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Laser Raman-Spectroscopy of Phase Transformation in the Near Surface of GaP

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When implanting GaP with boron and heavier argon ions, severe distortion of crystal structure occurs. Raman scattering has shown that with implanted ion dose change the crystal structure transforms gradually into disordered state, in which coexisting of crystalline, microcrystalline, nanocrystalline and amorphous phases is possible. At the certain stage of implantation the formation of continuous amorphous layer of GaP takes place. The critical doses of amorphization of GaP at implantation with B and Ar ions have been defined. The graph of dependence of LO phonon halfwidths upon implantation doses is also a characteristic of synthesizing of nano-GaP. We suggest a possible mechanism for structural transition dynamics in GaP caused by ion implantation.

Keywords: Raman Scattering, Implantation, Amorphization, Microcrystalline, Nanocrystalline Semiconductors.

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1. INTRODUCTION

The ion implantation is one of the main technological methods for semiconductors selective doping. An advantage of this method consists in the fact that at ion implantation it is possible to specify exactly the concentrations of doped ions as well as profiles of their distribution. On the other hand at implantation the crystal structure is destroyed - defects are produced. The defect production may increase so that after a certain critical limit the crystal transforms into a very disordered structure. Crystal structure transition into a disordered state depends upon implanted ion type and implantation conditions. Finally the crystal may transform into a continuous amorphous phase.

When implanting GaP with boron and heavier argon ions, severe distortion of the crystal structure occurs near the surface. Raman scattering has shown that with implanted ions dose change the crystal structure gradually transforms into a disordered state, in which coexisting of crystalline, microcrystalline, nanocrystalline and amorphous phases is possible. At the certain stage of implantation, the formation of continuous amorphous layer of GaP takes place.

Raman scattering is an important physical method to study such phase transformations. It should be noted that when studying Raman scattering an object under investigation does not undergo any damage.

Semiconductor surfaces implanted by various ions have been studed by the Raman spectroscopy. As a result it is stated that the crystalline structure of semiconductor substrate undergoes very important structural changes due to ion implantation. Other important physical-chemical changes also take place. In particular micro and nanocrystal clusters are synthesized [1-2]. The substrate surface transforms into continuous amorphous state [3-4]. Concentrations of free carriers increase greatly due to implantation with some ions and post annealing [5-7]. Mixed crystal synthesizing takes place by implantation with some ions [8-10]. It has been shown in these works that synthesizing of nanocrystalline phase is indicated by asymmetric broadening of half-widths of LO and TO phonons spectral bands, peak shift towards low frequencies and peak intensity decrease [1-2]. When the crystalline surface of substrate transforms into a continuous amorphous state due to implantation, then LO and TO phonons narrow spectral bands of Raman scattering peculiar to crystal structure are widening so that occurs their overlapping and a wide continuous spectral band without a structure is formed showing densities of phonon states [3-4]. When implanting occurs with electrically active impurities, then as the authors [5-7] have shown, the plasmon-phonon interaction becomes apparent. The intense increase of free carrier concentration points to this fact. As the authors [8-10] have shown in case of implanting of isomorphic impurities, the spectral bands peculiar to local, gap and mixed crystals are formed.

The objective of the present work is to study by Raman spectroscopy phase transformation of GaP crystalline surface when bombarding this semiconductor by various dosages of boron and argon ions.

2. EXPERIMENTAL CONDITIONS

The plates with surfaces oriented in (111) direction were cut from the single-crystalline GaP ingot. The both surfaces of the plates were polished optically. Argon ion implantation was carried out with the following doses: $D = 10^{12}$; 3×10^{12}; 9×10^{12}; 3×10^{13}; 8×10^{13}; 2×10^{14}; 6×10^{14}; 2×10^{15} ion/cm^2. Boron ion implantation was carried out with the following doses: $D = 1 \times 10^{13}$; 3×10^{13}; 1×10^{14}; 2×10^{14}; 6×10^{14}; 1×10^{15}; 2×10^{15}; 1×10^{16} ion/cm^2. The implanted ion energy was 110KeV. One half of the plate covered with

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the foil in which fast ions did not penetrate, was used as a standard at Raman spectra registration.

Raman spectra were recorded on the lab-type laser Raman spectrometer we had constructed on the basis of double monochromator DFS-12. A grating 600 grooves/mm, working in the first order of spectrum served as a dispersion element. Focal length of spectrometer was 800 mm. Photomultiplier FEU-79 served as a signal detector. Raman spectra were excited by argon laser wavelength 514.5 nm. All measurements were carried out at room temperature.

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

GaP belongs to cubic crystals with T_d symmetry. Raman scattering spectrum from surface (111) for such structure consists of two narrow spectral bands. One corresponds to LO longitudinal phonon at frequency LO = 402 cm^{-1}, and the other to TO transverse phonon TO = 365 cm^{-1}. Fig. 1 shows the Raman spectra we have recorded after doping GaP by 110 KeV argon ion with doses $9x10^{12}$, $6x10^{13}$, $2x10^{14}$, $6x10^{14}$ ion/cm^2. The spectra show distinctly that with increase of flow of implanted ions the LO and TO frequencies of substrate shift to lower frequencies. Intensities are decreased and halfwidths of spectral bands are broadened asymmetrically. Almost analogous experimental picture has been obtained in case of implantation of substrate GaP with various doses of boron ions. In this case of implantation the frequency shift, intensity decrease and broadening of halfwidth take place for higher doses than in case of heavier argon ions. Fig. 2 shows this case.

According to the spectra intensities of sharp LO and TO spectral bands for crystalline GaP strictly decrease after implantation with rather less doses; as for their half widths, they broaden with dose. Besides, spectral peak shifting to the low frequences takes place within 2.5 – 3.5 cm^{-1}. Further increase of dose causes such broadening of LO and TO phonon halfwidths that after joining they give a wide band without structure, Fig 1d and Fig.2d.

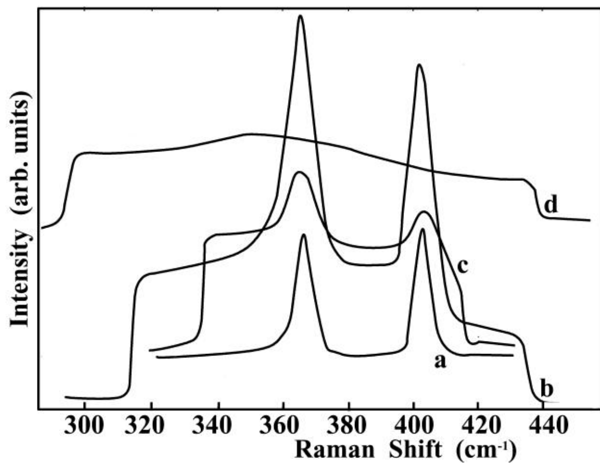

Fig. 1 – Raman spectra of GaP after implantation with various doses of Argon ions. a – $D = 9 \times 10^{12}$, b – $D = 6 \times 10^{13}$, c – $D = 2 \times 10^{14}$, d – $D = 6 \times 10^{14}$ ion/cm^2

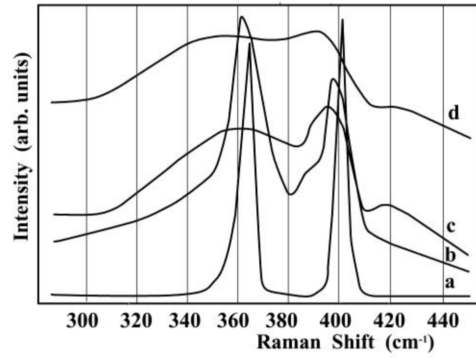

Fig. 2 – Raman spectra of GaP after implantation with various doses of Boron ions. a – $D = 1 \times 10^{13}$, b – $D = 1 \times 10^{14}$, c – $D = 2 \times 10^{14}$, d – $D = 1 \times 10^{15}$ ion/cm^2

Fig. 3 and Fig. 4 shows the dependence of LO TO phonon spectral band half width upon argon and boron ion implantation dose accordingly.

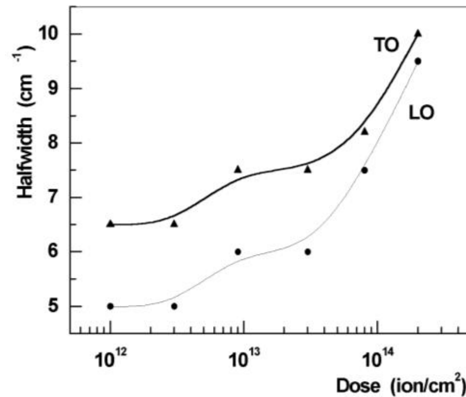

Fig. 3 – Dependence of halfwidths corresponding to LO TO phonon upon doses of implanted Argon ions at implantation with 110 KeV

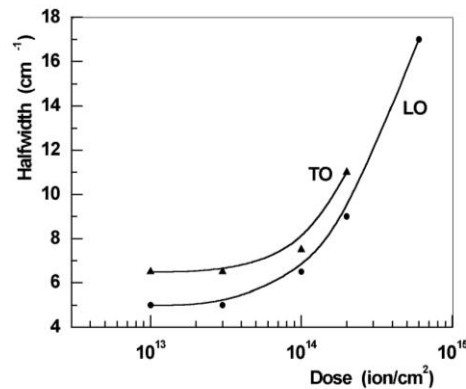

Fig. 4 – Dependence of halfwidths corresponding to LO TO phonon upon doses of implanted Boron ions at implantation with 110 KeV

With further increase of implantation dose the disorder of crystal lattice achieves the critical threshold and GaP crystal fully transfers into an amorphous state. To determine the critical dose of amorphization we have drawn the dependence of dose upon RS normalized intensity:

$$I_n = 1 - I/I_0,$$

when I_0 is RS intensity of standard GaP, and I is RS intensity of different doses of implanted GaP. Figures 5 and 6 show these dependences in the case of GaP:Ar and GaP:B accordingly. When the curve goes to the saturation, we suggest that the full amorphization takes place [1]. Critical dose of amorphization defined by the above method is 8×10^{13} ion/cm^2 for argon ion and 6×10^{14} ion/cm^2 in the boron ion case. The energy of each ion is 110 KeV. Probably GaP crystalline lattice transformation into amorphous state occurs at lower doses of implantation with Ar heavy ions than in case of implantation with B light ions.

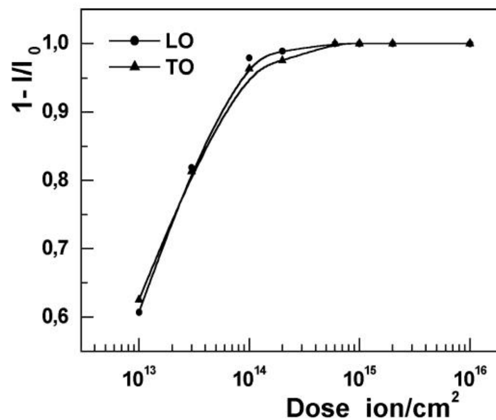

Fig. 5 – Dependence of normalized intensity I_n for LO and TO phonons on implantation dose in case of Argon ion implantation

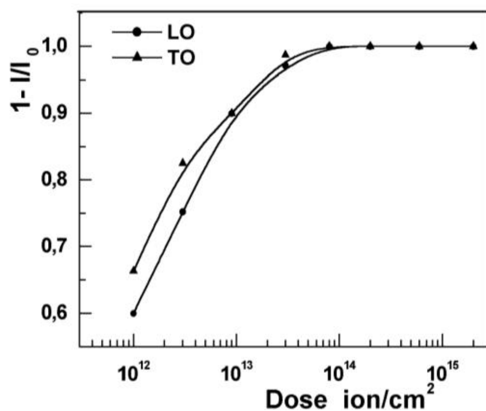

Fig. 6 – Dependence of normalized intensity I_n for LO and TO phonons on implantation dose in case of Boron ion implantation

In a perfect three-dimensional crystal the region over which the spatial correlation function of the phonon extends, is infinite. This leads to the fact that propagation of phonons is expressed by plane waves and at the first order Raman scattering the $q = 0$ selection rule is observed. Correlation function becomes finite when a great number of defects are formed at crystal bombardment with accelerated ions. In this case the $q = 0$ selection rule undergoes relaxation. Correlation function also decreases according to relaxation and becomes finite. Experimentally in such cases the shift of phonon frequencies towards low frequencies, decrease of intensities and asymmetric broadening of half widths of spectral band characterizing phonons take place in Raman scattering. The same experimental facts take place when Raman spectra of nanocrystalline compounds are being recorded. Just when studying a nanocrystalline semiconductor Si, Richter introduced the so-called "phonon confinement" conception [11], according to which the shift of phonon frequencies and asymmetric broadening of halfwidths take place in nanocrystalline materials. The reason is that in direct space the phonons of nanocrystalline materials are confined within spheres with diameter L. Description of such phonons is carried out in reciprocal space with wave packet with wave vector **k** in interval $\Delta k \approx L^{-1}$.

Thus shift of phonon frequencies towards low frequencies, asymmetric broadening of half widths and change of intensities indicate that due to ion implantation nano-GaP has been synthesized near the surface of GaP.

Thus the laser Raman-spectroscopy turns to be a very useful and informative method for diagnosis of physical-chemical properties of semiconductors surfaces modified by ion implantation.

4. CONCLUSION

When accelerated ions hit semiconductor target surface, multiform changes of crystal structure take place. Using Raman spectroscopy we have stated that near surface GaP nanocrystalline, microcrystalline amorphous and generally disordered structure phases are formed. We have stated that in the process of implantation the formation of the mentioned structural phases occurs in various dose ranges. Regularities of changes of experimental spectral parameters (halwidths, phonon frequencies and intensities) enable one to estimate approximately dose interval corresponding to structural transformation.

Critical doses of amorphization when implanting GaP by various doses of argon and boron ions have been estimated by Raman spectroscopy.

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