

Stabilization of GaAs Surface/Interface by Sulfur Treatment

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Stabilization of the GaAs surface/interface by the $(\text{NH}_4)_2\text{S}$ treatment has been investigated. Enhancement of Photoluminescence intensity and drastic improvement of Capacitance-Voltage characteristics on metal-insulator-semiconductor(MIS) structures prepared by this treatment lead to the reduction of surface recombination velocity and surface state density. Auger electron spectroscopy and low-energy electron energy loss spectroscopy indicate that the removal of oxide or As on the surface and the passivation of the GaAs surface by one monoatomic Sulfur layer.

1. Introduction

The sole dominance of silicon as VLSI material is accounted for the controllability of its surface. On the contrary, GaAs regarded as a material superior to silicon in many aspects, is yet to be controlled of defects, especially at the surface/interface, before GaAs will be extensively used in more electronic devices.

However, two processes of GaAs surface treatments give important and interesting results. One is "the photochemical washing¹⁾" whose effect remains only for a limited period. The other process is "the sulfides treatment²⁾" of which the best seems to give very stable and enduring surface/interface of GaAs.

Here we investigate the effect and the role of sulfur to account for the substantial reduction in surface trap density of GaAs by $(\text{NH}_4)_2\text{S}$ treatment.

2. Experimental

The investigation was performed mostly on the surface of n-type GaAs. Most of the time, it was done on (100) plane of the HB, LEC or VPE crystal with carrier concentration in the range of $5 \times 10^{15} \text{cm}^{-3}$. The sample was etched first in $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2\text{-H}_2\text{O}(5:1:1)$ solution at 60°C for 1 min, in the same solution with a different composition(5:1:40) at RT for 20 sec, and rinsed in deionized(DI) water. The cleaned sample was dipped into $(\text{NH}_4)_2\text{S}$ solution at RT for a certain period ranging from

several seconds to several hours. We chose $(\text{NH}_4)_2\text{S}$ rather than reported $\text{Na}_2\text{S}_9\text{H}_2\text{O}^{2,3)}$ in fear of the unknown contamination effect by the alkali metal. The $(\text{NH}_4)_2\text{S}$ solution was supersaturated with sulfur and we found the etching rate of the solution varied with the degree of supersaturation.

After taking the sample out of the treating solution, the droplet were blown off from the surface with dry N_2 . Existence of a very thin residual film was observable with naked eyes as whitish as a result of light scattering. Its thickness was measured to be about 10nm with Talstep[®], a piezoelectric surface profiler. This very thin film was found to disappear in a matter of half an hour in vacuum, while it remains unchanged in air. Without blowing-off, yellowish residue can accumulate as thick as $30\mu\text{m}$.

The evaluation of surface properties was performed by photoluminescence(PL) for surface recombination velocity change, capacitance-voltage(C-V) measurement on MIS structures for interface state density and band bending, and C-V measurements on Schottky barriers for barrier height. Auger electron spectroscopy(AES) and low-energy electron energy loss spectroscopy(LEELS) were also employed to study the atomic structure of the surface.

3. Results

The effect of $(\text{NH}_4)_2\text{S}$ treatment on the intensity of PL on GaAs(100) surface at RT in air is shown in

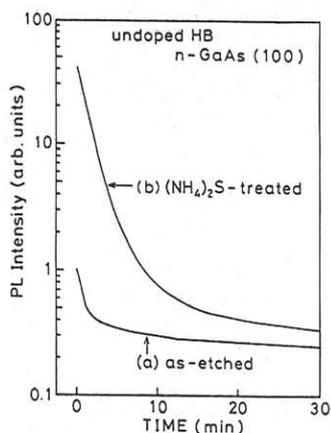


FIG.1. Degradation behavior of PL intensity in undoped HB GaAs($n; 5 \times 10^{15} \text{cm}^{-3}$) under 514.5nm Ar^+ laser excitation at 1.2KW/cm^2 . (a) as-etched and (b) $(\text{NH}_4)_2\text{S}$ -treated surface.

Fig.1. The initial intensity was improved by a factor of two orders of magnitude by the $(\text{NH}_4)_2\text{S}$ treatment. Also noted is that the rate of degradation was improved. Observation worth mentioning is that even after heavy ($>10^{-1}$) degradation the $(\text{NH}_4)_2\text{S}$ -treated surface is refreshable with another $(\text{NH}_4)_2\text{S}$ treatment.

Figure 2 shows C-V characteristics of metal-insulator-semiconductor(MIS) structures fabricated by an electron beam deposition of SiO_2 on the surface of VPE GaAs($n; 1.5 \times 10^{15} \text{cm}^{-3}$): (I) as-etched, (II) $(\text{NH}_4)_2\text{S}$ -treated, and (III) $(\text{NH}_4)_2\text{S}$ -treated and annealed at 300°C for 30 min. As can be seen, frequency dispersion in the accumulation region is markedly reduced from 50%(I) to about 10%(III), in the frequency range from 10^3Hz to 10^6Hz . The in-

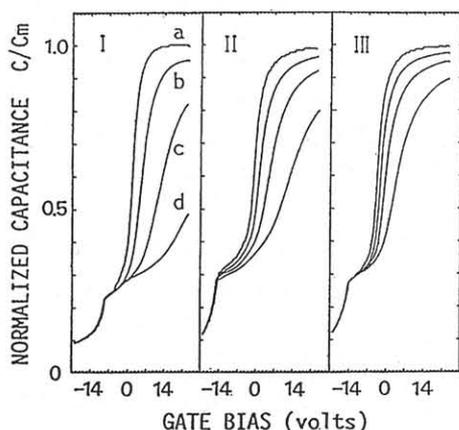


FIG.2. C-V characteristics of MIS structures measured at RT. (I) as-etched, $C_m = 41.0 \text{nF/cm}^2$, (II) etched and $(\text{NH}_4)_2\text{S}$ -treated, $C_m = 32.6 \text{nF/cm}^2$, and (III) same as (II) with additional $300^\circ\text{C}/30 \text{min}$ annealing, $C_m = 32.2 \text{nF/cm}^2$. Curves (a), (b), (c) and (d) are for measuring frequencies of 10^3 , 10^4 , 10^5 and 10^6Hz , respectively. The bias scanning rate is 0.1V/s .

terface state density N_{SS} , was estimated from the 10^6Hz C-V characteristics by Terman's method. The dominant pinning levels near 0.6eV below the conduction band minimum was found to reduce remarkably from $1.3 \times 10^{13} \text{cm}^{-2} \text{eV}^{-1}$ (I) to $2.2 \times 10^{12} \text{cm}^{-2} \text{eV}^{-1}$ (III). Detail of the analysis is reported elsewhere⁴.

It has been accepted that the barrier height of Schottky barriers on GaAs was almost fixed, independent of the work function of the deposited metal. We estimated the barrier height from C-V measurements and found the barrier height change for $(\text{NH}_4)_2\text{S}$ -treated GaAs. Table 1 shows the results for as-etched and $(\text{NH}_4)_2\text{S}$ -treated GaAs in comparison with theoretical values. It is obvious that the barrier height does change in case of Al close to the calculated value assuming no pinning traps. It suggests that the density of pinning traps decreases with $(\text{NH}_4)_2\text{S}$ treatment. However, in case of Pd and Pt, no change was observed. We may explain this observation by the temperature rise of the GaAs surface during Pd or Pt evaporation. We should add a word that the barrier height change is observed even with the shortest period (3 sec) of $(\text{NH}_4)_2\text{S}$ treatment and that the degree of the change seems to be independent of the dipping periods ($<10 \text{hrs}$).

The summed-up result of the study by means of AES on the surface is shown in Fig.3. For as-etched GaAs surface (a), presence of oxygen is revealed from the strong signals at 51, 77, and 104eV in addition to the signal at 510eV . After $(\text{NH}_4)_2\text{S}$ treatment (b), the above mentioned signals disappeared completely, implying the oxygen-free surface. Peak difference Δ near 1070eV is large, which means the stoichiometry is conserved (III-b)⁵. Surface degradation after 1 min of PL excitation at 10W/cm^2 can be seen for (c); Oxygen-related signals begin to increase. The tendency is further enhanced (d) for stronger excitation level (40W/cm^2 for 1 min). Degradation of the

Table 1. Variation of the Schottky barrier heights for Al, Pd and Pt/GaAs Schottky diode before and after $(\text{NH}_4)_2\text{S}$ treatment, on the n and p type HB GaAs(100) with carrier concentration of $2 \times 10^{16} \text{cm}^{-3}$ and $5 \times 10^{16} \text{cm}^{-3}$, respectively.

metal	work function (eV)	as-etched (eV)	$(\text{NH}_4)_2\text{S}$ -treated (eV)	theoretical values (eV)
Al	4.25	(n) 0.83	0.49	0.18
		(p) 0.62	1.10	1.24
Pd	4.80	(n) 0.98	0.94	0.73
Pt	5.30	(n) 1.05	1.05	1.23

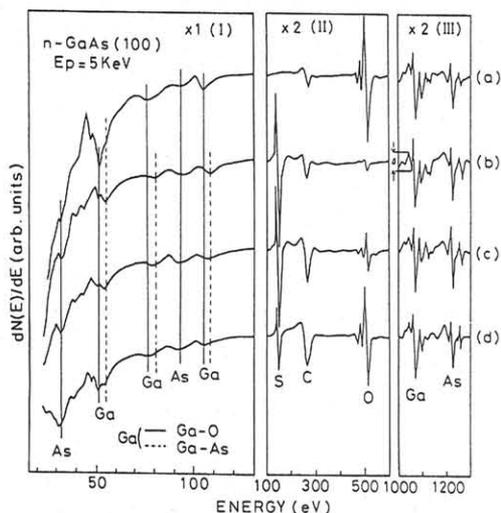


FIG.3. AES spectra from the n-GaAs(100) surfaces; (a) as-etched, (b) $(\text{NH}_4)_2\text{S}$ -treated, (c) and (d) $(\text{NH}_4)_2\text{S}$ -treated after exposed to Ar^+ laser irradiation for 1 min at 10 and 40 W/cm^2 , respectively, which correspond to the degradation of PL intensity.

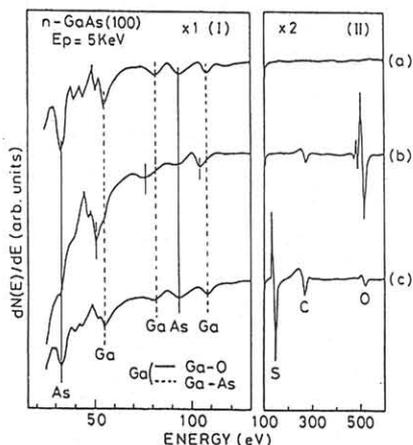


FIG.4. AES spectra from the n-GaAs(100) surfaces; (a) Ar^+ sputtered(fresh), (b) once fresh but exposed to air for 12h, and (c) $(\text{NH}_4)_2\text{S}$ -treated and exposed to air for 12h.

sample is more pronouncedly observed on the photochemically washed surface⁶). It is deduced by comparing the signal intensity of fresh GaAs and that from $(\text{NH}_4)_2\text{S}$ -treated surface(I-b), the sulfur layer is one or two monoatomic layers thick. The presence of one or two monoatomic layer of sulfur is consistently observed after the sample was kept in vacuum for more than 30 min.

Figure 4 shows the stability of the GaAs surface in air for (a) the cleaned Ar^+ sputtered- GaAs surface, (b) the once cleaned surface after 12h exposure to air, and (c) the $(\text{NH}_4)_2\text{S}$ -treated surface after 12h exposure to air. For the once cleaned surface (b), presence of oxygen can be seen from the chemical shifts, i.e., Ga(108 \rightarrow 104eV and 81 \rightarrow 77eV), as well as the depletion of As(33eV). On

the contrary, The $(\text{NH}_4)_2\text{S}$ -treated surface remains unchanged resembling the clean surface.

Thus AES data tentatively confirm the followings; (1) presence of one or two monoatomic sulfur, (2) the $(\text{NH}_4)_2\text{S}$ -treated surface is free of oxygen, (3) surface degradation by photoexcitation is related to the appearance of oxygen, and deviation from the stoichiometry.

More detailed study on the surface is performed by means of LEELS. Figure 5 shows the results with LEELS observation on $(\text{NH}_4)_2\text{S}$ -treated GaAs(100) surface. It must be noted that all spectra were taken with the energy resolution of about 0.5eV. The information depth changed from 2 to 10 Å for the primary electron energy, E_p (70-1600 eV), in Fig.5. Effect of sulfur on LEELS spectra are seen only for $E_p < 200\text{eV}$ and the spectra are nearly the same as those of clean GaAs surfaces for $E_p \geq 200\text{eV}$. Hence, we deduce the thickness of the covering sulfur to be less than 3 Å. The most remarkable effect of the sulfur coverage on LEELS spectra for $E_p < 200\text{eV}$ is the nonexistence of the peak at 20eV, which is observed clearly in the LEELS spectrum of a clean GaAs surface⁷).

Stability of the $(\text{NH}_4)_2\text{S}$ -treated surface against heat treatment in vacuum was studied. Spectra of LEELS were essentially unchanged for the isochronal(20 min) heat treatment up to 520°C except for the effect by carbon. Figure 6 shows the

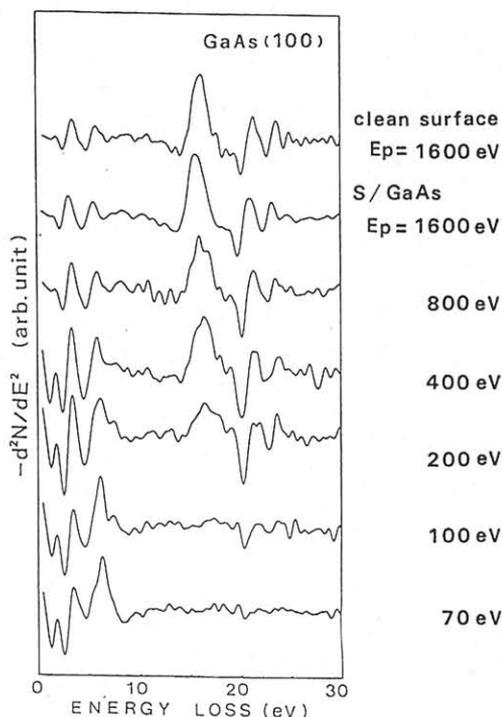


FIG.5. LEELS spectra of $(\text{NH}_4)_2\text{S}$ -treated GaAs(100) surface at RT for various primary electron energies.

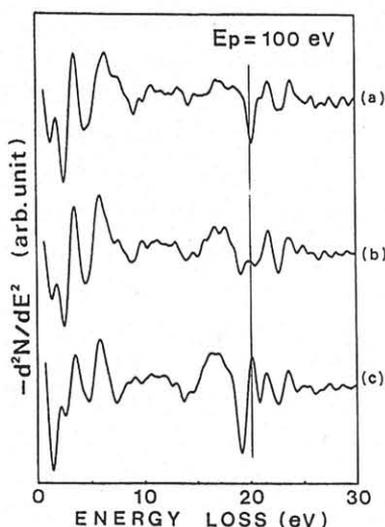


FIG.6. LEELS spectra of $(\text{NH}_4)_2\text{S}$ -treated GaAs surfaces heated for 20 min in vacuo at (a) 520°C, (b) 550°C, and (c) 570°C. The coverage ratios R_S of sulfur on the surface are $R_S=1, 0.6, \text{ and } 0$, respectively.

change by the heat treatment at higher temperatures. As seen in Fig.6(b) at 550°C, a new peak emerges at 20eV, which is assigned to excitation from the Ga 3d core level to the empty state - so-called dangling bond state⁷). The peak(20eV) grows(c) at higher temperature(570°C).

4. Discussions

We now sum up the effect of $(\text{NH}_4)_2\text{S}$ treatment on GaAs surface. (1) From the data of PL, we deduce that the surface recombination velocity is drastically reduced⁸), together with the degradation rate. (2) Analysis on the C-V characteristics tells us that the interface state density is reduced by a factor of ten. (3) Data of AES measurements indicates that the surface is covered with one or two sulfur atomic layer, free of oxygen adsorption, and kept at stoichiometry. Photoexcitation brings about surface degradation in the form of off-stoichiometry and chemical adsorption of oxygen⁹). Though it degrades, the degradation speed is much lower than for photochemically washed surface and simply etched surface. Finally, (4) the observation by LEELS reveals (i)that the sulfur layer is one monolayer thick, (ii)that the so-called dangling bond is unobserved after surface treatment, and (iii)that the sulfur atoms are removed by the heat treatment higher than 530°C.

We may give an interpretation here that by the $(\text{NH}_4)_2\text{S}$ treatment, after the surface oxides on GaAs is quickly etched, then the GaAs surface slowly etched⁴), and the pristine GaAs surface is covered

with a monoatomic layer of sulfur. The bond between sulfur and gallium (and/or arsenic) is so stable that the outflow of arsenic atoms by the adsorption of oxygen is hindered, because even oxygen, which is very active, is unable to adsorb on the stabilization layer of sulfur. This could be attributed to the layered structure of bulk GaS.

5. Conclusion

The change of GaAs(100) surface characteristics between as-etched and $(\text{NH}_4)_2\text{S}$ -treated samples were determined by means of PL, electrical measurements, AES, and LEELS. The physical and chemical stability at the sulfur(one monoatomic layer)/GaAs interface after $(\text{NH}_4)_2\text{S}$ treatment is considered to be due to both the oxides or As free surface and the passivating effect of sulfur atoms.

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