fig.4(c). Therefore, ArF excimer laser irradiation in H_2S gas ambient after surface cleaning is effective for prevention of oxygen chemisorption on the GaAs surface, though we cannot identify Ga-S bond.

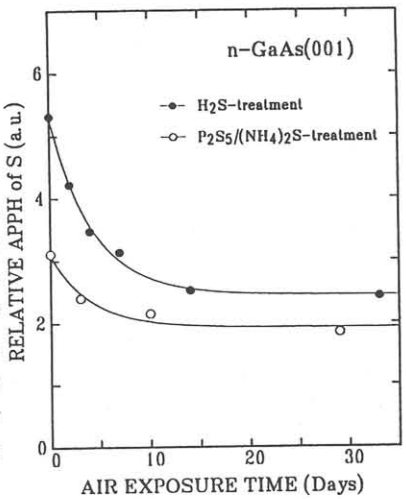

Fig.6. The time dependent decrease of the relative APPH of sulfur by air exposure. The exponential curves are fitted by method of least squares.

Figure 6 shows the dependence of the relative APPH of S/Ga upon air exposure time. The exponential curves are fitted by method of least squares using the following equation.

$$S=S_{sat}+(S_0-S_{sat})\exp(-at)$$

(where t: air exposure time(days), S_{sat}: saturation level of the relative APPH of S, S_0: S(t=0), a: attenuation constant)
Results of the fitting parameters are S_{sat}=2.44, a=0.233(for H_2S-treatment), and S_{sat}=1.92, a=0.241(for $P_2S_5/(NH_4)_2S$-treatment) The relative APPH of sulfur decreased rapidly by air exposure with almost the same attenuation constant in H_2S-treated and $P_2S_5/(NH_4)_2S$-treated samples. The saturation level of the relative APPH of sulfur(S_{sat}) in H_2S-treated sample is, however, higher than $P_2S_5/(NH_4)_2S$-treated sample. We suppose that it results from the superiority of H_2S-treatment in S-As bonding.

IV. SUMMARY

In summary, the native oxides of GaAs surface were etched away by surface cleaning procedure using ArF excimer laser irradiation in vacuum. Sulfur atoms deposited by the photolysis with ArF excimer laser on the surface had As-S bond. In addition, the superiority of dry passivation technique is shown compared with wet processes in terms of the reduction of oxygen, the sulfur coverage ratio, and the decrease of sulfur atoms by air exposure.

Acknowledgements

The authors would like to thank Benkan Corp. for the supply of many sterilized parts. They would also like to thank Douwa Kougyo Co., Ltd for the supply of the wafers.

References

1) C.J.Sandroff, R.N.Nottenburg, J.C.Bischoff, and R.Bhat, Appl.Phys.Lett. 51, 33(1987).
2) E.Yablonovitch, C.J.Sandroff, R.Bhat, and T.Gmmiter, Appl.Phys.Lett. 51, 439(1987)
3) Y.Nannichi, J.Fan, H.Oigawa, and A.Koma, Jpn.J.Appl.Phys. 27, 2367(1988)
4) K.C.Hwang, and S.S.Li, J.Appl.Phys. 67, 2162(1990)
5) H.Oigawa, J.Fan, Y.Nannichi, H.Sugahara, and M.Oshima, Jpn.J.Appl.Phys. 30, 322(1991)
6) Y.Wang, Y.Darici, and P.H.Holloway, J.Appl.Phys. 71, 2746(1992)