

RAMAN SPECTROSCOPY OF AMORPHOUS-CRYSTALLINE
PHASE TRANSITION INDUCED BY LASER ANNEALING

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Raman spectroscopy of laser annealed Gallium Arsenide made amorphous by ion implantation gives the possibility to follow the recrystallization of the material. For low irradiation density, the normal mode peaks of crystalline material appear but shifted toward the frequency of the band characteristic of the amorphous material and the selection rules are not obeyed. For a higher energy density, spectra tend to recover the characteristics of crystalline material. Scanning with the Raman laser spot across the annealed region shows a continuous variation from the amorphous state to the crystalline one. We account for this continuous variation of the crystallization by size effects due to the presence of microcrystallites.

Introduction

Among the various techniques of characterization of pulsed laser effect in semiconductors, the Raman spectroscopy has the advantage to be non destructive. Moreover, the ability to focus the Raman laser allows a local analysis of the annealing effects. Raman spectroscopy which is sensitive to the vibrational properties of solids can give valuable information on the crystalline order inside the annealed region of the material. Laser annealed Silicon samples have been studied [1] and show important shift of the first order degenerated phonon toward lower frequencies which has been interpreted as an effect of the dimensions of small crystallites [2]. It is interesting to study the same effect in Gallium Arsenide which is partially ionic and for which the long range electric forces splits the degenerate optical mode into transverse and longitudinal phonons at the center of the Brillouin zone.

Semi-insulating GaAs samples have been implanted and annealed at the L.C.R. of Thomson C.S.F. (Corbeville). The dose chosen was 2.10^{14} ions As/cm² and 2.10^{14} ions Ga/cm² under 300 keV. Annealing was realized by using a YAG laser with a frequency doubler which gives pulses of about 10 ns duration. The energy density was varied in the range 0.3 to 0.6 J/cm². Raman spectra were recorded using the 488 nm line of an Argon laser with a power of 400 mw.

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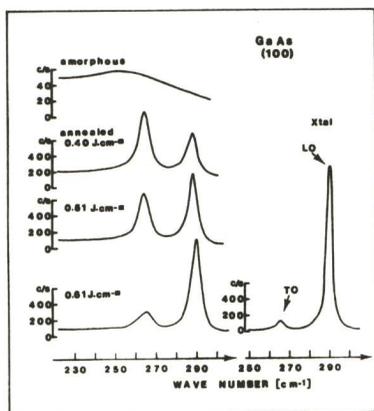


Fig. 1 Raman spectra on a (100) face of a GaAs sample for various irradiation energies: Intensities are measured in count per second

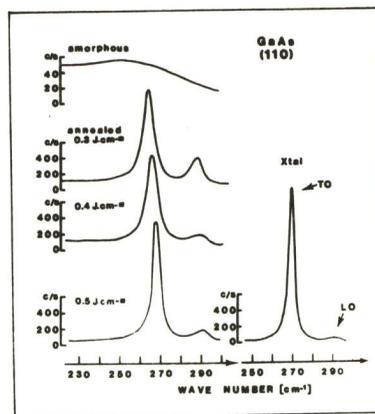


Fig. 2. Raman spectra on a (110) face of a GaAs sample for various irradiation energies: Intensities are measured in count per second

Experimental Results

Figures (1) and (2) present the Raman spectra of two GaAs samples in a backscattering geometry on faces (100) and (110). On these two different faces, the selection rules are complementary, the TO phonon being forbidden on the (100) face, the LO phonon forbidden on the (110) face. For perfectly crystalline samples, the selection rules are verified, the residual forbidden peaks in each case are due to residual misalignment. The frequencies of the lines are respectively $\omega_{TO} = 268 \text{ cm}^{-1}$, $\omega_{LO} = 291 \text{ cm}^{-1}$, their widths, measured with an instrumental resolution of 2 cm^{-1} , is equal to 3.6 cm^{-1} for both peaks. After an implantation of 2.10^{14} ion Gallium per cm^2 and 2.10^{14} ion Arsenic per cm^2 , the samples are rendered amorphous and the spectra observed are typical for this kind of amorphous material [3] i.e. a density of states spectrum.

After laser annealing, the spectra are drastically modified. For a low energy density, the forbidden peaks are respectively activated for each face; this is especially spectacular for the (100) face for which the forbidden TO is larger than the allowed LO. Moreover, the frequencies of these peaks are shifted towards the low frequency region and their widths are broadened to more than 6 cm^{-1} . As the annealing energy is increased, the forbidden peaks intensities tend to decrease, their frequencies shift and their widths reduce. However, the normal characteristics are not completely recovered at 0.6 J/cm^2 especially for the (100) face.

The spectacular behaviour of the (100) face for low energy annealing has led us to study the Raman spectra at the periphery of the annealed zone by sweeping the Raman laser spot across the limit of the annealed region where the irradiation energy continuously varies.

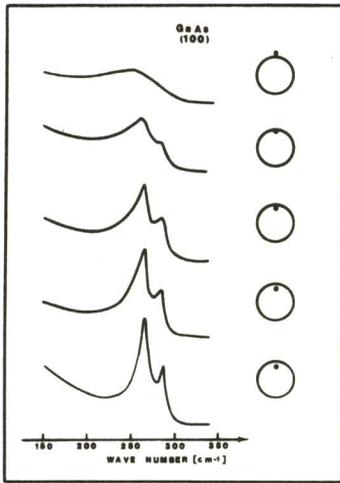


Fig. 3 Raman spectra on a (100) face of GaAs from various points near the periphery of a laser annealed region (energy 0.6 J/cm^2).

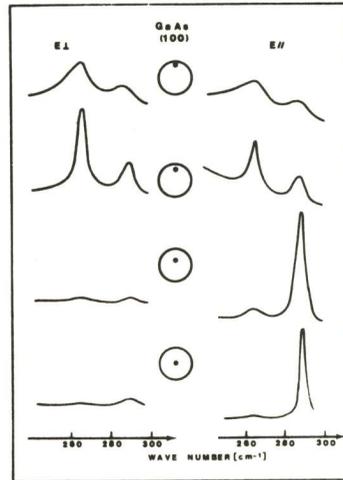


Fig. 4 Polarization measurements on a (100) face of GaAs from various points along a radius of a laser annealed region (energy 0.6 J/cm^2) E_{\perp} is parallel to $\langle 011 \rangle$ axis.

As can be seen on Figure (3), the spectra are continuously modified, the amorphous band at 250 cm^{-1} shifts and get structured changing into the TO phonon. The allowed LO phonon appears only as a shoulder on this band. The polarization analysis has been made on the (100) face sample, with the incident electric field parallel to the $\langle 011 \rangle$ axis, the scattered field has been either parallel or perpendicular to the incident field. For this last polarization both peaks TO and LO are forbidden in a perfectly crystalline sample whereas the LO phonon normally appears when both fields are parallel. On Fig. (4), it can be seen that the selection rules are well observed when the analysis is made at the center of the annealed zone but are not at the intermediate region, where spectra are rather identical for both polarization.

Discussion

The more important feature presented here seems to be the gradual transition from the amorphous spectrum to a crystalline one. This fact involves a continuous variation of the degree of order versus the annealing density energy. The late appearance of the longitudinal optical phonon when increasing the annealing energy conforms to this hypothesis as the existence of this phonon is due to long range Coulombic forces. A way of understanding such a continuous variation is to consider the presence of microcrystallites in the annealed region. Such crystallites have yet been observed in laser annealed Silicon and Gallium Arsenide [4,5]. There are very few published results on Raman spectroscopy of small crystals. The only extensively studied case is the graphite [6] where only very small size crystallites are available. In this material, new peaks as well as a shift of the high frequency E_{2g} first order peak are reported and attributed to the wave vector selection rules

relaxation. The shift observed is toward the high frequency region. This is not contradictory with our observation of a low frequency shift in GaAs if the special shape of the dispersion curves of graphite is considered. In this material, the highest branch of the dispersion curves reaches a region of higher frequency (~ 1600) than the zone center E_{2g} mode (1581 cm^{-1}) [7]. Furthermore, this E_{2g} mode is transformed into a band situated at higher frequency (1800 cm^{-1}) in the amorphous state of graphite (glassy Carbon) which is an opposite behaviour as compared to GaAs or Si. If the crystallites have systematically size of the order or larger than $10 \mu\text{m}$, as pointed by Tsu et al. [8] such a fact would contradict our explanation based on a size effect. But we have done some experiments on Silicon powders on grains of the order of $1 \mu\text{m}$. Such grains give Raman spectra comparable with the Raman spectra of laser annealed Si [1] with the first order Raman peak shifted towards low frequencies by more than 10 cm^{-1} . So it seems that only complete calculation of the Raman effect due to size effect in small crystal of GaAs would help to justify the hypothesis presented here.

Aknowledgments

We thank the Laboratoire Central de Recherches Thomson-C.S.F. for performing the implantations and laser annealings. This research was supported by the "Direction des Recherches Etudes et Techniques", Grant n° DRET 79/1101.

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