FORMATION AND STABILITY OF As-H BONDS IN H-IMPLANTED GaAs

H. J. Stein, Sandia National Laboratories

ABSTRACT

The chemical bonding and isochronal annealing of H implanted into GaAs at 80 K has been investigated by infrared absorption measurements. Based upon the frequency shift when deuterium is substituted for H, and an equivalent band formation in InAs, assignment of a new band at 2029 cm^{-1} is made to As-H centers. Bonding of H at interstitial As of an As-vacancy pair which anneals between 150 and 250K is suggested as the structure for the defect. A previously-reported absorption band at 1834 cm^{-1} assigned to Ga-H centers in H-implanted GaAs increases in intensity when H is released from As-H centers.

INTRODUCTION

Ion beam modification of semiconductor materials is an important method for: 1) the processing of semiconductor wafers and circuits, 2) the ongoing development of microelectronics, and 3) the study of defects, impurities and defect-impurity interactions in semiconductors. Hydrogen in semiconductors has received widespread attention for its ability to passivate dangling bond defects, and to neutralize acceptor and donor activity¹. Hydrogen ion implantation of GaAs can be used to create high resistivity regions for electrical isolation in devices and circuits fabricated in this material²⁻⁵. While the implantation

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effects in GaAs are primarily due to displacement damage, a correspondence has been noted⁶ between displacement damage annealing near 500 K and the annealing of Ga-H centers following H implantation at room temperature.

Recovery from displacement damage in GaAs is also known to occur below room temperature⁷⁻⁹. There is an interest, therefore, in H-defect interactions in these lower temperature annealing stages. In the present study, the behavior of H following implantation into GaAs at 80 K and during subsequent isochronal annealing to 525 K has been examined by infrared absorption. Substitution of deuterium (D) for H, and InAs for GaAs, has been used to establish assignment of an absorption band in H-implanted GaAs to As-H centers which anneal below room temperature.

EXPERIMENTAL DETAILS

Samples (0.63 x 0.63 cm) diced from a two-side-polished 635 μm semi-insulating 3 inch diameter <100> Czochralski GaAs wafer and a sample of one-side polished undoped InAs were utilized for H and D implantations at 80 K. The implantations were performed in a liquid-nitrogen refrigerant cryostat with a gate valve to allow removal of the cryostat¹⁰ from the implanter and insertion into a Nicolet 60SX FTIR spectrometer. Infrared absorption measurements were made near normal incidence with 4 cm^{-1} resolution. Implant doses and energies used in the experiments introduced H (D) concentrations between 10^{19} and $10^{20}/\text{cm}^3$ into 2 to 3 μm thick surface layers of the samples. Hydrogen implantations into GaAs were performed at 250, 200, 150 and 100 keV to doses of 10, 7.5, 5,

and $2.5 \times 10^{14} \text{ cm}^{-2}$, respectively, into both optical faces of the samples. Deuterium implantations into GaAs were performed at 200, 100, 50, and 25 keV at doses of 1, 1, 1.4, and $1 \times 10^{15} \text{ cm}^{-2}$, respectively. The InAs sample was implanted on one side with 10, 7.5, 5, 3, and $2 \times 10^{14} \text{ cm}^{-2}$ at 330, 300, 250, 200, and 150 keV of H, respectively. Isochronal annealing in 20 min. periods was performed utilizing a heater and temperature sensor on the cold finger in the cryostat for temperatures $\leq 300 \text{ K}$, and in flowing N_2 for temperatures $\geq 300 \text{ K}$.

RESULTS AND DISCUSSION

Infrared absorption spectra between 1300 and 2200 cm^{-1} measured after H and D implantation into GaAs at 80 K are plotted in Fig. 1. The broad features in the spectra are caused by interference effects associated with a displacement-damage-produced change in the refractive index. Deuterium implantation produced more damage than that for H, and hence larger interference effects. Well-defined localized vibrational mode (LVM) absorption bands appear at 2029 cm^{-1} and 1460 cm^{-1} for H and D implantation, respectively. The frequency ratio of 1.39 for these new absorption bands indicates that they are due to a vibrational mode of H(D), and the frequencies are approximately those expected for vibrational modes of As-H (As-D) centers^{6,11}. A weaker band appears at 1834 cm^{-1} after H implantation which is the band previously assigned to Ga-H centers^{6,11,12}.

To further establish an As-H assignment for the 2029 cm^{-1} band in H-implanted GaAs, a sample of InAs was implanted with H at 80 K .

An absorption band very similar to that in H-implanted GaAs is produced at 2021 cm^{-1} by implantation of H into InAs, as shown in Fig. 2. This shift is larger than expected for an oscillator imbedded in the two materials since they have nearly equivalent static dielectric constants, and it is much smaller than the 7 percent lattice parameter difference between InAs and GaAs. Displacement damage and chemistry, therefore, must be the dominant factors in determining the LVM frequency for As-H in these compound semiconductors.

Trapping of implanted H by As at 80 K is obviously favored over trapping by Ga since 80 percent of the absorption intensity is in the As-H band. Assuming all of the implanted H is trapped by either As or Ga, the absorption cross section per As-H center is $6 \times 10^{-18}\text{ cm}^2$ at the peak of the As-H absorption band. This value is in good agreement with that deduced from reported values¹² of absorption by Ga-H centers after H implantation at room temperature.

Isochronal annealing between 80 and 300 K was performed to examine the thermal stability of the As-H center in GaAs, and to compare the results to previously reported displacement damage recovery⁷⁻⁹. Spectra measured after implantation and after subsequent annealing at 200 and 300 K are shown in Fig. 3. Annealing at 200 K reduced the As-H band intensity by a factor of two while the intensity of the Ga-H band increased. The As-H band was no longer observed after annealing at 300 K and the Ga-H band intensity has increased to approximately one half that for the As-H band after implantation.

A more complete view of the isochronal annealing characteristics is given in Fig. 4 where peak intensities for the As-H and Ga-H bands are plotted as a function of isochronal annealing temperature. Removal of the As-H band by annealing at 250 K is consistent with previously-reported Stage I annealing of displacement damage after electron irradiation⁷. First order kinetics and an activation energy of 0.7 eV were reported for Stage I annealing, and closely-spaced vacancy-interstitial pairs were suggested for the responsible defects⁷. The intensity of the Ga-H band increases slowly between 150 and 400 K before annealing near 500 K as previously reported^{6,11}. Annealing near 500 K has been labeled⁷ Stage III. First order kinetics has been reported¹³ for Stage III annealing and is, therefore, suggestive of close pair annealing. Thommen⁷ noted that the fractional annealing in Stage III relative to Stage I increased with decreasing electron bombardment energy which might be expected if Stage III defects were produced on the Ga (lighter ion) sublattice and Stage I defects are produced on the As sublattice.

Assuming that annealing of the As-H and Ga-H centers are associated with Stage I and Stage III annealing of closely-spaced interstitial As-Vacancy ($\text{As}_\text{I}\text{-V}$) and interstitial Ga-Vacancy ($\text{Ga}_\text{I}\text{-V}$) pairs, respectively, a sketch of potential energy versus relative vacancy-interstitial positions for H trapped at these pairs is depicted in Fig. 5. The annealing is assumed to be controlled by close-spaced pair recombination plus H diffusion to give the broad annealing temperature range for the increase in Ga-H centers after H is released from As-H centers. The activation energies for As-H

and Ga-H are those reported for Stage I and Stage III annealing^{7,13}, and the relatively low energy for diffusion of H was assumed from published calculations on diffusion of neutral H in GaAs¹⁴. Linking annealing of As-H centers in H-implanted GaAs to displacement damage annealing below room temperature is analogous to results from earlier studies on H-implanted Si which showed a correlation between the annealing of Si-H centers¹⁵ and vacancy annealing.

A significant fraction of displacement damage and electrical isolation produced in GaAs by H implantation²⁻⁵ remain at temperatures which remove both As-H and Ga-H centers. Electrical isolation produced in GaAs by proton bombardment, therefore, is not dependent upon centers formed by chemical bonding of the implanted hydrogen.

SUMMARY

A strong new absorption band with a frequency close to that expected for As-H centers in GaAs has been observed after H-ion implantation at 80 K. Substitution of D for H confirms H(D) vibrational origin of the band, and formation of an equivalent band in InAs further supports assignment of the new band to As-H centers. The As-H centers anneal in a stage between 150 and 250 K which coincides with previously-reported displacement damage annealing attributed to recombination of closely-spaced vacancy-interstitial pairs. Bonding of H to interstitial As of interstitial-vacancy pairs is suggested for the As-H defect observed in the present study with annealing controlled by recovery

of displacement damage. Intensity of an absorption band for Ga-H centers increases upon release of H from As-H centers and the increase continues to ≈ 400 K, suggestive of diffusion before retrapping to form Ga-H centers in GaAs.

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REFERENCES

- 1) S. J. Pearton, J. W. Corbett, and T. S. Shi, Appl. Phys. A43, 153 (1987).
- 2) A. G. Foyt, W. T. Lindley, C. M. Wolfe, and J. P. Donnelly, Solid State Electron. 12, 209 (1969).
- 3) D. C. D'Avanzo, IEEE Trans. on Elect. Devices ED-29, 1051 (1982).
- 4) O. Nakajima, K. Nagata, Y. Yamauchi, H. Ito, and T. Ishibashi, Electronics Lett. 22, 1317 (1986).
- 5) J. P. Hohimer, D. R. Myers, T. M. Brennan, and B. E. Hammons, Appl. Phys. Lett. 55, 531 (1989).
- 6) R. C. Newman and J. Woodhead, Rad. Effects 53, 41 (1980).
- 7) K. Thommen, Rad. Effects 2, 201 (1970).
- 8) F. L. Vook, Phys. Rev. 135, A1742 (1964).
- 9) H. J. Stein, J. Appl. Phys. 40, 5300 (1969).
- 10) H. J. Stein and R. H. Baxter, Rev. Sci. Instrum. 45, 1537 (1974).
- 11) Pajot, J. Chevallier, A. Chaumont, and R. Azoulay, in Defects

in Electronic Materials, Edited by M. Stavola, S. J. Pearton and G. Davies, MRS Proc. Vol. 104 (1988) p. 345.

12) L. P. Wang, L. Z. Zhang, W. X. Zhu, X. T. Lu, and G. G. Qin, *physica (b)* 158, 113 (1990).

13) L. W. Aukerman, P. W. Davis, R. D. Graft, and T. S. Shilliday, *J. Appl. Phys.* 53, 3590 (1963).

14) L. Pavesi, P. Giannozzi and F. K. Reinhart, *Phys. Rev. B* 42, 1864 (1990).

15) H. J. Stein, *Appl. Phys. Letters* 43, 1030 (1979).

LIST OF FIGURES

1) Infrared absorption versus wavenumbers for semi-insulating GaAs after hydrogen ($5 \times 10^{15} \text{ cm}^{-2}$) and deuterium ($9 \times 10^{15} \text{ cm}^{-2}$) implantation at 80 K. Spectra arbitrarily positioned on absorbance axis.

2) Comparison of infrared absorption in InAs following hydrogen implantation ($2.75 \times 10^{15} \text{ cm}^{-2}$) at 80 K to that for GaAs (same as Fig. 1). Spectra arbitrarily positioned on absorbance axis.

3) Infrared absorption in hydrogen implanted GaAs measured at 80 K after implantation subsequent annealing to 200 and 300 K. Spectra arbitrarily positioned on absorbance axis.

4) Peak intensities for As-H and Ga-H absorption bands as a function of isochronal annealing temperature.

5) Suggested defect structures and annealing mechanisms for As-H and Ga-H centers.

SCHEMATIC ENERGY DIAGRAM FOR TRAPPING OF IMPLANTED H IN GaAs

RELATIVE POSITIONS FOR H-TRAPPING
AT As_V - As_I AND Ga_V - Ga_I PAIRS

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