ISSN 1512-1461

LASER RAMAN SPECTROSCOPY OF GAAS AFTER AR, B, P IONS IMPLANTATION

Sergo V. Gotoshia, Lamara.V. Gotoshia
(Institute of Inorganic Chemistry and Electrochemistry, Tbilisi 0186, Mindeli 11, sergotoshia@yahoo.com)

Abstract:
When implanting GaAs with boron and heavier argon ions, severe distortion of crystal structure occurs. Raman scattering has shown that with change of fluence of implanted ions the crystal structure gradually transforms into disordered state, where coexistence of crystalline, microcrystalline, nanocrystalline and amorphous phases is possible. At the certain stage of implantation the formation of continuous amorphous layer of GaAs takes place. The critical fluences for amorphization of GaAs 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 amorphization. We suggest a possible mechanism for structural transition dynamics in GaAs caused by ion implantation. We implanted polish surfaces of GaAs also with 70 and 40 KeV phosphorous with $1.8x10^{17}$ *and* $1x10^{17}$ *ion/*cm^2 *fluences accordingly. The orientations of surfaces were (111). The implantation was carried out at room and* 450^0 *C temperatures accordingly. In these two cases a disordered structure of the ternary compound GaAsP is formed. When implanting at room temperature a ternary compound is synthesized in amorphous phase and at hot implantation besides amorphous phase microcrystalline nuclei are formed as well. By following thermal treatment the amorphous phase changes into crystalline.*

Keywords: *Raman scattering, ion implantation, amorphization, microcrystalline, nanocrystalline, mixed semiconductors.*

1. Introduction

Ion implantation is one of the main technological methods for selective doping of semiconductors. An advantage of this method consists in the fact that at ion implantation it is possible to specify exactly 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. 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 continuous amorphous phase.

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 studied by Raman spectroscopy. As a result it is stated that the crystalline structure of semiconductor substrate undergoes very important structural changes by 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 by implantation with some ions and with post annealing [5-7]. Mixed crystal synthesizing takes place by implantation with some ions [8-10]. It

ISSN 1512-1461

has been shown in these works that synthesizing of nanocrystal phase is indicated by asymmetric broadening of half-widths of LO and TO phonons spectral bands, peaks shift towards low frequencies and peak intensity decrease [1-2]. When crystalline surface of substrate transforms into 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 their overlapping occurs and 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, a plasmon-phonon interaction becomes apparent. This indicates intense increase of concentration of free carriers. As the authors have shown [8-10], in case of implanting of isomorphic impurities, spectral bands peculiar to local, gap and mixed crystals are formed.

The objective of the present work is to study by Raman spectroscopy the dynamics of crystal structure transition of GaAs into amorphous when bombarding this semiconductor by various dosages of boron and argon ions. It is also interesting what happens on the surface of substrate GaAs when bombarding it with high doses of isomorphic phosphorous ions, the substrate at implantation being at room and high (450^0 C) temperatures.

2. Experimental conditions

From the single-crystalline high-resistance GaAs ingot plates with surfaces oriented in direction (111) had been cut. The both surfaces of the plates were polished optically. One half of optically polished surface was covered with aluminum foil; the second half was implanted by argon, boron ions. The implanted energy of ions was 110 KeV, fluences varied in the wide range. Current was marginally small at the implantation so as not to happen damaged crystal structure recovering due to annealing during implantation process. This current did not exceed 0.4 μA/cm^2. Argon ion implantation was carried out with the following fluences: D=10^{12}; $3x10^{12}$; $9x10^{12}$; $3x10^{13}$; $8x10^{13}$; $2x10^{14}$; $6x10^{14}$; $2x10^{15}$ ion/cm^2. Boron ion implantation was carried out with the following fluences: D=$1x10^{13}$; $3x10^{13}$; $1x10^{14}$; $2x10^{14}$; $6x10^{14}$; $1x10^{15}$; $2x10^{15}$; $1x10^{16}$ ion/cm^2. One half of the plate covered with foil in which fast ions could not penetrate, was used as a standard at Raman spectra registration.

Raman spectra were recording on the lab-type laser Raman spectrometer we had constructed on the basis of double monochromator DFS-12. A grating 600 grooves/mm producing reflected light concentration in red-yellow area of spectrum and working in the first order of spectrum served as a dispersion element. The focal length of spectrometer was 800 mm. Photomultiplier FEU-79 served as a signal detector. Raman spectra were excited by argon ion laser wavelength 514.5 nm. All measurements were carried out at room temperature.

3. Implantation of GaAs by ions Ar and B

GaAs 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 292 cm^{-1} and the other to TO transverse phonon at 268 cm^{-1}.

Fig.1 shows the Raman spectra we have recorded after doping GaAs with various fluenses of Boron ions. The standard Raman spectrum of GaAs is also presented in the same picture. 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 GaAs with various fluences of argon ions. In this case of implantation the frequency shift, intensity decrease and broadening of halfwidth occur for lower fluences than in case of light boron.

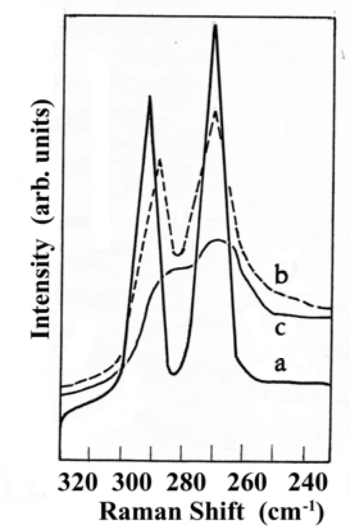

Fig. 1 Raman spectra of GaAs after implantation with various fluences of boron ions. a - standard GaAs; b – D=1x10^{14} ion/cm^2; c – D=6x10^{14} ion/cm^2.

On the basis of the above experimental data, the dependences of halfwidths of spectral bands corresponding to LO phonon, on fluences of implanted boron and argon ions at implantation with 110 KeV energies have been plotted. These dependencies in Fig.2 show that LO phonon halfwidths are broadened according to the nonlinear law by fluence increase.

At the same time the graphs show that at implantation with heavier ions (for instance, argon) implantation with lesser fluence is needed to achieve the same broadening as in case of light ions (boron, for instance).

Maximum frequency shift has been fixed at 3.5 cm^{-1}.

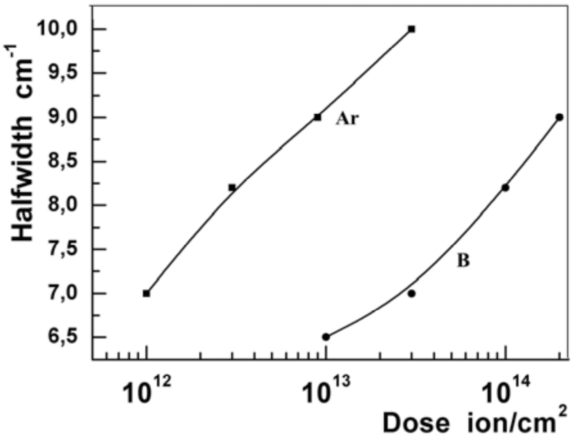

Fig. 2 Dependence of halfwidths corresponding to LO phonon upon fluences of implanted boron and argon ions at implantation with 110 keV.

As mentioned, the third parameter changing at ion implantation is LO and TO phonons intensities. Fig.1 shows that these intensities decrease gradually when implantation fluence increase. But after the certain fluence called critical fluence, narrow peaks of LO and TO phonons almost disappear and the spectrum takes shape of wide band without any structure. Such a character of the spectrum indicates that at implantation with the mentioned fluence, crystal phase has transformed into amorphous phase.

The graph for dependence of normalized intensity I_n on fluence of implanted ions has been plotted to analyze quantitatively the dynamics of crystalline GaAs transformation into amorphous phase.

$$I_n = 1 - \frac{I}{I_0} \qquad (1)$$

Where I_0 is RS intensity of crystalline (standard) GaAs, I- RS intensities of GaAs implanted with various doses.

Normalized intensity is zero, when there are no defects in substrate, but it is equal to unity when the crystal is completely transformed into amorphous phase.

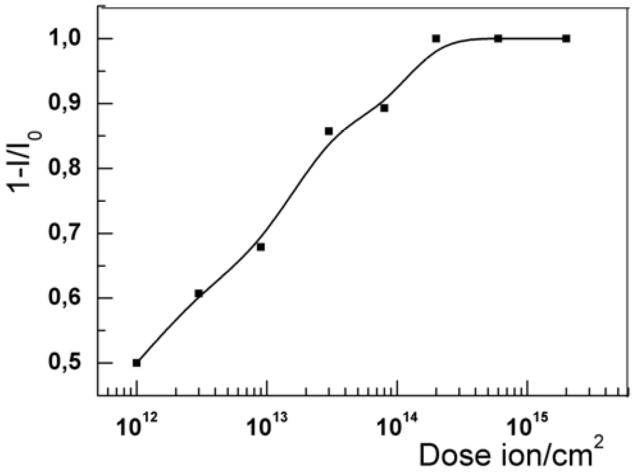

Fig.3 Dependence of normalized intensity I_n on fluence of implanted ions in case of argon ion implantation.

Fig.3 shows the mentioned dependence in case of argon ion implantation. Fig. 4 shows the mentioned dependence in case of boron ion implantation. The graphs show that defect concentration in crystal lattice increases with implantation fluence increase. The defects cause crystal structure transition into disordered state. After achievement a critical fluence there are such a great number of defect clusters that due to their overlapping the crystal structure changes into amorphous state. The critical fluence of amorphization is $2x10^{14}$ ion/cm^2 when doping GaAs with110 KeV argon ions at room temperature. When doping by boron ions with the same energy at room temperature the critical fluence of amorphization is $2x10^{15}$ ion/cm^2. The mentioned quantities are obtained from graphs in Fig. 3 and Fig. 4 accordingly.

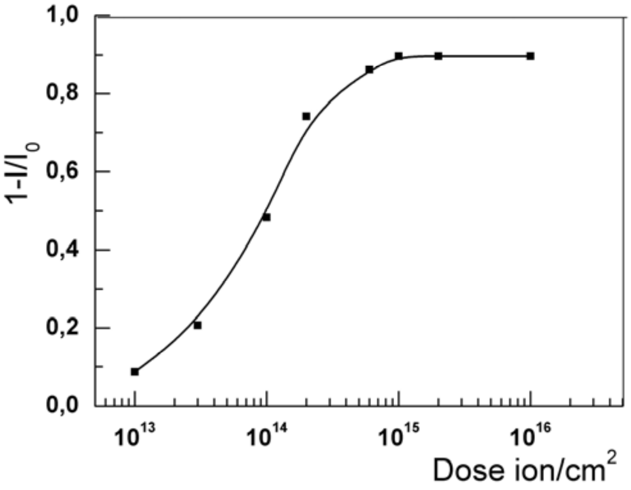

Fig. 4 Dependence of normalized intensity I_n on fluence of implanted ions in case of boron ion implantation.

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 shift of phonon frequencies towards low frequencies, decrease of intensities and asymmetric broadening of half widths of spectral bands characterizing phonons take place in Raman scattering. The same experimental manifestation occurs when Raman spectra of microcrystalline compounds are being recorded. Just when studying a microcrystalline semiconductor Si, Richter introduced the so-called “phonon confinement” conception [11], according to which the shift of frequencies of phonons and asymmetric broadening of halfwidths take place in microcrystalline materials. The reason is that in direct space the phonons of microcrystalline 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 $\mathbf{\Delta k \approx L^{-1}}$.

Thus shift of frequencies of phonons towards low frequencies, asymmetric broadening of half widths and change of intensities are characteristics not only for microcrystalline nonmetallic materials. Defects induced in crystals also cause the same effects.

Consequently, with the aid of these parameters qualitative and quantitative estimation of crystal quality is possible.

The spectra in Fig.1b and 1c show the picture of destruction of crystal structure of substrate and indicate that at boron implantation with such fluences and energy at room temperature the crystal lattice of GaAs is transformed into disordered structure phase. These spectra show that Raman spectra consists of two additive components: peaks of LO and TO phonons with decreased intensities, maxima of which are shifted by little amounts towards the standard substrate frequencies and their half widths are broadened asymmetrically; the second component as seen from the spectra is a wide band without structure. The first part of the spectrum we ascribe to microcrystalline GaAs, and the second component-to amorphous α-GaAs. As to Raman spectrum in Fig. 1c, it almost entirely corresponds to Raman spectrum of α-GaAs.

The same discussion may be carried out in case of argon ion doping, but the quantitative result will be different from case of boron ion doping. Partially, critical fluence of amorphization for lighter boron will be higher. This is illustrated in Fig. 3 and Fig. 4.

ISSN 1512-1461

On the basis of our experiments and data from literature the following destruction mechanism of crystal structure GaAs through ion implantation is offered. In the crystal structure clusters of small dimensions are formed at implantation with small fluences and the local point symmetry is conserved in these clusters. These clusters are of small dimensions. In spaces between the clusters the crystal structure of a lot more volume is conserved containing defects in small quantity, which do not affect the Raman spectra appreciably. As a result, the Raman spectra show small decrease of LO and TO phonon intensities, slight broadening of halfwidths and small shift towards low frequencies of peaks. According to the Raman spectra in this stage of implantation in GaAs coexist microcrystalline clusters with dimensions 60-100 nm in small concentrations and a large amount of spaces with lattice periodicity with small amount of defects in them. At implantation with moderate fluences the quantity of defect areas increases. Simultaneously quantity of microcrystalline clusters increases too. In this stage of implantation a share of crystalline indestructible structure in total structure becomes very small. At the same time the sizes of microcrystalline grains decrease also. Synthesizing of nano-GaAs in large amount takes place. The sizes of these nanocrystals are less than 60 nm. The intensities of LO and TO phonons decrease in large amount, larger shift of peaks maxima towards the low frequencies and vast broadening of halfwidths (this broadening being very asymmetric) indicate this fact. In this stage of implantation microcrystalline, nanocrystalline and a disordered structure of GaAs still co-exist in the crystal. Their ratio is defined by intensity ratios of Raman bands. In the next stage of high fluence implantation the defective areas are broadening with fluence increase and the clusters overlap each other. This leads to synthesis of amorphous α–GaAs. This is proved by transformation of Raman spectrum into a broad band without any structure.

4. Implantation of GaAs by ions P

When bombarding surface GaAs with high fluence of isomorphic impurity, phosphorous, synthesizing of a new ternary compound $GaAs_xP_{1-x}$ is possible. It is interesting in this case: is the new phase synthesizing directly, under the influence of accelerated ions only or additional thermal treating is necessary? What is the substrate temperature effect at implanting of GaAs: is it possible at hot implantation to decrease defect formation in crystalline substrate so much that to obtain crystalline phase of a new compound $GaAs_xP_{1-x}$ without additional thermal treatment; is it possible to obtain by thermal annealing the ternary semiconductor $GaAs_{1-x}P_x$ when the substrate is implanted at room temperature?

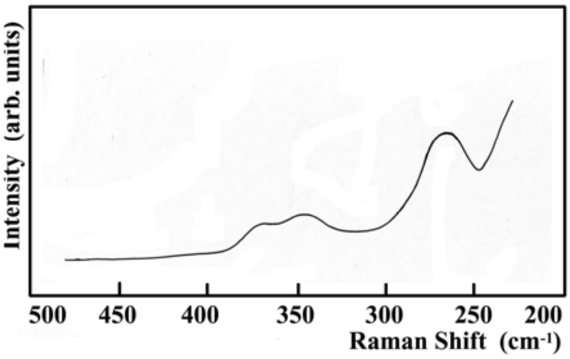

Fig. 5 Raman-spectra of α-GaAsP synthesized by P ion implantation at room temperature.

Fig. 5 shows the Raman-spectrum, which reflects the picture created by phosphorous ion implantation in GaAs. The implantation occurs at room temperature; the fluence of implantation being 1x10^{17} ion/cm^2. Implantation energy is 40 KeV. Two wide bands at proximity of about 275cm^{-1} and 375 cm^{-1} are distinctly seen in the Raman-spectrum. These bands are sharply shifted from the characteristic spectra of α-GaAs and α-GaP. Their ion syntheses and identification by Raman has been done in our work [12]. Thus the Raman-spectra in Fig. 5 characterizes a new compound α-GaPAs, where the band at about 275 cm^{-1} corresponds to Ga-As pair vibration; the band at about 375 cm^{-1} shows Ga-P pair vibration. Thus when the substrate is at room temperature, at implantation with high fluences the crystalline long range ordering is so broken that only amorphous phase synthesizing takes place. But after implantation the amorphous phase already corresponds to different (from substrate GaAs) chemical composition α-GaPAs. Thus the Raman spectra show clearly that at room temperature synthesis long range ordering peculiar to crystallinity is broken completely; but near ordering, local tetrahedral bonds are retained.

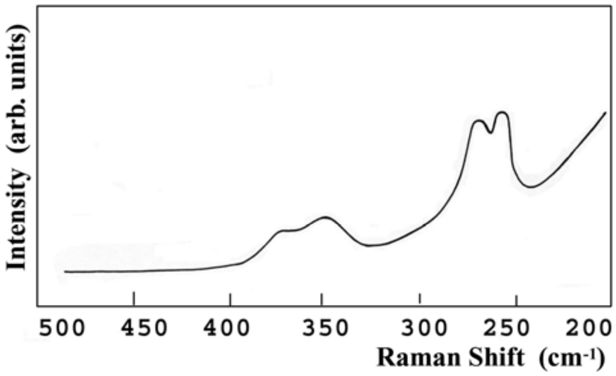

Fig. 6 Raman-spectra of α-GaAsP synthesized by P ion implantation at 400^0 C.

Let us see what happens at hot implantation. Fig.6 shows the Raman spectrum of a new compound synthesized by hot implantation. This spectrum is almost analogous to the Raman spectrum of the same amorphous compound (Fig.5).

However because of its characteristic spectral bands being slightly narrower and more intensive we can conclude that in this case radiation defects are probably smaller. In this case we think that in this regime of implantation synthesizing of a new ternary compound GaPAs takes place. It is expedient to call it a disordered structure δ–GaPAs. We imagine such structure as nano or micro structural small crystals suspended mosaically in amorphous phase. At any case in amorphous phase synthesized at hot implantation local tetrahedral symmetry of α-GaPAs may be enlarged upon some lattice parameters. In the Raman spectrum in Fig.6 at 275 cm^{-1} a spectral band peculiar to Ga-As bond vibration splitting is observed distinctly. This evidently indicates a crystalline nucleus formation of small dimension.

So, when implanting surface GaAs with high doses of isomorphic phosphorous ions a new ternary compound α-GaPAs is synthesized at room temperature implantation. And at hot implantation under the same conditions the disordered structure δ-GaPAs is synthesized. This structure consists of amorphous α-GaPAs phase in big amount with micro crystalline μ–GaPAs suspended in it.

When implanting GaAs with phosphorus, the ion path with its correction does not exceed 100 nm. That is, the synthesized amorphous α-GaAsP is of the same order. At wavelength of 514.5 nm the skin-layer of GaAs, calculated by absorption coefficient, 1/α is about 100 nm, whereas for synthesized amorphous layer the absorption coefficient increases still more. So, in that case only a nanodimensional amorphous layer is studied with excitation 514.4 nm; therefore only the characteristic layer of amorphous layer without substrate spectrum is manifested in the Raman spectrum.

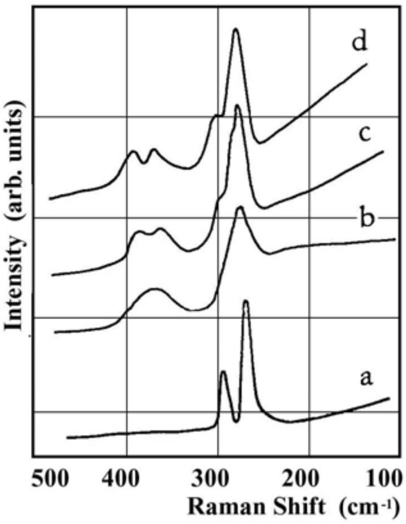

Fig. 7. The Raman spectra indicating the crystallization process of α-GaAsP:
a-the spectrum of the standard GaAs with orientation (111); b, c,
d-the spectra of crystals received after quenching at 500, 700, 850^0 C,
respectively.

When implanting surface GaAs at room temperature with 70 KeV phosphorous ions and fluence $1.8x10^{17}$ ion/cm^2 again the ternary compound GaAsP in amorphous phase has been formed.

To recover the crystal structure we used the thermal annealing in the high vacuum. Before annealing we coated the surface of implanted GaAs with about 100 nm thickness protective layer of SiO_2 to avoid the phosphorous and arsenic evaporation from the crystalline surface. We carried out annealing at 500, 700 and 850^0 C during an hour. The general picture of the Raman spectra recorded after annealing at the above temperatures, is represented in Fig. 7. It is clearly seen that as a result of annealing, α-$GaAs_xP_{1-x}$ transforms gradually into a crystalline state and at the 850^o C nearly entirely recovering of crystalline phase takes place, although a small amount of radiation defects are still felt. This fact is confirmed by narrowing of wide bands typical for amorphous phase with rising the annealing temperature and formation of new peaks at 370$cm^{-1}$and 345cm^{-1} frequencies respectively. We refer these peaks to LO_1 and TO_1 phonons vibration of ternary compound GaAsP accordingly. These spectral bands correspond to phonon vibrations of GaP- type crystalline sub-lattice of new ternary compound GaAsP.

The synthesizing of the mentioned ternary compound is confirmed by formation of a peak at the 280 cm^{-1} displaced by 12 cm^{-1} from the LO phonon of the standard GaAs. This peak relates to the LO_2 phonon vibration of the synthesized crystalline GaAsP and
corresponds to LO phonon vibration of GaAs-type sublattice.

5. Conclusion

When accelerated ions hit semiconductor target surface, multiform changes of crystal structure take place. Using Raman spectroscopy we have stated that near surface GaAs are formed nanocrystalline, microcrystalline amorphous and generally disordered structure phases. By Raman spectroscopy we estimated critical fluences of amorphization when implanting GaAs by various fluences of argon and boron ions.

At implantation surface GaAs with isomorphic impurity, phosphorous, a new ternary compound GaAsP is synthesized. In this case we compared two regimes of implantation: implantation at room temperature and hot implantation, 450^0 C. It turned out that in both cases the crystalline ternary compound $GaAs_{1-x}P_x$ does not synthesize directly only by implantation process. In both cases to recover crystalline long-range ordering it is necessary extra thermal processing. By Raman spectroscopy we have shown the dynamic process of gradual recovering of substrate crystalline structure. It has been proved that at phosphorous implantation of GaAs at room temperature, with post thermal annealing at 850^0 C during an hour synthesizing of crystalline $GaAs_{1-x}P_x$ is possible.

A difference between implantation at room temperature and hot implantation is that in the first case only amorphous compound α-GaAsP is synthesized and in the second case at hot implantation disordered structure δ-GaAsP is synthesized. This structure mainly consists of amorphous phase, α-GaAsP, and few amount of microcrystalline μ-GaAsP suspended in it.

References

[1]. Hiroshi Yoshida, Takashi Katoda, J.Appl.Phys. **67,** 7281-7286, (1990)
[2]. M. Holtz, R. Zallen, O.Brafman, Physical Review **B37**, 2737-2740, (1988)
[3]. J. Wagner and C. R. Fitzsche, J.Appl.Phys. **67,** 808, (1988)
[4]. M. Holtz, R. Zallen, Art E. Geissberger and R.A. Sadler, J.Appl.Phys. **59,** 1946, (1986)
[5]. T. Nakamura and T. Katoda, J.Appl.Phys. **57,** 1084, (1985)
[6]. R. Ashokan and K.P Jain, J.Appl.Phys. **65,** 2209-2213, (1989)
[7]. S. Hernandez, R. Cusco, N. Blanco, G. Gonzalez-Diaz, L. Artus, J.Appl.Phys. **93,** 2659, (2003)
[8]. I.I. Novak, V.V. Baptizmanski, N.S. Smirnova, A.V.Suvorov, FTT, **20**, 2134, 1978
[9]. R. Ashokan, K.P Jain, H.S.Mavi, M. Balkanski, J.Appl.Phys. **60,** 1985-1993, (1986)
[10]. V. Heera, F. Fontaine, W. Scorupa, B. Pecz and A.Barna, Applied Physics Letters, **77**, 226, (2000)
[11]. H. Richter, Z. P. Wang, L.Ley, Solid State Commun. **39,** 625, (1981)
[12]. S. Gotoshia. L. Gotoshia, Bulletin Of the Georgian Academy of Sciences, **160**, 234, 1999

7 figures

Article received: 2010-04-26