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RAMAN VIBRATIONAL STUDIES OF TRANSIENT ANNEALING OF GaAs AMORPHOUS THIN FILMS

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Résumé - Des couches endommagées par implantation ionique, à forte dose, dans GaAs ont été reconstruites à l'aide d'un laser Ruby pulsé (nsec), d'un laser Nd-YAG pulsé (psec) ou d'un système de lampes à halogène. La reconstruction du réseau cristallin par ces différentes techniques de recuit rapide est étudiée par diffusion Raman des phonons.

Abstract - A nanosecond pulsed ruby laser, a picosecond pulsed Nd-YAG laser and a set of halogen lamps are used to induce the reconstruction of the damage layer obtained by high dose ion implantation in single crystal GaAs. The lattice reconstruction by these different rapid irradiation sources has been examined by Raman scattering from the phonons.

INTRODUCTION

Lasers, electron beams or incoherent lamps provide a way to locally heat the surface of an implanted semiconductor. A rapid local heating followed by a fast cooling after irradiation are induced by these different beams (transient annealing) and both crystal recovery and dopant activation are obtainable during an annealing cycle. These techniques are widely used in Silicon Technology. Gallium Arsenide which contains two different kinds of atoms is more chemically unstable than Silicon and surface degradation is more likely to occur at high temperatures.

Raman scattering by phonons is an unique tool for characterization, after an annealing cycle, of the lattice reconstruction, the surface degradation as well as the nature (donors or acceptors) and concentration of dopants introduced by implantation.

LIQUID PHASE RECRYSTALLIZATION

Two kinds of laser pulses have been used : a Q-switched Ruby laser (25ns) and a picosecond (30 ps) pulse from a mode-locked Neodymium : Yttrium Garnet laser. It is believed that melting of the implanted layer occurs under irradiation, followed by a liquid phase epitaxial regrowth.

a - STUDY OF THE LATTICE RECONSTRUCTION BY THE RUBY LASER :

A set of two different Indium ion implantations have been performed in (001) GaAs substrates to obtain an uniform distribution of defects over 1000 Å from the surface, one, at 330 KeV (dose $3 \times 10^{15} \text{ cm}^{-2}$) and the other at 170 KeV (dose $1.5 \times 10^{15} \text{ cm}^{-2}$). Such bombardment conditions allow the formation of an amorphous layer of thickness larger than the argon-ion laser radiation (5145Å) used to perform the Raman measurements.

The scattered light intensity $I(\omega)$ of an amorphous material is given [1] by

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$I(\omega) = C_b [n(\omega, T) + 1] g_b(\omega) / \omega$, where $n(\omega, T)$ is the Bose-Einstein distribution at temperature T for first-order Stokes scattering at energy shift ω and $g_b(\omega)$ represents the vibrational density of states in band b ; C_b is the coupling constant given by $C_b \approx |e_i R_{ij}(\omega) e_j|^2$ with \vec{e} and \vec{e} as the polarization vectors of the incident and scattered light, and R_{ij} the Raman tensor components; C_b is proportional to ω for $\omega < 50 \text{ cm}^{-1}$ (Ref 2) and is taken constant for higher ω values in GaAs. The amorphous GaAs spectrum at room temperature is represented in Fig 1 (upper curve). Two main bands can be distinguished: one which corresponds to the modes belonging to the transverse acoustic branch and the other which is associated to the frequency range of the optical branches in the crystal. The amorphous density of states which appears on this spectrum is very similar to that of the corresponding crystal (Fig 2) but broadened by a convolution with a Gaussian factor of the order of 25 cm^{-1} (Ref 3). The first band peaks at the frequency corresponding to the transverse acoustic branch at the Brillouin zone edge and is labelled DATA (Disorder Activated Transverse Acoustic band). The similarities between the density of states of amorphous and crystalline GaAs are due to the conservation of the short-range order of the crystalline phase and the near-neighbor character of the atomic interaction.

Fig 1 - Ruby laser annealing of implanted amorphized GaAs Raman scattering study at different density of energy. The horizontal lines indicate the zero level. For 0.6 J/cm^2 the resolution is 3 cm^{-1} and 5 cm^{-1} for the other spectra

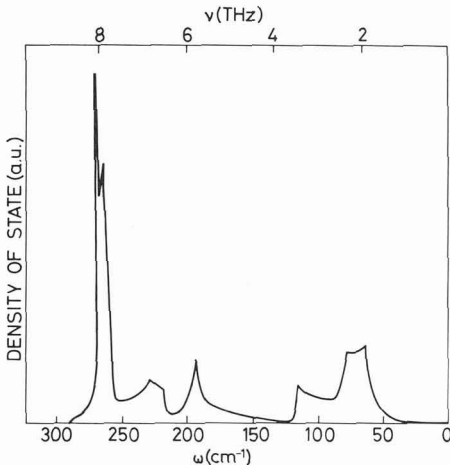
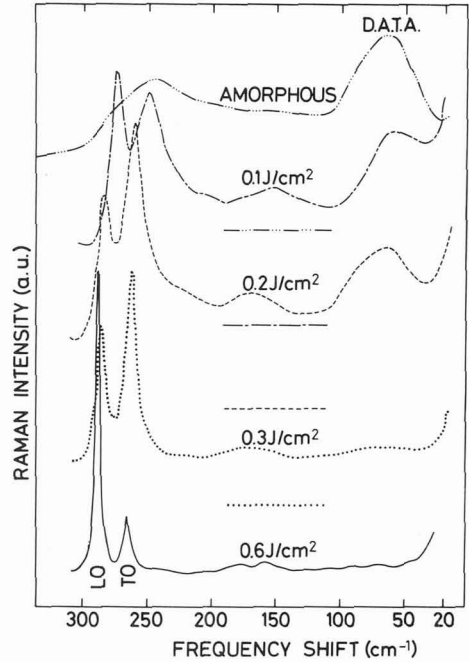


Fig 2 - Phonon density of states in GaAs crystal from Dolling and Cowley, Proc. Phys. Soc. London 88, (1966) 463

An irradiation with of a Ruby laser pulse of 0.6 J/cm^2 allowed complete reconstruction of the crystal since the spectrum of the annealed sample (lowest curve of Fig 1) is very similar to the one of the GaAs crystal (LO line at 292 cm^{-1} and a small TO at 269 cm^{-1} owing to departure from strict backscattering). The LO line corresponds to the highest phonon energy of the diagram of the crystal density of states. It is clear on Fig 1 that the DATA becomes less and less active with increasing values W of the density of energy of the Ruby pulse and practically disappears for $W = 0.6 \text{ J/cm}^2$. The high energy Raman peak of amorphous GaAs split into two lines which we call LO-like and TO-like as their frequency, width and intensity tend to the LO and TO of the crystal as the lattice is reconstructed. More precisely as the long-range order is restored the LO-like and TO-like shift to higher frequencies, their width decreases while the LO-like intensity increases drastically with respect to the intensity of the TO-like.

b - STUDY OF THE MULTIANNULAR PATTERN PRODUCED BY A PICOSECOND LASER

The lattice reconstruction depends on the resolidification velocity of the surface layer melted under irradiation by the pulsed beam. There is a threshold in the speed of the resolidification process above which the crystalline structure does not recover, resulting in amorphous material formation [4]. Extremely short pulses (psec) or strongly absorbed light pulses (U.V. photons) produce resolidification rates above this threshold in semiconductor.

Single pulses of overage duration 27 ps at $1.06 \mu\text{m}$ were extracted from a mode locked Nd : YAG laser [5] and were used for annealing. The samples were GaAs (001) substrates amorphized with Te ions at a dose of $1 \times 10^{15} / \text{cm}^2$ and at an energy of 250 KeV. The amorphized layer was about 1000 \AA thickness. The gaussian laser beam was focused on the sample at a diameter of $450 \mu\text{m}$.

The annealed spot is composed of concentric rings [5] of different contrast which can be viewed under a conventional Normarski optical microscope. This multiannular pattern is probably due to a multiple melting-resolidification process [6,7] during the pulse duration. The best optical contrast was obtained at 1.5 J/cm^2 , above the damage threshold of the substrate and the annealed spot was degraded at the center (see Fig 3 left top edge). Raman scattering measurements were performed using a microprobe and the incident laser was focused on a $1 \mu\text{m}$ -diam spot scanned across the area irradiated by the picosecond pulse. All the spectra are taken in the same experimental conditions. The first ring surrounding the damaged center is essentially recrystallized but the LO peak is downshifted by 2 cm^{-1} . Furthermore a very small peak appears at 267 cm^{-1} which is assigned to the TO mode and is probably a consequence of a slight disorder or misorientation. The spectra (C) and (D) obtained from the other rings of the pattern are clearly intermediate states between crystalline (A) and amorphous (E) GaAs. One can notice the striking similarities between the lines of (C) and (D) and the TO-like and LO-like of Fig 1. Then the region D appears more ordered than the region C and the annealed pattern is clearly formed of rather ordered and rather disordered rings.

SOLID PHASE RECRYSTALLIZATION-HOLOGEN LAMPS ANNEALING

When a C.W. laser or an incoherent lamp is used, the annealing mechanism is usually a solid phase epitaxial regrowth which proceeds at rates comparable to those obtained for conventional thermal annealing. The role of the laser and the lamp is only to heat the implanted region to a temperature (1000-1300C) high enough to induce solid phase regrowth.

A system [8] of two 150 W halogene lamps have been built in the laboratory in order to anneal implanted GaAs samples ($1 \times 10^{15} \text{ Te ions/cm}^2$ at 250 KeV) ; contact protection of the substrate was obtained by mounting the sample in a sandwich configuration between a silicon plate and a quartz plate. The reconstruction of the lattice by irradiation was accompanied by a slight surface degradation evidenced by traces of crystalline As. The presence of As can be attributed either to an evaporation and recrystallization of As at the surface of the sample due to the confinement [8], or

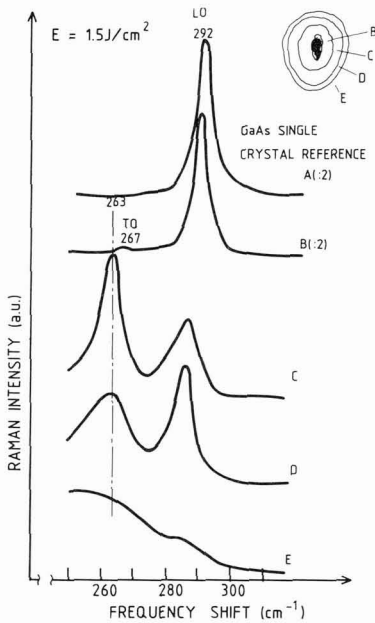


Fig 3 - Raman spectra of the different regions of the multiannular pattern induced by a picosecond pulse ($\lambda : 1.06 \mu m$) in an amorphized GaAs sample

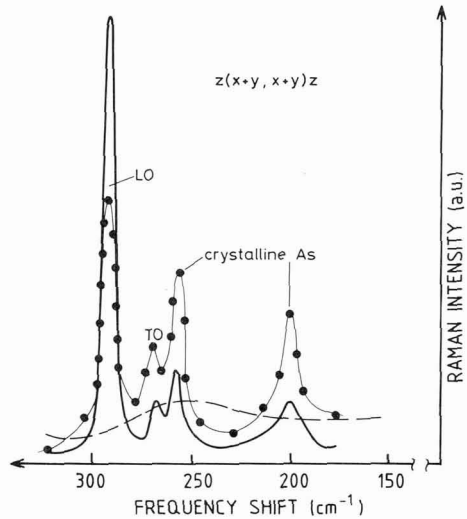


Fig 4 - Raman scattering spectra of amorphized GaAs irradiated with Halogen lamps ; ----- amorphous reference
 _____ irradiated for 30 s ; -●-●-●- irradiated for 45 s

a thermal oxydation with As retained in the interfacial region during growth [9]. Raman scattering allows a simultaneous study of the lattice reconstruction and the surface degradation. Several irradiation times have been selected between 5 and 45s. The presence of crystalline As detected by the two first-order Raman lines A_{1g} and E_g was clearly an increasing function of the exposure time. Yet, the As layer at the surface was thin enough to allow transmission of incident and scattered photons from the implanted region. The best operating conditions for Halogen lamps annealing were obtained for a time exposure t of 30s for which the intensity of the LO was maximized (60 % of the intensity of a crystalline reference. For $t > 30s$ (Fig 4) the LO decreases while the As lines continue to increase versus t . For $t < 30s$ both the As lines and LO decrease.

CONCLUSION

This is an experimental survey of transient annealing of implanted amorphous layers of GaAs. The rapid irradiation sources used induced either a melting followed by a recrystallization, or a complete solid phase regrowth. The Raman active modes are studied in the transformation amorphous-crystal. The study have evidenced TO-like and LO-like modes associated with intermediate states. The nature of these intermediate states is not yet elucidated (are they polycrystalline agregates ?) Only the use of other technique (electronic microscopy for instance) could bring an answer. The fact that no coupled LO phonon plasmon modes appeared in the spectra of Te implanted GaAs in spite of the good reconstruction of the lattice after annealing by Halogen lamps indicates that no significant electrical activation has been obtained.

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