Extended Abstracts of the 15th Conference on Solid State Devices and Materials, Tokyo, 1983, pp. 177-180

B-3-9

Local Modes from Si at Gallium and Arsenic Sites and Electrical Activation in Implanted GaAs

T. Nakamura and T. Katoda
Institute of Interdisciplinary Research
Faculty of Engineering, The University of Tokyo
4-6-1 Komaba, Meguro-ku, Tokyo 153

Local vibrational modes based on Si implanted in GaAs were studied by laser Raman spectroscopy. From the dependence of intensities of the local modes due to Si at As sites and pairs of Si at Ga sites and As sites on annealing temperature, Si are considered to occupy As sites with annealing at a temperature lower than 550°C and Ga sites at higher than 550°C accompanying generation of carriers. Depth profiles of the local mode intensities and carrier concentration obtained after annealing at 850°C indicate that Si at As sites prevent generation of carriers and Si at Ga sites have no contribution to generation of carriers if they form pairs with nearest neighbor Si at As sites.

§1. Introduction

Mechanism of electrical activation of impurities implanted into gallium arsenide has not been made clear especially in the case of amphoteric impurities such as silicon.(1,2) It is necessary at least to know lattice sites of the impurities in order to make clear the mechanism. Impurities such as P, Al, and Si in GaAs are known to activate localized vibrational modes.(3-8) Vibrational energy of the mode for the light impurity is extremely localized and generally extends over less than one lattice constant. Local modes, therefore, provide important informations on impurity-site distributions and local environment of the implanted species.

Many studies on infrared absorption have reported local vibrational modes of Si in GaAs.(3-7) Depth profile of implanted Si in lattice sites, however, has not been obtained and hence no apparent correlation with electrical activation by annealing has been shown by the measurement of infrared absorption. Sensitivity of infrared absorption method is not high enough to discuss change of the local mode through the depth. On the other hand, Raman spectroscopy using a laser beam of a relatively shorter wavelength such as Ar^+ laser is very useful to measure depth profile of local mode intensity because a depth measured by the method is as small as several hundred angstroms.(9)

In this paper, the depth profiles of the local vibrational modes from implanted Si in GaAs and the carrier concentration measured by laser Raman spectroscopy will be reported. In addition, correlation between the local modes and longitudinal optical phonons appearing with annealing will be shown.

§2. Experiment

The samples were Cr-doped semi-insulating (100)GaAs implanted with Si ions to a dose ranging from 1×10^{14} to $1\times10^{16}\text{cm}^{-2}$ at 175KeV followed by annealing at a temperature between 200 and 550°C with no surface encapsulant and at 850°C with CVD SiO_2 film. Some samples were etched with a solution of 200 H_2O:5 NH_4OH:1 H_2O_2 at 24°C to study the depth profile of the local mode intensity and the carrier concentration. The Raman spectra were measured in a quasi-backscattering geometry with a 514.5nm line of an Ar^+ laser whose penetration depth into GaAs is estimated to be less than 100 nm. In the configuration, the direction of propagation of the incident beam was at an angle of about 40° with respect to the normal against the sample surface. The electric vector of the incident beam was polarized in the plane of incidence (H) and the scattered light was unanalyzed (U) or perpendicular to the plane of incidence (V).

§3. Results and Discussion

Figure 1 shows Raman spectra from GaAs implanted with Si ions to doses 2×10^{15} and 1×10^{16} cm^{-2} followed by annealing at 550°C. A strong peak at $292cm^{-1}$ and a weak peak at $268cm^{-1}$ are the LO and TO phonons at the Γ point, respectively. A broad shoulder from 300 to $480cm^{-1}$ and a broad peak from 510 to $540cm^{-1}$ are based on the second order Raman scattering.(10) A sharp peak at about $390cm^{-1}$, whose intensity increases with the dose of Si, is local modes of lattice site Si in GaAs.

Figure 2 shows Raman spectra of the local modes from Si implanted GaAs before and after annealing at various temperatures. The local mode at $390cm^{-1}$ appeared only after annealing at a temperature higher than 200°C at which the LO phonon intensity started to increase due to recrystallization of damaged structure.(11) The intensity of the local mode at $390cm^{-1}$ increased with annealing temperature from 200 to 550°C and was nearly constant after annealing above 550°C. It means that the implanted silicon atoms occupy the substitutional sites with structural recovery due to annealing. Electrical activation, however, has not been obtained at the point. It is well known that annealing above 800°C is required to obtain the enough activation of implanted Si. We studied, therefore, changes of the local vibrational mode with annealing at a temperature between 550 and 850°C. Figure 3 shows Raman spectra in the spectral range in which the local modes appear with annealing. In order to eliminated the influence of second order Raman spectra (10) Raman measurements were performed under HV configuration, that is, the incident and scattered lights were polarized to horizontal and vertical to the incident plane, respectively.

According to the assignment of local vibrational modes in infrared absorption spectra which measured at 77K,(5,6) the local vibrational frequencies of Si at Ga site (Si_{Ga}), As site (Si_{As}), and nearest-neighbor Si_{Ga}-Si_{As} pairs are 384, 399 and $393cm^{-1}$, respectively. To interpolate the frequencies of the local mode in Fig. 3 which were measured at room temperature to those at 77K, temperature dependence of Raman frequencies were measured between room temperature and 77K. The frequencies based on the local modes and the LO

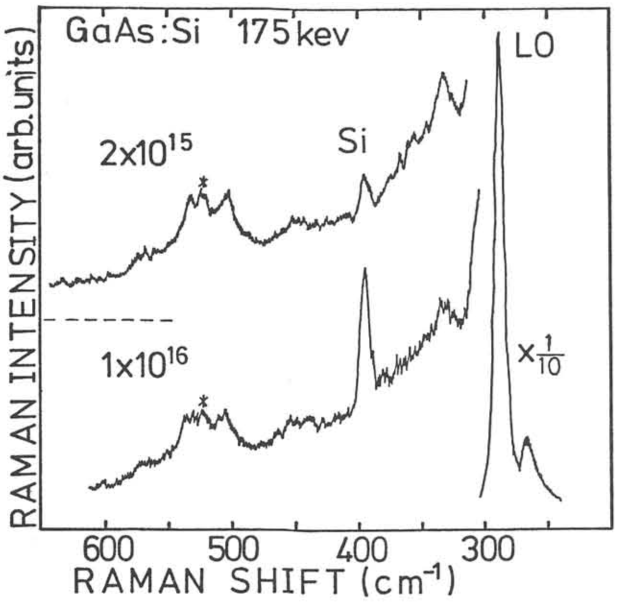

Fig. 1. Raman spectra from GaAs implanted with Si ions to doses 2×10^{15} and $1\times10^{16}cm^{-2}$ followed by annealing at 550°C.

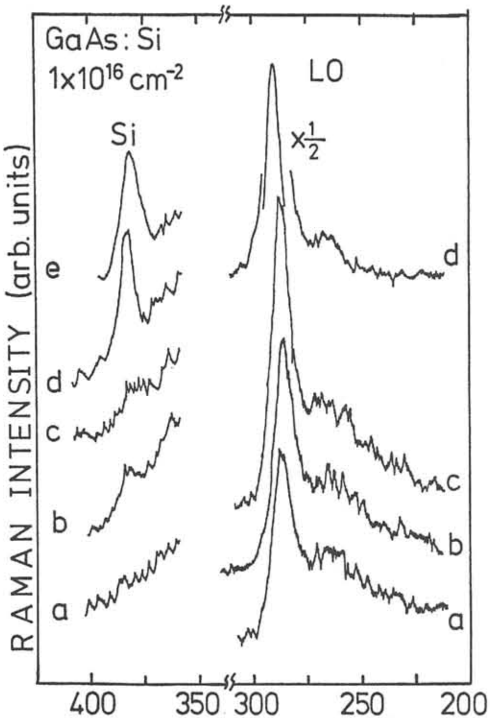

Fig. 2. Raman spectra of the local modes and the LO phonon from Si implanted GaAs before (a) and after annealing at 200°C (b), 300°C (c), 550°C (d), and 850°C (e).

phonon decreased linearly at -0.018cm^{-1}/K with increase in temperature. The linear dependence of the LO phonon frequency has been ensured by Chang et al. below 50K.(12) Assuming that frequencies of the LO phonon and the local modes have a temperature dependence -0.018cm^{-1}/K below room temperature, three peaks at 380, 396 and 391cm^{-1} in Fig. 3 are shown to be identical to the modes due to Si_{Ga}, Si_{As} and the Si_{Ga}-Si_{As} pairs at 77K, respectively.

It is clear from Fig. 3 that the intensity of the Si_{As} mode remains nearly constant after annealing above 550°C as previously described while that of the Si_{Ga}-Si_{As} mode increases with annealing temperature up to 850°C. The results means that Si take arsenic sites with annealing at a relatively lower temperature while concentration of Si in gallium sites increases with annealing at a temperature higher than 550°C. That is, carrier concentration increases with that of Si in gallium sites. Intensity of the Si_{Ga} mode was too weak to be discussed its change.

Role of Si at various sites on electrical activation can be made clear by comparing depth profiles of local mode intensities and carrier concentration. Figure 4 shows depth profiles of relative intensities of the Si_{As} and Si_{Ga}-Si_{As} modes to the LO phonon of the semi-insulating GaAs before implantation, carrier concentration, and concentration of Si calculated according to the LSS theory in the case that Si-implanted GaAs was annealed at 850°C for 15 min. The plotted data of local mode intensities are those obtained at the plotted positions. Therefore the peak position, where the intensity of the Si_{As} mode is maximum, is in slightly deeper region because penetration depth of the incident laser beam is about several hundred angstroms. The carrier concentration was estimated by measuring relative intensity of the LO phonon because the relation between the relative intensity of the LO phonon and carrier concentration for n-GaAs is determined definitely by experiment. The theoretical profile of Si was calculated by assuming the simple diffusion mechanism in which the diffusion coefficient of Si in GaAs at 850°C was taken as $1\times10^{-13}\text{cm}^2/\text{sec}$.(13)

The carrier concentration decreases near the surface and a dip is observed at a position where

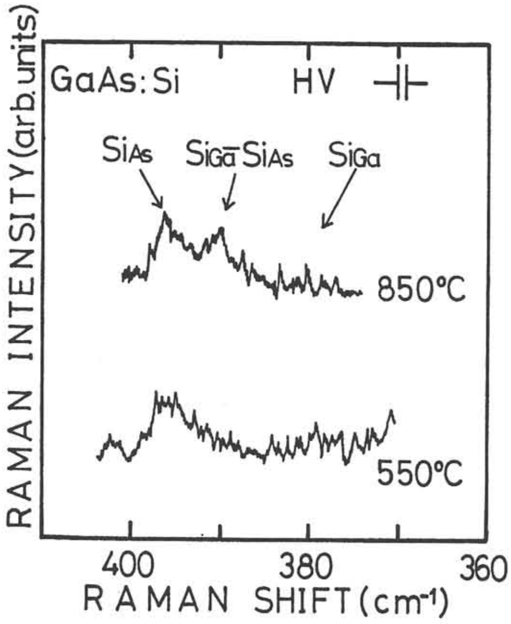

Fig. 3. Assignment of the local vibrational modes in the Raman spectra measured after annealing at 550 and 850°C.

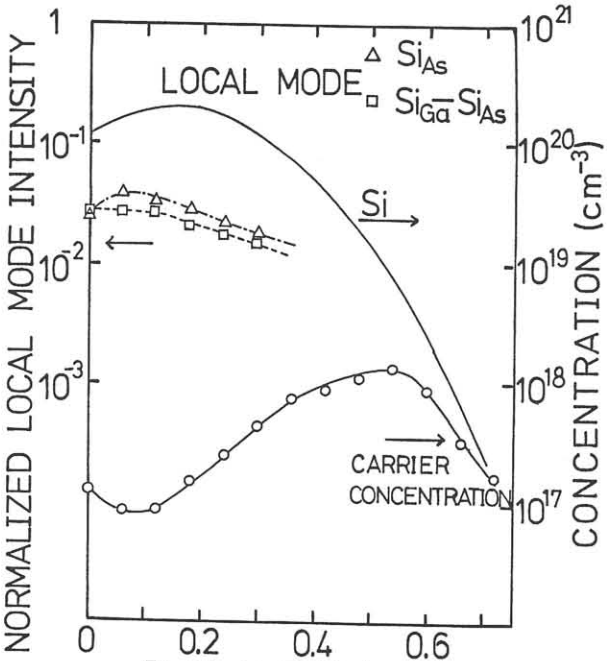

Fig. 4. Depth profiles of the relative intensities of the Si_{As} and Si_{Ga}-Si_{As} modes to the LO phonon of the semi-insulating GaAs before implantation, carrier concentrations, and concentration of Si caluculated according to the LSS theory.

the intensity of the Si_{As} mode has a maximum. The carrier concentration increases again with decrease in the Si_{As} intensity. It means that Si at arsenic sites prevent generation of carriers. The intensity of the Si_{Ga}-Si_{As} mode decreases also with increase in the carrier concentration although its depth profile has no peak near the surface. The result indicates that silicon pairs in gallium and arsenic sites have at least no contribution to generation of carriers although it means increase in Si in gallium sites accompanying increase in carriers. The reason that the curve of the Si_{Ga}-Si_{As} pair mode is rather flat is speculated that it is determined by the diffusion of gallium vacancy(14) from the suface with annealing.

In addition to the influence of Si_{As} and Si_{Ga}-Si_{As} pairs other effects such as point defects introduced by implantation(15) and redistribution of Cr(16) are considered to have some roles in forming the profile of carrier concentration. Although it is necessary to analyze in detail profiles of the local modes and carrier concentration in the deeper region where effects of defects introduced at the surface and redistribution of Cr can be neglected, intensities of the local modes are too weak to be discussed.

§4. Conclusion

Local vibrational modes of substitutional Si in GaAs on Raman spectra were observed for the first time. Local mode based on Si at arsenic sites Si_{As} appeared with structural recovery by annealing at relatively low temperatures. On the other, local mode due to silicon pairs at gallium and arsenic sites Si_{Ga}-Si_{As} appeared only after annealing at temperatures higher than 550°C. Intensity of the Si_{Ga}-Si_{As} pair mode increased with annealing temperature while that of the Si_{As} mode remained constant. Increase in carrier concentration occured also after annealing at higher than 550°C. The results means that implanted Si occupy arsenic sites by annealing at relatively low temperatures and occupy gallium sites at relatively high temperatures.

It was made clear from the depth profiles of the local modes and carrier concentration that Si at arsenic sites prevent generation of carriers and those at gallium sites have no contribution to generation of carriers if they form pairs with Si at arsenic sites. However, increase in pairs of Si at gallium and arsenic sites accompanying increase in carrier concentration indicates that Si at gallium sites without forming pairs with those at arsenic sites are sources of carriers.

The authors wish to thank Dr. H. Nishi, Fujitsu Laboratories Limited, for his supply of the samples and helpful discussions.

References

1) A. Masuyama, M.-A. Nicolet, I. Glecki, J. L. Tandon, D. K. Sadana, and J. Washburn, Appl. Phys. Lett. 36, 749(1980).
2) R. S. Bhattacharya, A. K. Rai, Y. K. Yeo, P. P. Pronko, S. C. Ling, S. R. Wilson, and Y. S. Park, J. Appl. Phys. 54, 2329(1983).
3) O. G. Lorimor and W. G. Spitzer, J. Appl. Phys. 37, 3687(1966).
4) W. G. Spitzer and W. Allred, Appl. Phys. Lett. 12, 5(1968).
5) W. G. Spitzer and W. Allred, J. Appl. Phys. 39, 4999(1968).
6) L. H. Skolnik, W. G. Spitzer, A. Kahan, F. Euler, and R. G. Hunsperger, J. Appl. Phys. 43, 2146(1972).
7) R. T. Chen, V. Rana, and W. G. Spitzer, J. Appl. Phys. 51, 1532(1980).
8) L. H. Skolnik, W. G. Spitzer, A. Kahan, and R. G. Hunsperger, J. Appl. Phys. 42, 5223 (1971).
9) M. Balkanski, J. F. Morhange, and G. Kanellis, J. Raman Spectrosc. 10, 240(1981).
10) T. Sekine, K. Uchinokura, and E. Matsuura, J. Phys. Chem. Solids. 38, 1091(1977).
11) T. Nakamura and T. Katoda, J. Appl. Phys. 53, 5870(1982).
12) R. K. Chang, J. M. Ralston, and D. E. Keating, *Proceeding of the International Conference on Light Scattering Spectra of Solids, New York,* p. 369(Springer-Verlag, 1969).
13) J. Kasahara and N. Watanabe, *Semi-Insulating III-V Materials, Evian,* p. 238(Shiva Pulishing, 1982).
14) S. Y. Chiang and G. L. Pearson, J. Appl. Phys. 46, 2986(1975).
15) R. K. Surridge, B. J. Sealy, A. D. E. D'Cruz, and K. G. Stephens, *Inst. Phys. Conf. Ser. No. 33a*, p. 161(1977).
16) C. A. Evans, Jr., V. R. Deline, T. W. Sigmon, and A. Lidow, Appl. Phys. Lett. 35, 291(1979).