

Invited**The Effect of Sulfur on the Surface of III-V Compound Semiconductors**

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The surface of III-V compound semiconductors has been mysterious and uncontrollable. Of recent, treatment with sulfide solution offered a series of remarkable improvements with possibility of permanent stabilization. We present characteristic improvements and understanding of the surface/interface structure in various combination of the substrate semiconductor and the treatment chemicals. Prospects are also presented.

I INTRODUCTION

Defects at surface as well as in bulk of III-V compound semiconductors have long been mysterious and uncontrollable. It was first claimed in 1986 that GaAs surface was finally under control by photochemical washing process as photoluminescence intensity increased. The effect was connected with the deletion of cluster As, which became soluble upon photoexcited oxydation. However, the surface was not permanently stabilized as As was found to reaccumulate in the oxide.

In 1987 was reported the surface treatment with Na_2S solution reduced remarkably the surface recombination velocity. However, in this case also, the effect was again temporary only so long as a film of Na_2S remained on the treated surface.

In 1988, we presented¹⁾ that by treating GaAs surface with $(\text{NH}_4)_2\text{S}_x$ the improvement could be more effective. The effect is very much different from that with Na_2S . Here, we

discuss the effects of various sulfides and sulfur treatments.

II WET PROCESS OF SULFIDE TREATMENT

The wet process of sulfide treatment is simple and straightforward. An etched GaAs wafer is dipped into Na_2S , $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{S}_x$ solution followed by blow drying immediately after taking it out of the solution.

The natural oxide is quickly etched in the last solution but not so quickly in the second, and unetched in Na_2S . The etching speeds for GaAs are much slower, but their order for the three solutions is preserved. The difference may well come from pH and the presence of excess S^{2-} .

After either treatment, the surface is covered with a visually recognizable residual coverage and the surface recombination velocity is reduced, which is confirmed by an increase in photoluminescence or in the current amplification factor of a transistor.

However, there is an essential

difference between Na_2S treatment and $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{S}_x$ treatment. In the first, the residual film is not flat (Fig. 1-A) and an accumulation of Na is observed by Scanning Auger Electron Microscopy (Fig. 1-B). The film is readily soluble in water or deliquescent in moisture. The magic effect of Na_2S is thus easily lost, while the process is reapplicable with reproducibility.

In contrast, the covering film after $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{S}_x$ treatment is smooth (Fig. 1-C) and uniform (Fig. 1-D).

Further surface analyses reveal the cause of the difference. AES analysis shows that the surface after Na_2S treatment contains Na and S. Presence of O at surface and interface is observed (Fig. 2-B). After rinsing in water, the residual film is almost completely removed and the growth of oxide is observable on the surface same as that on the freshly etched surface (Fig. 2-A).

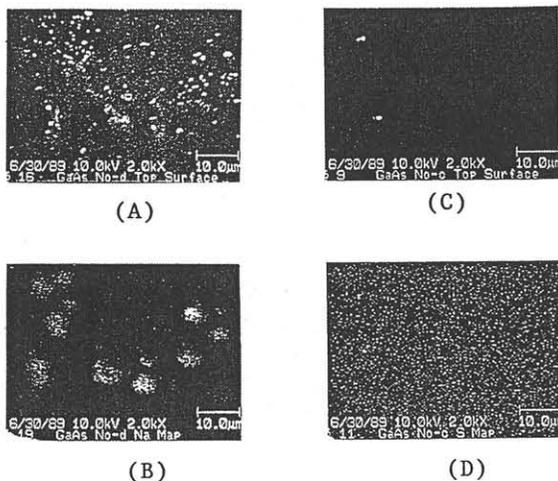


Fig. 1 Surface Observation; Smoothness by SEM on (A) Na_2S - , and (C) $(\text{NH}_4)_2\text{S}_x$ -treated GaAs. Surface distribution by SAM of (B) Na on Na_2S - , and (D) S on $(\text{NH}_4)_2\text{S}_x$ -treated GaAs, respectively.

In the case of $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{S}_x$ treatment, originally yellowish residual film disappears when kept in vacuum for analyses. So the compositional analysis of the film is difficult to perform. However, amorphous sulfur would be a reasonable guess from its vapor pressure and the contamination of the vacuum chamber. The treated surface is almost completely free from adsorbing oxygen as seen in Fig. 2-C. This is meaningful in that active oxygen is prohibited of chemisorption on the treated GaAs surface.

Observations on the bond states at the interface of $(\text{NH}_4)_2\text{S}$ or $(\text{NH}_4)_2\text{S}_x$ treated GaAs clearly shows the absence of O-As and/or O-Ga bonds, which was not the case with Na_2S treatment.

III STRUCTURES OF TREATED SURFACE AND INTERFACE³⁾

We present a simplified model of the treated surface as schematically illustrated in Fig. 3:

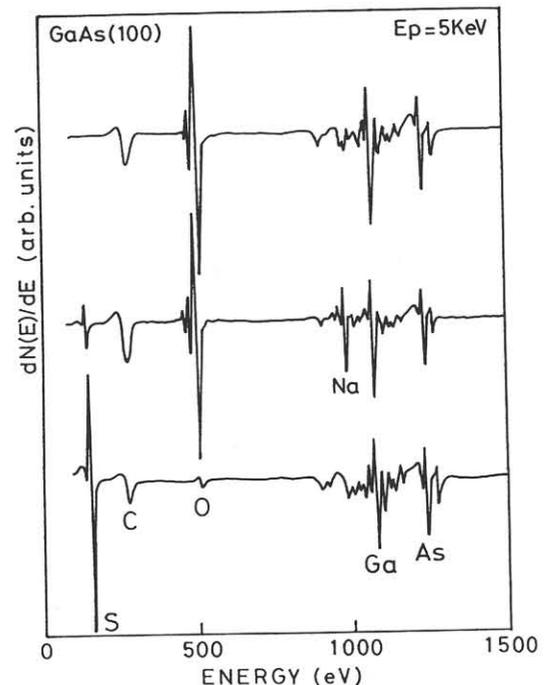
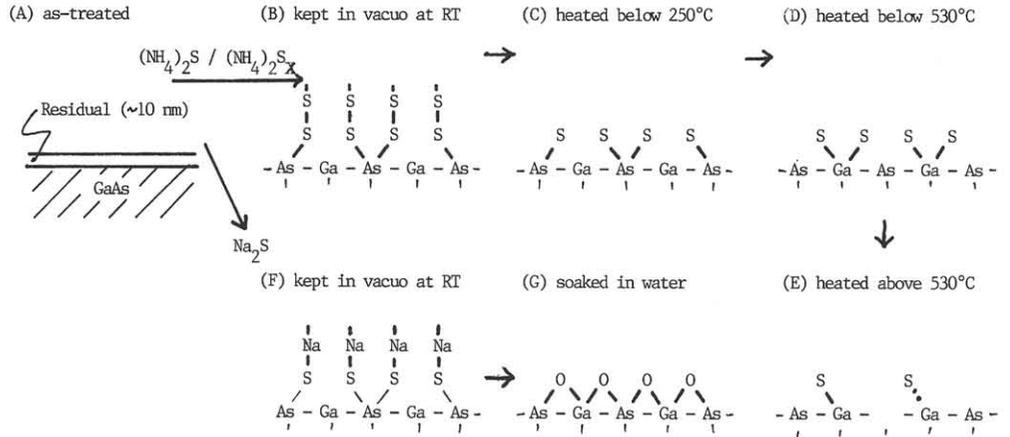


Fig. 2 Atomic identification on the surface by AES; (A) as-etched, (B) Na_2S - and (C) $(\text{NH}_4)_2\text{S}_x$ -treated GaAs.

Fig. 3 A simplified scheme of the change of the residue (A); Sulfur bonds after $(\text{NH}_4)_2\text{S}_x$ treatment change with temperatures (B - C - D - E). But Na_2S treatment gives a different behavior (F - G).



A) As-treated surface is covered with a visible, about 10nm-thick film of amorphous S (or Na_2S).

B) Kept in vacuum at RT, amorphous sulfur sublimates quickly but some S-S bonds still remaining. No oxygen is observed, and S-As bonds are dominant. S-Ga bond is barely observable or masked by the peak of S-As.

C) By heating in vacuum, S-S bonds disappear forming a monolayer of sulfur. Sulfur atoms correspond one to one with the substrate alignment resulting in a 1x1 structure. The exact positioning of S atoms is uncertain and now eagerly sought.

D) Heated at higher temperatures above about 250°C, S atoms on the surface undergo reconstruction by forming a 2x1 structure. This transition is characterized by disappearance of the dominant S-As bonds replaced by S-Ga bonds.

E) S-Ga bonds are stable up to 500°C. Above that, S atoms gradually disappear. Sulfur atoms are losable by other means such as irradiation of light or electron beam.

F) In case of Na_2S residual, nothing

happens in vacuum.

S-Na and S-As as well as O-As and O-Ga bonds are observed.

G) S-As bonds are lost by rinse in water which implies that the S-As bond for Na_2S differs from that for ammonium (poly)sulfide.

When we deposit Al on the treated surface, new bonds of Al-S are observed to form³⁾ as shown in Fig. 4.

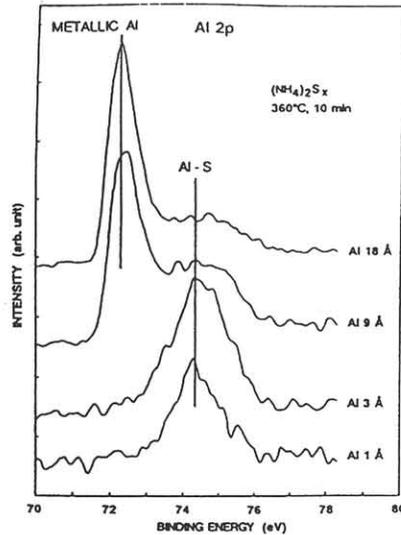


Fig. 4 Bond of Al-S is formed on deposition of thin(1 18Å) aluminum.

IV REDUCTION IN SURFACE/INTERFACE DEFECT DENSITY

Electrical characteristics of Schottky and MIS structures give a good index as to the interface defect density. The barrier height is fixed for normally treated surface, whereas that for S-treated surface varies fairly proportionally with the work function of the contact metal (Fig. 5).

Interface state density is calculated from C-V curves in MIS structures in Fig. 6, which clearly shows the reduction is achieved by sulfide treatment⁴⁾.

Though a phenomenological interpretation of the effect of defect an-

nihilation is presented²⁾, a full account for the improvement could not be given before a complete comprehension of surface defect itself is obtained.

However, it is somehow agreed upon that one of the cause for the defectful interface of natural oxide/GaAs is the reacting oxygen. Some of IIIb-VIb compounds tend to form the layered structure which has a rather weak interlayer coupling. Therefore, it is, by any means, not surprising when we find a similar effect in a good number of combinations of S or Se with (GaAl)As, GaP, InAs, InP, etc.

V FUTURE PROSPECTS

The treatment is readily applicable to the modification of the barrier height either for lower contact resistance or for higher breakdown voltage.

The specific effect of sulfur treatment appears to lie in the ability: a) to expose fresh surface of III-V compound, and b) to cover instantly with sulfur monolayer forming a sort of layered structure. In those days, dry process is preferred over wet process.

When the fresh surface is provided, there seems no problems as to the sulfurization of the surface.

From a different point of view, the wet process can provide a slow etch rate, a mask of monolayer thickness, sensitivity to light or particle beam, etc. Then, why not use it for superfine lithography?

The process is also applicable to epitaxial growth when the electrical doping is not of primary concern.

It is evident that the sulfur reacts with air or moist, even though, slowly and mildly. It is absolutely necessary to find out an effective means to prevent the reaction.

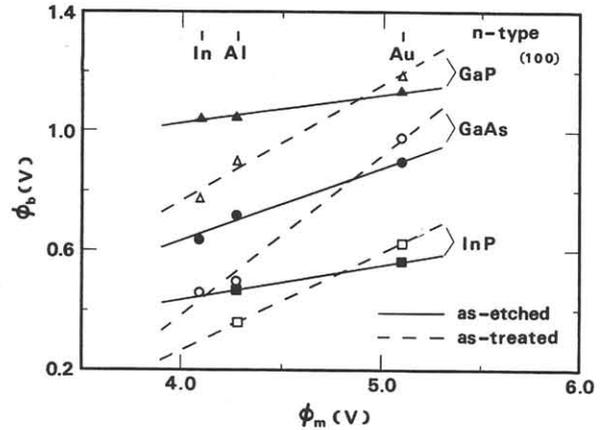


Fig. 5 Barrier height dependency on as-etched and treated surfaces.

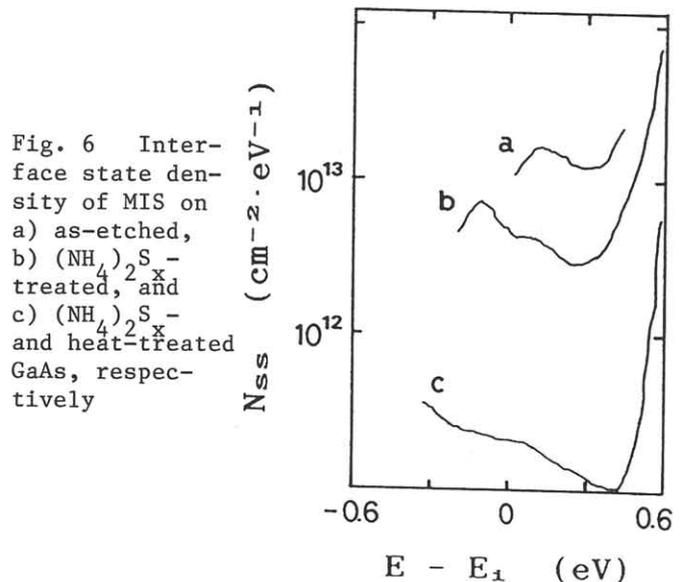


Fig. 6 Interface state density of MIS on a) as-etched, b) $(\text{NH}_4)_2\text{S}_x$ -treated, and c) $(\text{NH}_4)_2\text{S}_x$ - and heat-treated GaAs, respectively

In conclusion, We stress that this process can supply invaluable data to the understanding of surface defects, which can help the technology to develop, in turn.

ACKNOWLEDGEMENTS

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