



ELSEVIER

Journal of Molecular Structure 348 (1995) 33–36

**Journal of
MOLECULAR
STRUCTURE**

Raman study of damage processes in Si⁺-implanted GaAs

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Ion-induced damage in GaAs as a function of ion dose following 100 keV Si⁺ implants has been investigated by Raman spectroscopy. A new approach for decomposition of Raman scattering intensity on to the crystalline and amorphous phase components has been used in analysis of Raman spectra. With increasing ion dose the following was observed: a) the widths of vibrational bands of a-phase significantly increase, while the width of the LO(Γ) phonon band of c-phase remains unchanged; b) the longitudinal optical phonon band of c-phase completely disappears, while the transverse optical phonon mode evolves in to a new band of a-phase; c) the wavenumbers of all vibrational bands of a- and c-phase shift to lower values by ~ 10 -15 cm⁻¹. A number of mechanisms possibly accountable for these shifts were analysed and evaluated.

1. INTRODUCTION

Ion implantation is a key technology for precise doping in semiconductor processing. The electrical activation of dopants and performance of the devices fabricated using ion-implanted materials can be seriously affected by the lattice damage introduced during implantation process. Thus, a detailed understanding of the lattice defects and structural changes in the ion-implanted semiconductors is increasingly important as device sizes in integrated circuits are decreased. A powerful technique for probing the atomic-scale structure of the implanted layer is the use of Raman scattering experiments in which the optical penetration depth of the incident laser beam is chosen to be less than, or comparable to, the ion penetration depth. Raman spectra have been used to characterize ion-implanted GaAs [1]. The Raman spectrum of ion bombarded GaAs is a superposition of the defect-modified crystalline longitudinal and transversal optical phonon lines (LO(Γ) and TO(Γ)), second-order spectrum of c-phase, disorder-activated first-order spectrum of a-phase and broad background signal. However, many previous studies, which reported the experimental shifts and widths as a function of ion fluence or annealing, have not been based on the clear separation of these contributions. Here, we present the Raman study of damage process in high energy ion bombarded GaAs, analysing separately each component in the Raman scattering spectrum.

2. EXPERIMENTAL

Commercial undoped GaAs (100) wafers were implanted at room temperature with 100 keV Si⁺ ions. The applied ion doses were in interval: 1×10^{14} - 3×10^{15} ions/cm². The dose rate was 0.05 μ A/cm². The Raman spectra were recorded from samples in vacuum (to 10^{-4} Torr) with a DILOR Z-24 triple spectrometer. The laser power of 0.5 W of the 514.5 nm line of a Coherent Innova 100 Ar-ion laser was focused on a spot with dimension: 0.1×0.4 mm². The HH polarized Raman spectra were radiometrically corrected and temperature reduced. The intensity of the second-order Raman spectrum of c-phase is comparable with the intensity of the first-order Raman spectrum of a-phase and may significantly influence results of the fitting. Therefore, we have subtracted the second-order contribution from the Raman spectra. The difference spectra were then decomposed by a computer fitting program on the background signal, the TA, Π A and TO vibrational bands of a-phase, and the LO(Γ) and TO(Γ) vibrational bands of c-phase. The details of fitting procedure are presented elsewhere [2].

3. RESULTS AND DISCUSSION

The linewidths of the TO and LO modes of a- and c-phase for various fluences are shown in Figure 1. The relative large value of the TO-c mode bandwidth in comparison to the LO-c, and its unusual additional rapid increase at higher fluence which is also observed by Rao et al. [3], is still unclear. Figure 2 shows intensities of the LO-c and TO-c modes normalized to the intensity of the TO-a mode as a function of fluence. We note here that with the highest

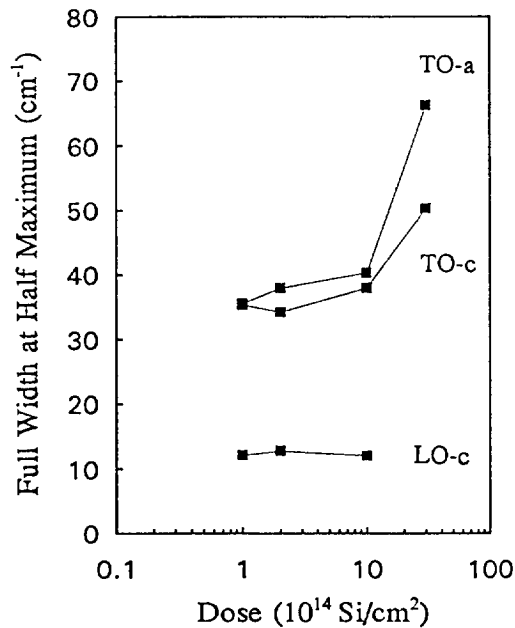


Figure 1. Broadening vs fluence for the modes of crystalline (TO-c and LO-c), and amorphous phase (TO-a).

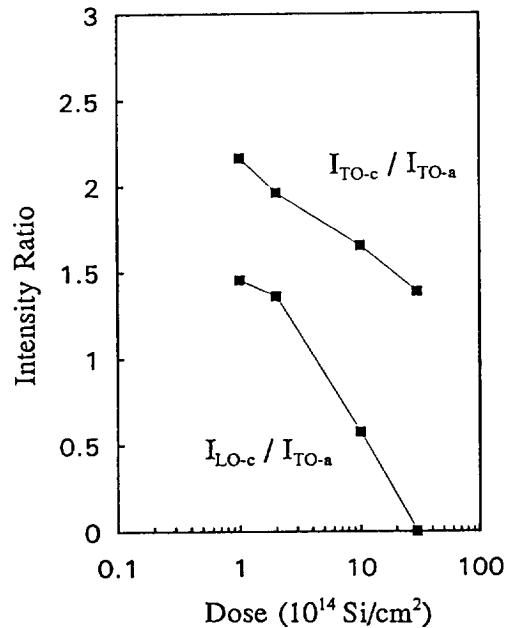


Figure 2. Relative intensities of the TO-c and LO-c modes vs fluence.

applied fluence (3×10^{15} Si/cm²) the c-phase in Raman and RBS spectra completely disappear [1]. In this case the remaining observation of the TO-c mode means that its origin should be in a-phase. Therefore, the TO-c mode should be considered as a superposition of two overlapping modes from which one (previously known mode) belongs to c- and the other (new) mode to a-phase. This explains the much larger width of the TO-c mode in comparison to LO-c. The wavenumber of the new mode in a-phase is at the position of the TO feature in the phonon density of states (PDOS) [3], while the mode which we considered in the fitting procedure as the TO-a mode is at the position of the LO feature. Therefore, we suggest the following assignment for the modes in a-GaAs (Fig. 3): TA (~ 70 cm⁻¹), IIA (~ 160 cm⁻¹), LO (~ 220 cm⁻¹) and TO (~ 260 cm⁻¹). This assignment differs from the previous ones in the region of optical modes, where the hump at ~ 250 cm⁻¹ was interpreted as the TO mode only.

The abrupt increase of the TO-a linewidth at the highest applied fluence should be connected with the disappearance of the c-phase and will be discussed in more detail in a following paper.

Figure 4 shows the phonon wavenumber shifts as a function of fluence for all fitted modes of a- and c-phase. According to this new assignment, the TO-c mode is designated as TO-m (mixture of TO-c and TO-a) and the mode supposed in fitting as TO-a is now designated as LO-a. All modes shift to lower wavenumbers by 10-15 cm⁻¹. The following mechanisms have been considered for the explanation of the modes shift in GaAs [4,5]:

- (a) phonon confinement,
- (b) defect induced changes in the ionic plasma frequency,
- (c) strain,

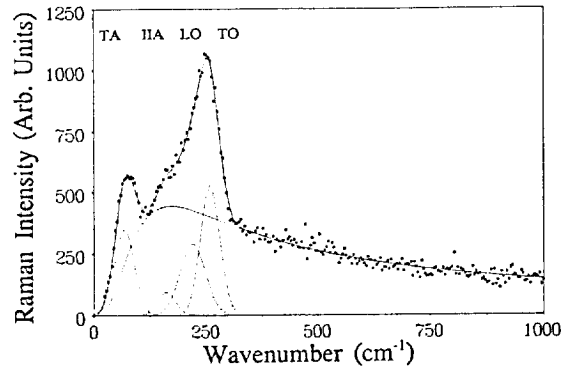


Figure 3. Raman spectrum of GaAs implanted with 3×10^{15} Si/cm². The spectrum is decomposed on the phonon bands and broad background signal (boson peak [2]).

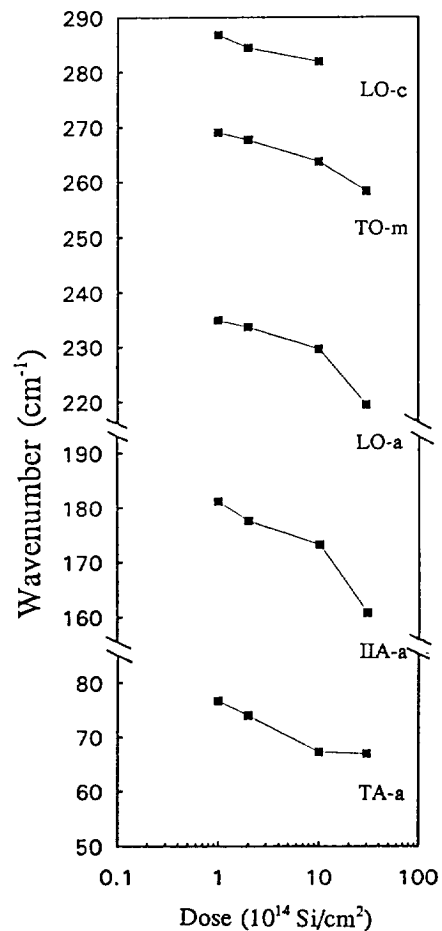


Figure 4. Wavenumbers of the phonon modes of a- and c-phase as a function of fluence.

- (d) changes in average atomic mass and volume of GaAs,
- (e) changes in the force constants.

In the phonon confinement model the shift of the LO-c mode should be correlated with its simultaneous broadening. Since in our analysis the shift is not accompanied by such changes in the linewidth, we conclude that phonon-confinement should not play a significant role in shifting of the modes.

In polar media, in which the effective charge is nonzero, the wavenumbers of the LO phonons are higher than the TO phonons. Therefore, defect induced changes in the effective charge can explain the relative shift of these modes. But this relative shift is not observed in our spectra, instead the LO and TO modes shift in parallel. On the other hand the modes of a-phase should be mainly sensitive to the PDOS and not to the effective charge. Also, the same type of dependence of wavenumbers of the modes of a- and c-phase on fluence show their common origin.

From the measured elastic strains in the bombarded samples, the strain-induced shifts can be calculated using the experimentally derived coefficients for the phonon deformation potentials. This calculation shows only $\sim 1\text{cm}^{-1}$ contribution to the shift [4]. The change in the average mass caused by adding the lighter element Si contributes to the frequency shift as $\omega \propto m^{-1/2}$, and a change in the average volume will affect the frequency through the Grüneisen parameter. According to Ashokan et al. [5], the calculated shift should be also $\sim 1\text{cm}^{-1}$.

The above mentioned mechanisms have been applied with reasonable success to lightly damaged GaAs layers, where shifts from undamaged values are relatively small (up to few cm^{-1}). However, they cannot explain shifts of order of $\sim 10\text{-}15\text{ cm}^{-1}$, observed in heavily perturbed layers. Hence we believe that the remaining mechanism, the defect induced changes of the short range force constant, have to be predominant, as - in principle - it allows for the large shifts. If the bombardment induced defects are either isotropic or anisotropic, but enter into cubic equivalent positions, they will produce the same change in the short range force constants for the LO-c and TO-c phonons. This should be reflected in the same way by the vibrational modes of a-phase since the PDOS is mainly sensitive to the short range force constant. A detailed model based on this mechanism, which enables a quantitative estimate of the damage-induced shift will be presented separately.

Acknowledgments: This research was financed by the European Communities under contract nr. ERBCIPACT 92-2095, and in parts by the Ministry of Science and Technology of Croatia and US Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The supports are highly acknowledged.

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