

Sulfur-Treatment and Hydrogenation Effects in GaAs

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Photoluminescence (PL) and photorefectance (PR) measurements on a Si-doped GaAs bulk and a nominally undoped GaAs layer have been carried out to investigate the surface state behavior for sulfur-treated GaAs as well as the neutralization of the carbons and the variation of the charges for hydrogenated and nitrogenated GaAs. A variation of the surface states and neutralization of the ions affect the intensity of the PL spectra and the intensity and the broadening parameter of the PR signal.

I. Introduction

GaAs compound semiconductors have many advantages for high-speed devices, such as high mobilities and high saturation drift currents, in comparison with Si semiconductors. Although GaAs has many merits, it is still impossible to fabricate a metal-insulator-semiconductor field-effect transistor (MISFET) with a high-quality insulator-semiconductor interface because of the Fermi-level pinning on the GaAs surface [1-3]. When a Schottky metal is evaporated on the GaAs, the Schottky barrier height does not depend on the work function of the metal.

Many studies have been based on the goal of solving the Fermi-level pinning problem. Recently, passivation of the defects, and subsequent improvement of the quality of devices based on GaAs, through sulfur treatment was reported [4-6].

The role of the hydrogen atom is also very attractive because of the significant improvement in the electrical and optical properties of GaAs due to hydrogen-atom injection into the semiconductor materials [7-9]. Although Hall-effect and capacitance-voltage measurements are usually used to investigate the charge distribution in such materials, metal contacts are required for those measurements. Modulation spectroscopy methods are also powerful tools for optically investigating the variation of the charge distribution, and they do not need metal contacts [10-11].

This paper reports the results of photoluminescence (PL) and PR measurements which were performed in order to investigate the variation of the surface states and the Fermi level-pinning effect after sulfur treatment and to investigate the neutralization of the carbons and the variation of the charges by hydrogenation and thermal treatment of GaAs. Although the intensity of the PR signal was considered to be related to the surface electric field, in this study, it has also been deeply related to the surface state density.

II. Experimental Detail

The samples used in the sulfur-treatment study were Si-doped GaAs bulks ($n \approx 1 \times 10^{18} \text{ cm}^{-3}$) grown by the horizontal Bridgmann (HB) method and nominally undoped GaAs layers grown by molecular beam epitaxy. The GaAs bulks were cleaned with trichloroethylene (TCE), acetone, and methylalcohol, sulphated with a solution of $(\text{NH}_4)_2\text{S}_x$ at 60°C for 20, 40, 110, 150, 200, and 250 min, and dried with a nitrogen gas. The MBE grown undoped-GaAs thin-film layers were cleaned with trichloroethylene (TCE), acetone, and methylalcohol, etched in a mixture of H_2SO_4 , H_2O_2 , H_2O (4:1:100), sulphated with a solution of $(\text{NH}_4)_2\text{S}_x$ at 60°C for 10, 20 and 30 min, dried with a nitrogen gas, and annealed at 250°C and 400 °C in a nitrogen atmosphere for approximately 5 min.

MBE grown undoped-GaAs thin layers were exposed to a hydrogen plasma at a pressure of 0.5 Torr for 60 min at a power density of 0.06 W/cm² using a capacitively coupled rf (13.56 MHz) plasma system. The hydrogenated GaAs was annealed at 400, 500, and 600°C in a nitrogen atmosphere for approximately 5 min. The PL measurements were carried out using a 75-cm monochromator equipped with an RCA 31034 photomultiplier tube. The excitation source was the 5145-Å line of an Ar-ion laser, and the sample temperature was controlled between 10 K and 300 K by using a He displacer system. The PR measurements were performed using a 75-cm monochromator equipped with 750-watt tungsten lamp as a probe source and using the 6328-Å line of a He-Ne laser as a modulation source.

III. Results and Discussion

Figure 1 shows the results of the room-temperature PL and PR signals for the HB grown Si-doped GaAs and sulfur-treated GaAs. The total intensity of the PR spectrum for the sulfur-treated GaAs increased in comparison to that of the as-grown GaAs until the sulfur-treatment time became 110 min. When the sulfur-treatment time are above 150 min, the intensity of the PR spectrum decreased. The intensity of the PL spectra of the sulfur-treated GaAs increased continuously as the sulfur-treatment time increased. The intensities of the PR and PL spectra as a function of the sulfur-treatment time are shown in Fig. 1. The value of the broadening parameter was not affected by the sulfur treatment.

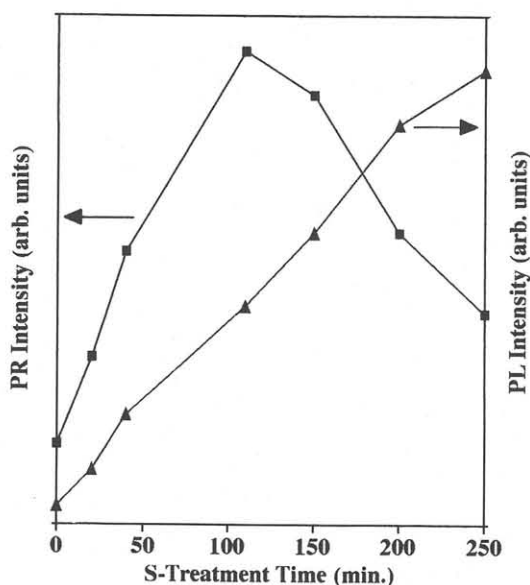


Fig. 1. PR and PL intensity variation with S-treatment time.

The surface electric field is determined from the magnitudes of the internal charge, negative surface state concentration (N_s), and positive surface state concentration (P_s). Although the value of the total concentration of surface states ($N_s + P_s$) does not affect the magnitude of the surface electric field, it is a very important factor for the determination of the pinning magnitude of the surface Fermi level. When two samples have the same value of the F and large values of ($N_s + P_s$), the variable magnitude of the band width (ΔV_p) becomes smaller as the pinning of the Fermi level becomes stronger. Thus, the intensity of the PR signal for the surface states of the sample obeys the following equation:

$$\Delta R/R \propto H_p / (N_s + P_s) \quad (1)$$

where H_p is the number of the holes forming at the valence band near the surface due to the modulation source. However, when the surface flat band is formed by ΔV_p as a result of the small magnitude of ($N_s + P_s$), the intensity of the PR signal is given by

$$\Delta R/R \propto F. \quad (2)$$

The increase of the PR intensity according to the increase of the sulfur-treatment time is due to the decrease of the ($N_s + P_s$) magnitude in Eq. (1). The decrease of the PR intensity for the sulfur-treated GaAs with sulfur-treatment times above 150 min is caused by the decrease of F in Eq. (2). The PL intensity originating from the band-to-band transitions increases linearly as the sulfur-treatment time increases. The continuous increase in the PL intensity of the sulfur-treated GaAs in comparison to the as-grown GaAs results from the passivation of the surface states, acting as a nonradiative recombination centers due to the sulfur treatment.

Figure 2 shows results of the PR spectra for the MBE as-grown, the sulfur-treated, and the sulfur treated and annealed GaAs at 400°C measured at 300 K. The clear third-derivative functional form of the PR signal for the as-grown GaAs is observed. However, the PR spectrum was undetectable after sulfur treatment; it appeared again after thermal treatment at 400°C. Since the intensities of the PL spectra of the sulfur-treated GaAs were raised by as much as 75 times in comparison to that of the as-grown GaAs, the disappearance of the PR spectra of the sulfur-treated GaAs was not due to the damage of the crystallinity of the GaAs. Thus, the disappearance of the PR

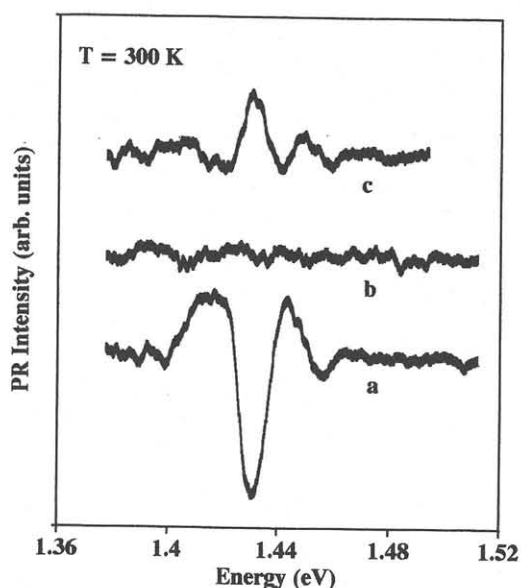


Fig. 2. PR spectra of (a) as-grown GaAs, (b) S-treated GaAs, and (c) S-treated GaAs annealed at 400°C, measured at 300 K.

spectrum results from the formation of a quasi-flat band at the GaAs surface. The appearance of the PR signal originates from the reformation of the surface states after thermal treatment, and this result is in good agreement with the results of the PL spectra.

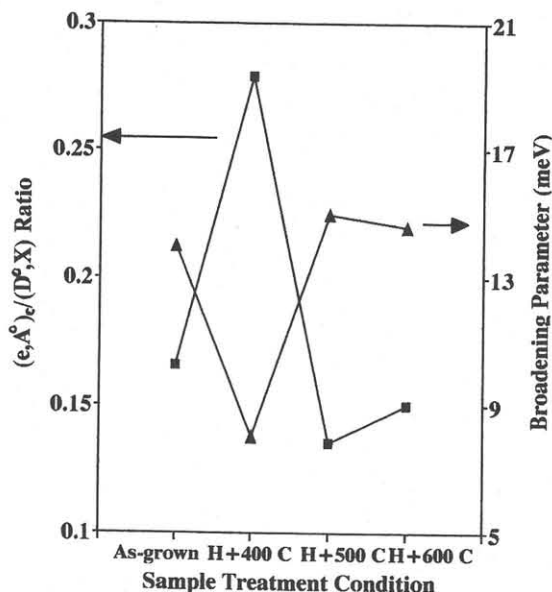


Fig. 3. Comparison of the broadening parameter with the ratio of the free-to-carbon acceptor $(e, A^0)_e$ signal to the neutral donor bound exciton (D^0, X) signal for the as-grown and hydrogenated GaAs annealed at (a) 400°C, (b) 500°C, and (c) 600°C.

The variation of the broadening parameters in the PR spectra correlated with the intensity of the $(e, A^0)_e$ peak.

Figure 3 shows a comparison of the broadening parameter and the intensity ratio of the $(e, A^0)_e$ to (D^0, X) taken from the PR and PL spectra for the as-grown GaAs and the GaAs annealed at 400°C, 500°C, and 600°C after hydrogenation. When These results indicate that the decrease of the surface potential caused by the decrease in the carriers reduces the value of the broadening parameter after hydrogenation and that the increase of the surface potential due to the ionized carbon acceptors resulting from thermal treatment increases the value of the broadening parameter.

IV. Summary and Conclusions

This result indicates that the sulfur treatment is an effective passivation method of the GaAs surface. The intensity of the PR signal was proportional to $H_p / (N_A + P_A)$ or F. While the variation of the broadening parameter in the PR spectra for the hydrogenated GaAs was caused by a neutralization or an ionization of the carbon acceptors, that for the nitrogenated GaAs did not change.

References

1. R. Williams, Modern GaAs Processing Methods (Artech House, Boston, 1990).
2. A. Callegari, P. D. Hoh, D. A. Buchanan, and D. Lacey, *Appl. Phys. Lett.* **54**, 332 (1989).
3. S. D. Offsey, J. M. Woodall, A. C. Warren, P. D. Kirchner, T. I. Chappell, and G. D. Pettit, *Appl. Phys. Lett.* **48**, 475 (1986).
4. S. Shikata and H. Hayashi, *J. Appl. Phys.* **70**, 3721 (1991).
5. Y. Nannich, J. Fan, H. Oigawa, and A. Koma, *Jpn. J. Appl. Phys.* **27**, L2367 (1988).
6. C. J. Spindt, D. Liu, K. Miyano, P. L. Meissner, T. T. Chiang, T. Kendelewicz, I. Lindau, and W. E. Spicer, *Appl. Phys. Lett.* **55**, 861 (1989).
7. M. Kobayashi, T. Yokoyama, and S. Narita, *Jpn. J. Appl. Phys.* **22**, 10 (1983).
8. W. C. Dautremont-Smith, J. C. Nabity, V. Swaminathan, M. Stavola, J. Chevallier, C. W. Tu, and S. J. Perton, *Appl. Phys. Lett.* **49**, 17 (1986).
9. A. Callegari, P. D. Hoh, D. A. Buchanan, and D. Lacey, *Appl. Phys. Lett.* **54**, 4 (1989).
10. M. Cardona, Modulation Spectroscopy (Academic Press, New York, 1969).
11. D. E. Aspnes, Handbook on Semiconductors (North-Holland, New York, 1980), Vol. 2.