Laser Raman-Spectroscopy Identification of Ion-Synthesized Ternary Mixed $Ga_{1-x}Al_xP$ in Amorphous and Crystalline Phases

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A ternary semiconductor $Ga_{1-x}Al_xP$ has been synthesized for the first time by hot implantation of aluminum in GaP. Two mixed crystals of various compositions have been synthesized when implanting by two different fluencies of aluminum ions. The identification of the above mentioned mixed semiconductors in the amorphous as well as in the crystalline phases has been carried out by the laser Raman spectroscopy. The synthesis of the ternary compositions has been carried out at different depths from the substrate surface by implantation of aluminum ions of various energies. $Ga_{1-x}Al_xP$ synthesized by the ion implantation shows the behavior of two-mode mixed semiconductors. The synthesized compounds are defective and the Raman spectra prove the fact. The share of disordered structure of the composition synthesized with high fluencies of aluminum ion implantation, 2.5×10^{17} ion/cm^2, is especially big.

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1. Introduction

As is known, the ion implantation method is widely used for the modification of semiconductor materials. Particularly in some papers binary and ternary semiconductor synthesis by ion implantation is considered [1–3]. In some works [4–15] optical methods (Raman spectroscopy, photoluminescence, IR spectroscopy) are used for the identification of compounds synthesized by the ion implantation.

The ion implantation is an extreme technological process. Because of forming radiation defects and intermediate disordered structures of various types during the implantation process it is difficult to determine preliminarily at what combination of accelerated ions and corresponding substrates is synthesized the planned compound with a preliminarily calculated composition. A mixed crystal is not always synthesized as a consequence of any substrate implantation with any ion. Generally the result of synthesizing by ion implantation is seen in the process of experiment. Thus, the technological parameters of ion synthesis, conditions and results for all individual cases, for synthesis of a concrete compound, are necessary to be investigated. Everything must be taken into consideration: types of ions, their energies and fluencies, the substrate properties and temperature; kinetic processes of energy transfer between ions, defects and the substrate orientation are also important. Probably, because of these reasons only few ternary semiconductor compounds are synthesized by the ion implantation.

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In the given paper a ternary semiconductor $Ga_{1-x}Al_xP$ synthesized by hot aluminum implantation on substrate GaP has been studied by laser Raman spectroscopy. Our aims are to investigate: if there is possible the synthesis of $Ga_{1-x}Al_xP$ by hot implantation of substrate GaP with aluminum ions at various depths of surface of substrate GaP; the technological conditions of ion synthesis and the vibration dynamics of synthesized mixed crystals; if the defects induced by the implantation can be neutralized by quenching; how the implantation of aluminum with high fluencies influences upon the structural perfection of synthesized mixed crystal.

We have used only the Raman scattering with the purpose of monitoring the dynamics of structural transformations of synthesized mixed crystals. Of course, employment of other structural methods simultaneously would be very important as an additional informational source but we have been limited to use those methods. Besides, it is known that both monitoring of crystal structure transformation into amorphous and the dynamics of recovering processes almost unambiguously are carried out by the Raman scattering.

We have not met the analogous work yet except our works [14, 15].

As is known, the ion implantation produces various degrees of disorder in a crystalline material ranging from point defects and clusters to the amorphous state. Most of the methods used to characterize the disorder, like the Rutherford backscattering technique, transmission electron microscopy, and electrical measurements, are destructive in nature. The Raman scattering, on the other hand, is a powerful, nondestructive method for studying the structure of the disordered solids. A quantitative distinction between a crystalline lattice and a lattice with

some degree of disorder can be made by Raman spectroscopy [16]. This is done by investigating the broad-band characteristic of the disordered state and the narrow peaks appropriate to crystalline structure. For example, the Raman spectrum of amorphous GaAs shows [17] a broad structure around 250 cm^{-1}, while the spectrum of crystalline GaAs shows a sharp peak at LO = 292 cm^{-1} corresponding to zone-center phonons (ZCP). Also, the Raman spectrum of amorphous GaP shows [17] a broad structure around 380 cm^{-1}, while the spectrum of crystalline GaP shows a sharp peak at LO = 402 cm^{-1} corresponding to ZCP. The ternary mixed semiconductors have the same properties, too, when their crystalline structure changes into amorphous by any technological method. In this case in contrast to double semiconductors two wide bands are formed at different frequencies; every band corresponds to two sublattices constituting the mixed crystal. For example, the Raman spectrum of amorphous GaAsP shows [18] two broad structures around 250 cm^{-1} and 380 cm^{-1}. From these two wide bands one at 250 cm^{-1} characterizes Ga–As bond vibration in GaAs like sublattice and the other at frequency 380 cm^{-1} characterizes Ga–P bond vibration in GaP like sublattice. The spectrum of crystalline $GaAs_{1-x}P_x$ shows [19] two sharp peaks at LO_1 = 289 cm^{-1} and LO_2 = 392 cm^{-1} corresponding to ZCP, which characterizes the vibration of GaAs and GaP like sublattice in ternary semiconductor $GaAs_{1-x}P_x$, respectively. As is seen, in case of changing the crystalline phase into amorphous, the narrow spectral bands LO, TO, the characteristics of a crystallinity, are broadening greatly and overlapping each other. In the same time the wide spectral bands, the characteristics of amorphism, are shifting towards low frequencies. As to intensities of the wide bands, they decrease greatly than that of crystalline sharp band. In case of double amorphous semiconductors only one wide spectral band is produced while the ternary amorphous semiconductors unambiguously are characterized with too wide spectral bands. The Raman spectroscopy is therefore a versatile tool for studying the amorphous-to-crystalline transition, which is affected by annealing the implanted material.

It is worthwhile to note that we use the term "amorphous" concerning an entire amorphous solid matter; but in case when the compound is not an entire amorphous solid matter and it consists of partially amorphous and crystalline phases, it is more appropriate to mention the term "disorder".

The vibrational dynamics and phonon behavior of crystalline lattice GaAlP of ternary compounds synthesized by implantation and thermal treatment have not been studied. As is known there are two types of mixed ternary crystals according to phonon behavior: one- and two-mode crystals [20–22]. In the one-mode crystals the frequencies of LO and TO phonons observed by infrared and Raman spectroscopies shift according to concentrations from the frequency of one sublattice to the frequency of the second sublattice. In this case no new frequencies, that is, no local vibrations, are observed. Two curves are observed which show the dependence of frequencies of LO and TO phonons on the composition of the ternary crystal. In the two-mode ternary compounds with concentration increase besides the frequencies of LO and TO phonons of one sublattice, the frequencies of local vibrations appear in the infrared and Raman spectra. Due to increase of the concentration of the third component the local vibrations are splitting into the frequencies of LO and TO phonons of the second sublattice. As a result four curves are formed. Each pair shows the dependence of the frequencies of LO and TO phonons of each sublattice of the ternary compound upon the concentration.

2. Experiment

We carry out the implantation of substrate GaP of orientation (001) by 100 keV ions of aluminum with fluencies $D_1 = 2.8 \times 10^{16}$ and $D_2 = 2.5 \times 10^{17}$ ion/cm^2. We carry out the implantation at substrate temperature 400 °C. The ion implantation is carried out also by 60 keV aluminum ions with fluencies $D_3 = 8.7 \times 10^{16}$ ion/cm^2 at 400 °C. The aim of using of two different energies is to synthesize a ternary compound in various depths of the substrate. Besides, it is interesting to see if the form of wide Raman spectral band characterizing the synthesized amorphous compound changes with the increase of implantation energy. But as is known, due to high temperature implantation, radiation defects decrease noticeably in the process of synthesizing. It is interesting to know if synthesizing the crystalline phase directly is possible when implanting GaP with low fluencies at 400 °C. Interpreting and comparing our results we receive the Raman spectra of amorphous GaP synthesized with implantation inert Ar ions of crystalline substrate GaP at 100 keV and fluencies 1×10^{15} ion/cm^2. During the implantation process we cover one half of substrate GaP with a foil and use it as a standard. The uncovered part of the substrate is implanted.

The registration of the spectra is carried out on home-made block Raman spectrometer constructed on the ground of double 800 mm monochromator DFS-24, with diffraction gratings 1200 groove/mm. An argon ion laser with emission of 514.5 nm and 488.0 nm is used to excite the Raman spectra. All Raman scattering measurements are carried out at room temperature.

3. Results and discussion

The crystalline GaP is of cubic symmetry with point group symmetry T_d. Therefore on the basis of the group theory analysis, according to the selection rules, when exciting (001) surface by laser emission, only LO_{GaP} phonon is observed in the Raman spectrum. As for surface (111), here both LO_{GaP} and TO_{GaP} phonons are observed, LO_{GaP} at 402 cm^{-1} and TO_{GaP} at 365 cm^{-1}. A standard spectrum of (001) GaP is shown in Fig. 1a. The picture shows an intense spectral peak at 402 cm^{-1}corresponding to phonon LO_{GaP}

and a peak at 365 cm^{-1} of low intensity corresponding to phonon TO_{GaP}. The reason of generating the peak of very low intensity is that the Raman backscattering is not a real backscattering configuration in our experiment. Figure 1b shows the Raman spectra of (001) GaP implanted by aluminum ions with 100 keV, $D_1 = 2.8 \times 10^{16}$ ion/cm^2.

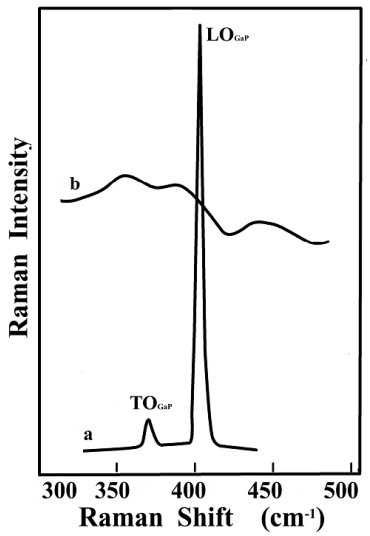

Fig. 1. Raman spectra of standard (001) GaP (a) and GaP after Al^+ hot implantation with 100 keV and fluencies 2.8 × 1016 ion/cm^2 (b); $\lambda_L = 514.5$ nm.

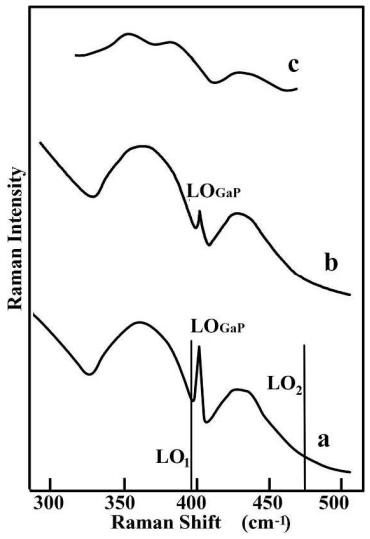

Fig. 2. Raman spectra of α-$Ga_xAl_{1-x}P$ synthesized by Al^+ implantation with two different energies and excitation: 60 keV (a) and 100 keV (c) and $\lambda_L = 514.5$ nm; 60 keV (b) and $\lambda_L = 488.0$ nm.

Figure 2 shows the Raman spectra of amorphous GaAlP in case when α-$Ga_xAl_{1-x}P$ is synthesized by aluminum ion implantation with two different energies, 100 keV and 60 keV. Figure 2c shows the Raman spectra of α-$Ga_xAl_{1-x}P$, when it is synthesized by the bombardment of substrate GaP with comparatively high-energy, 100 keV aluminum ions. Figure 2a shows the characteristic spectrum of α-$Ga_xAl_{1-x}P$ when bombarding GaP substrate with low-energy, 60 keV aluminum ions. In both cases exciting of the spectra occurred with 514.5 nm wavelength. Figure 2b shows the characteristic spectrum of α-$Ga_xAl_{1-x}P$ when bombarding GaP substrate with low-energy, 60 keV aluminum ions. In this case shorter excitation, 488.0 nm has been used to excite the spectra. It is interesting to analyze the spectra presented in Fig. 2c, Fig. 2a and Fig. 2b, showing amorphous layers formed by the implantation with 100 and 60 keV aluminum ions in GaP and exciting by 514.5 nm and 488.0 nm, respectively.

At implantation with 100 keV aluminum ions in GaP the ion path is about $R_p = 90$ nm, and at implantation with 60 keV, about $R_p = 50$ nm [23]. Here R_p is a projection of implanted ion path of an average depth in the substrate on the primary direction of an incident ion. At wavelength 514.5 nm the absorption coefficient $\alpha \approx 350$ cm^{-1} is lower for GaP and the skin-layer, $1/2\alpha$ for this wavelength is almost 14 μm; at wavelength 488.0 nm the absorption coefficient $\alpha \approx 1500$ cm^{-1} and the skin-layer, $1/2\alpha$ for this wavelength is 5 μm [24]. Our preliminary measurements show that synthesizing of α-$Ga_xAl_{1-x}P$ causes sharp increase of absorption coefficient at 514.5 nm and 488.0 nm. It becomes about 6×10^3 cm^{-1} and 2×10^4, respectively, far greater than that of crystalline GaP and its magnitude depends on fluencies and energies of implanted ions. At implantation with aluminum ions of 100 keV the production of absorption coefficient, α, by thickness of amorphous layer d, that is, αd, is of such a size that radiation of 514.5 nm is entirely absorbed in amorphous layer. Because of this the Raman spectrum characterizes only the amorphous layer as is shown in Fig. 2c. At implantation with aluminum ions of 60 keV, αd is not of such magnitude to absorb the radiation of 514.5 nm entirely; the radiation passes through the amorphous layer and stimulates excitation of the Raman spectra from substrate GaP. As a result, in the Raman spectrum two wide bands, characteristics of α-$Ga_xAl_{1-x}P$ and a narrow band of LO_{GaP} phonon of crystalline substrate GaP at 402 cm^{-1}, are fixed simultaneously. These are shown in Fig. 2a. In this case the narrow band of LO_{GaP} phonon is a very good reference point for measuring precisely the frequency shift of wide band of synthesized α-$Ga_xAl_{1-x}P$. Therefore, Fig. 2a shows exactly the magnitude of shift of wide bands characterizing the amorphous phase α-$Ga_xAl_{1-x}P$ synthesized by ion implantation from the reference LO_{GaP}; this value for GaP-like band is 26 cm^{-1}. Thus, at high-temperature implantation entire amorphous new ternary compound α-$Ga_xAl_{1-x}P$ is synthesized on surface GaP. Continuity of the synthesized amorphous phase is proved by the fact that the narrow spectral peak corresponding to phonon LO_{GaP} we have fixed, belongs to the substrate of crystalline LO_{GaP} located under the amor-

phous phase and not to crystalline fragments suspended in amorphous phase. Figure 2c also indicates the mentioned fact. In case of suspended crystalline phase the characteristic phonon of LO_{GaP} was to appear here, too. Figure 2b also proves this consideration, its comparison with Fig. 2a shows that the intensity of phonon LO_{GaP} decreases distinctly with decrease of exciting wavelength (by increase of absorption coefficient on this wavelength). Thus, when exciting by 488 nm, comparatively small signal is imposed to the Raman spectrum of α-$Ga_xAl_{1-x}P$ from GaP substrate than that by exciting with 514.5 nm. In case of crystalline phase suspended into amorphous phase the intensity of peak corresponding to LO_{GaP} was to be the same during the both excitation. Simultaneously the ratio of the intensity of the peak corresponding to LO_{GaP} to the intensity of wide strip representing the amorphous phase was not to be changed. Figure 2a and b shows clearly that this ratio is far too small at excitation of 514.5 nm than at excitation of 488.0 nm. In case of suspended crystalline phase the mentioned ratios were to be almost unchanged, at any rate not with such difference in ratios as in our case.

We have mentioned above the thickness of the amorphous phase, d, the absorption coefficients of which at 514.5 nm and 488.0 nm are a lot more than in case of crystalline phase. Under this thickness we mean the approximate measure of the thin layer of α-$Ga_xAl_{1-x}P$ synthesized near the surface of substrate GaP, forming after critical fluencies of implantation of aluminum ions. We do not need to determine its absolute value in this case.

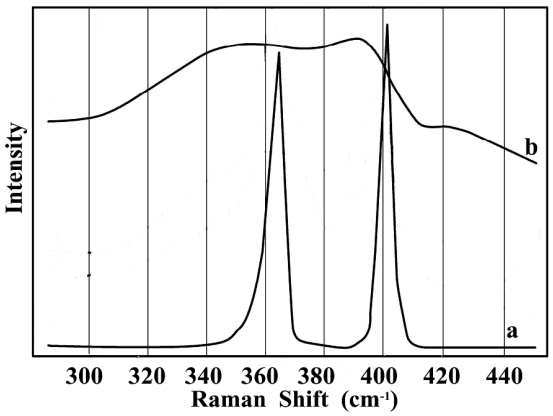

Fig. 3. Raman spectra of standard (111) GaP (a) and α-GaP synthesized with 100 keV Ar^+ implantation, fluencies 2.8×1015 ion/cm^2 (b); $\lambda_L = 514.5$ nm.

According to [17], when implanting the substrate (001) GaP by inert argon ions the crystalline substrate transforms into an amorphous phase. The entire amorphous phase of α-GaP synthesizes after reaching the critical fluencies of implantation. Figure 3 shows the Raman spectrum giving a picture of changing crystalline GaP to amorphous when implanting by inert argon ions with 100 keV and fluencies 1×10^{15} ion/cm^2. The spectrum characterizing the amorphous GaP is given by a wide spectral band. The sharp spectral lines in Fig. 3 at 402 cm^{-1} and 365 cm^{-1} correspond to LO and TO phonons of crystalline GaP, respectively. When transforming into an amorphous phase the narrow lines of LO and TO phonons of crystalline GaP are widening gradually. According to fluencies, their intensities decrease noticeably and on reaching the critical fluencies of amorphization they overlap each other. The amorphous phase of the substrate is formed. Besides, as is known and seen from the given figures, the wide spectral bands of the amorphous phase are shifted to lower frequencies from the corresponding crystalline LO and TO phonon frequencies. All A^3B^5 semiconductors in the amorphous condition are characterized with such an unambiguous picture [17]. The same properties are possessed by the Raman spectra of covalent Si, Ge and many other compounds [17]. As is known [25, 26], the Raman spectra of the amorphous semiconductors reflect the picture of density of vibration modes.

When implanting GaP with aluminum ions, two wide spectral bands are formed in contrast to the case of implanting with inert argon ions,one at 400–350 cm^{-1} and the other at about 443 cm^{-1} (Fig. 1b and Fig. 2). To compare with, the characteristic Raman spectrum of the crystalline GaAlP is shown in Fig. 4 [26]. In this case the crystalline GaAlP is synthesized on substrate GaP of orientation (001) by liquid-phase epitaxy. As is known from [27], the high-frequency narrow spectral band 472 cm^{-1} of crystalline GaAlP corresponds to LO_2 phonon of mixed crystal GaAlP and shows the vibration of AlP-like sublattice. As to the low-frequency spectral band at 397 cm^{-1}, it corresponds to LO_1 phonon of the mixed crystal and shows the vibration of GaP-like sublattice. Right here, together with LO_1 and LO_2 characteristic phonons of the mixed crystal, LO_{GaP} and TO_{GaP} characteristic phonons of GaP substrate at 402 cm^{-1} and 365 cm^{-1}, respectively, are seen. According to [28], LO_{AlP} and TO_{AlP} phonons corresponding to AlP are located at 501 cm^{-1} and 439 cm^{-1}, respectively.

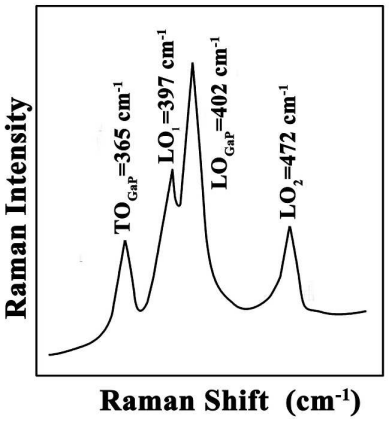

Fig. 4. Raman spectra of crystalline GaAlP grown by liquid-phase epitaxy, $\lambda_L = 514.5$ nm.

As is seen from Fig. 1b and Fig. 2, after implantation Al with fluencies $D_1 = 2.8 \times 10^{16}$ ion/cm^2 and $D_3 = 8.7 \times 10^{16}$ ion/cm^2 (the fluencies are more than the critical fluencies of amorphization of GaP at implantation with aluminum ions of the same energy) two wide bands are originated in the Raman spectrum. These bands are shifted from the corresponding frequencies of LO_{GaP}, LO_1, LO_2 phonons of the crystalline GaP and $Ga_{1-x}Al_xP$, respectively, to the lower frequencies. The comparison of Figs. 1–4 shows this fact. In contrast to the implantation of GaP with argon ions, the formation of a wide spectral band of high-frequency takes place besides. The band is located at about 443 cm^{-1}. The mentioned facts indicate that a ternary compound, different from AlP and GaP, has been formed. As is known the mentioned picture characterizes the amorphous phase. Thus, the comparison of Raman spectra in Figs. 1–4 unambiguously indicates that when implanting GaP with aluminum fluencies $D_1 = 2.8 \times 10^{16}$ ion/cm^2 and $D_3 = 8.7 \times 10^{16}$ ion/cm^2, synthesizing of ternary mixed amorphous phase of GaAlP takes place.

As we have mentioned above, the frequency of the wide band showing the vibration of AlP-like sublattice of α-$Ga_{1-x}Al_xP$ is 443 cm^{-1}. The frequency of this band is very likely greatly lower than that of amorphous AlP. We have not found the Raman-spectrum of amorphous AlP in the literature but our opinion is based on the following argumentation: according to the above-mentioned, the frequency of α-GaP band is shifted about12 cm^{-1} from the crystalline LO phonon towards low frequencies. The wide bands of other amorphous semiconductors (GaAs, InP) of A^3B^5 type are shifted approximately the same distance from the corresponding frequency of LO phonon. The cited frequency of LO phonon of crystalline AlP from the literature is equal to 501 cm^{-1}. Therefore the frequency of the wide band of amorphous AlP probably will not be lower than 480-490 cm^{-1}. The isotopic substitution of Al by heavier gallium in α-$Ga_xAl_{1-x}P$ causes a great shift of the wide band corresponding to AlP-like sublattice from the frequency of α-AlP. On the whole with the aid of such discussion we come to a conclusion that the single-phase α-$Ga_xAl_{1-x}P$ has been synthesized and no segregation of separate phases GaP and AlP takes place.

For recovering the crystal structure, high temperature annealing in vacuum has been used. After implantation we cover GaP plate with SiO_2 protective capsule to avoid the outlet of light volatile phosphorus from the substrate. After implantation GaP with 100 keV Al^+ ions and fluencies 2.8×10^{16} ion/cm^2, we carry out annealing at 500, 700, and 850 °C during an hour. After each annealing stage we receive the Raman spectra of standard and implanted parts of the substrate together with the quartz capsule. The corresponding spectra are shown in Fig. 5. In the same picture a vertical line shows LO_{GaP} phonon in the Raman spectra of crystalline (001) GaP. It is seen from the spectra (Fig. 5a) that after annealing at 500 °C the signs of crystal lattice recovering become apparent.

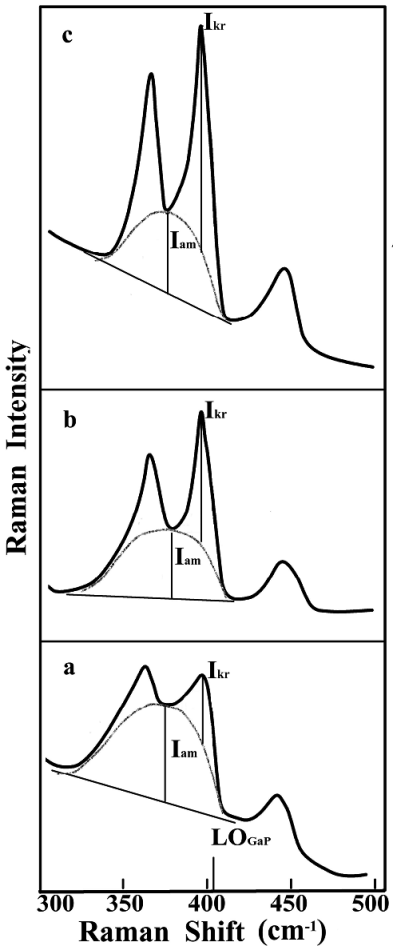

Fig. 5. Raman spectra of GaP implanted with 100 keV Al^+ and fluencies 2.8 × 1016 ion/cm^2 after annealing; annealing temperature: (a) 5000 °C; (b) 7000 °C; (c) 8500 °C; $\lambda_L = 514.5$ nm.

This is expressed by splitting the wide spectral band, the characteristics of the amorphization, into two narrower bands. The mentioned bands correspond to LO_1 and TO_1 phonons of synthesized film $Ga_{1-x}Al_xP$ which show the vibration of GaP-like sublattice. The structureless spectrum in Fig. 5a represented by the dotted line shows the portion of amorphous α-$Ga_xAl_{1-x}P$ remained after annealing at 500 °C. We observe the co-existence of two phases of system $Ga_{1-x}Al_xP$ in this stage of annealing — the amorphous in great quantity (the structureless spectrum represented by the dotted line) and the crystalline (the Raman spectrum represented by narrower bands) in small quantity. In the post-annealing stages at 700 and 850 °C the Raman spectra show clearly the crystal lattice recovering dynamics. The above-mentioned are illustrated in Fig. 5b and c, respectively. It is seen that in those stages of annealing sharp, narrow bands appear at 363 cm^{-1} and 399 cm^{-1}. Those peaks correspond to TO_1 and LO_1 phonons of recrystallized $Ga_{1-x}Al_xP$, which show the vibration of GaP-like sublattice. Besides, a new well-shaped small peak appears at 445 cm^{-1}

which represents LO_2 phonon of the synthesized film and characterizes the vibration of AlP-like sublattice, respectively. As is known, due to high-temperature annealing the wide Raman spectrum, the characteristic of amorphous semiconductor, changes into the narrow Raman spectrum, the characteristic of crystalline phase. On this stage of annealing also a background of wide structureless spectral band, represented with the dotted line, is observed clearly. This indicates that $Ga_{1-x}Al_xP$ synthesized by the implantation and post thermal treatment contains a disodered structure in small quantity.

With the aid of parts of vertical lines the Raman intensities of shares of disordered structure and crystalline $Ga_{1-x}Al_xP$, I_{dis} and I_{cr}, respectively, are indicated in the Raman spectra (Fig. 5). As is seen from Fig. 5a–c the ratio I_{cr}/I_{dis} increases proportionally with the increase of annealing temperature. This fact indicates to recovering of the crystal structure. It is also seen clearly that even after annealing at 850 °C, I_{dis} does not become infinitesimal, though the ratio I_{cr}/I_{dis} is far bigger than after early stages of annealing. This fact proves once more the coexistence of a small disordered structural phase with the synthesized crystal phase $Ga_{1-x}Al_xP$.

Comparing Fig. 1 with Fig. 5 one can see that in the Raman spectra of standard GaP of orientation (001) the forbidden TO phonon becomes visible after Al^+ implantation and annealing. That is, a new compound synthesized by the implantation does not repeat the substrate orientation. Moreover, spectra in Fig. 5 show that with the increase of annealing temperature the half widths of peaks corresponding to LO_1, TO_1, and LO_2 phonons get narrower and their intensities increase sharply. This fact indicates that the contribution of crystalline ternary compound increases distinctly and radiation defects decrease due to annealing at high temperatures.

On the basis of the above-mentioned experimental facts we can say that at hot (400 °C) implantation of substrate GaP with 100 keV aluminum ions and fluencies 2.8×10^{16} ion/cm^2, the crystalline phase of ternary compound $Ga_{1-x}Al_xP$ is not formed directly. The amorphous phase of the above semiconductor is synthesized and after the further high temperature treatment the crystalline $Ga_{1-x}Al_xP$ is synthesized. It should be noted that the synthesized compound does not repeat the substrate orientation; the Raman spectra show that the synthesized semiconductor is polycrystalline. It contains small quantities of radiation defects, which decrease with the temperature increase.

When carrying out the hot implantation (400 °C) of substrate GaP of orientation (001) with 100 keV aluminum ions and fluencies 2.5×10^{17} ions/cm^2, the amorphous phase of system $Ga_{1-x}Al_xP$ is formed again and the Raman spectrum unambiguously shows it. The spectrum is similar to that in Fig. 1b. Afterwards we put the implanted plates GaP in vacuum furnace according to the above-mentioned procedure and anneal at 500, 700, 850 °C during an hour. The implanted substrates with both 2.8×10^{16} and 2.5×10^{17} ions/cm^2 fluencies are annealed in high vacuum simultaneously. Thus the plate annealing conditions for the both fluencies are the same.

Figure 6 shows the recrystallization process dynamics of synthesized amorphous compound α-$Ga_xAl_{1-x}P$. It is seen from the spectra (Fig. 6a), that when annealing at 500 °C the compound remains in the amorphous state. This fact differs from the result when the implantation occurred with fluencies 2.8×10^{16} ions/cm^2. When annealing at 700 °C (Fig. 6b) the wide band characterizing the Ga–P bond vibration in the amorphous phase, is split into two narrow peaks corresponding to LO_1 and TO_1 phonon vibrations of crystalline phase of $Ga_{1-x}Al_xP$. Accordingly, the band reflecting Al–P bond vibration in the amorphous phase, near 451 cm^{-1} grows narrower distinctly. Those experimental facts indicate that recovering re-crystallization of long-range ordering is begun at this stage of annealing. In the further stage of annealing, at 850 °C, the peaks corresponding to TO_1 and LO_1 phonons at 362 and 396 cm^{-1}, respectively, are distinctly seen in Fig. 6c and they are far sharper and narrower than in case of annealing at the former stage. Those peaks belong to GaP-like sublattice vibration. At the same time a sharp peak formed at 453 cm^{-1}, belonging to LO_2 phonon, represents AlP-like sublattice vibration. Besides, the Raman spectra show the radiation defects in quantity in recrystallized lattice. In Fig. 6a a vertical line shows LO_{GaP} phonon in the Raman spectra of crystalline (001) GaP.

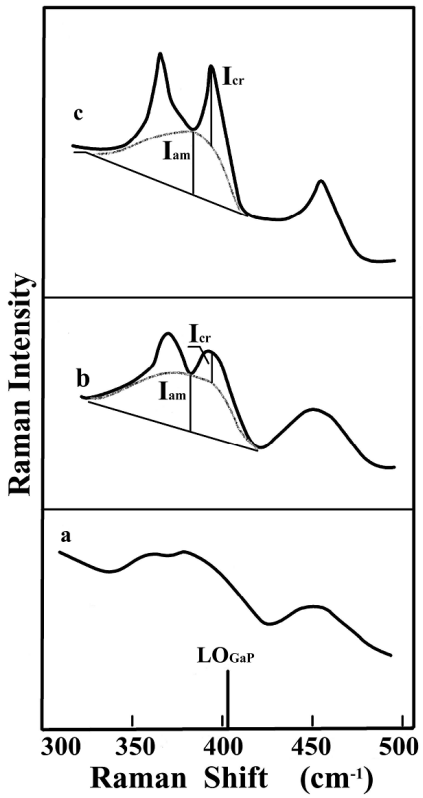

Fig. 6. Raman spectra of GaP implanted with 100 keV Al^+ and fluencies 2.8 × 1017 ion/cm^2 after annealing; annealing temperature: (a) 5000 °C; (b) 7000 °C; (c) 8500 °C; $\lambda_L = 514.5$ nm.

In this case just as in the previous case (Fig. 5) the ratio I_{cr}/I_{dis} shows the ratio of shares of recrystallized and remained in the amorphous phase $Ga_{1-x}Al_xP$. From the analyses of the Raman spectra in Fig. 5 and Fig. 6 it is obvious that the ratio I_{cr}/I_{dis} increases with the increase of the annealing temperature. At the implantation with fluencies 2.5×10^{17} ions/cm^2 and post annealing at 850 °C this ratio is equal about to one. It is much smaller than the same ratio at implantation with fluencies 2.8×10^{16} ions/cm^2 and annealing at 850 °C. That is, by increasing the fluencies of implanted aluminum ions the process of recrystallization becomes more difficult, the annealing temperature increases.

Thus, when implanting GaP of (001) orientation with 100 keV aluminum ions by fluencies of 2.5×10^{17} ions/cm^2, the substrate being at 400 °C, the direct crystalline phase of ternary compound $Ga_{1-x}Al_xP$ is not formed, but amorphous α-$Ga_xAl_{1-x}P$ is synthesized. To recover the crystalline phase, the higher temperatures are needed for annealing, than in case of destruction of the crystalline structure of the substrate by aluminum implantation with the fluencies 2.8×10^{16} ions/cm^2.

Comparing the Raman spectra of the two crystalline $Ga_{1-x}Al_xP$ synthesized by different fluencies one can see that the frequencies corresponding to their characteristic LO_1, LO_2, and TO_1 phonons are different. Table indicates these frequencies. The phonon frequencies of ternary $Ga_{1-x}Al_xP$ synthesized at implantation with higher fluencies of aluminum ions are shifted by certain quantities from that of synthesized by the lower fluencies. This fact indicates directly that when bombarding with aluminum ions of different fluencies, ternary mixed semiconductors $Ga_{1-x}Al_xP$ of two different compositions are synthesized on GaP surface.

TABLE

LO_1 and TO_1 frequencies of GaAlP synthesized by ion implantation, liquid phase epitaxy and LO, TO frequencies of substrate GaP.

Sample history	LO_1 [cm^{-1}]	TO_1 [cm^{-1}]	LO_2 [cm^{-1}]
GaP etalon	402	365	
Liquid phase epitaxy GaAlP	397		472
2.8×10^{16} ion/cm^2	399	363	445
2.5×10^{17} ion/cm^2	396	362	453

The regularity of the concentration shift of LO_1 phonon frequencies and the formation of a new peak LO_2 with its concentration shift prove that system $Ga_{1-x}Al_xP$ formed by the ion implantation synthesis belongs to the mixed semiconductors of the two-mode behavior. This conclusion is in agreement with the results we have received [27], as well as with the data of other authors [29–33], in which the mode structure of mixed crystals $Ga_{1-x}Al_xP$ synthesized by the ordinary chemical methods, have been studied by the Raman spectroscopy.

4. Conclusion

We can say that we, the first, have shown that by the hot implantation of substrate GaP with aluminum ions and post annealing, synthesizing of ternary semiconductor $Ga_{1-x}Al_xP$ is possible. Two ternary compounds $Ga_{1-x}Al_xP$ of different compositions have been synthesized by aluminum ion hot implantation in GaP crystalline substrate with different doses. The dynamics of lattice destruction and its recovering by annealing have been studied by the laser Raman spectroscopy. We have proved experimentally that during the hot ion implantation the ternary compound $Ga_{1-x}Al_xP$ cannot be received directly in crystalline form, but an amorphous phase of α-$Ga_xAl_{1-x}P$ is formed. The additional high temperature heat-treatment is necessary in the following stage to recover the crystalline structure. To recover the crystalline structure in case of increased implanted ion fluencies, higher annealing temperatures are needed but in spite of this, the synthesized ternary compounds still will contain radiation defects in fair quantity. Thus, one may suppose that α-$Ga_xAl_{1-x}P$ synthesized by the implantation with higher fluencies (2.5×10^{17} ions/cm^2) of aluminum ions, cannot be changed into the perfect crystalline phase after the high temperature annealing. But in case of implanting with low fluencies (2.8×10^{16} ions/cm^2) the synthesized mixed α-$Ga_xAl_{1-x}P$ changes into the crystalline phase almost entirely at high temperature annealing.

The ternary mixed semiconductors $Ga_{1-x}Al_xP$, we have first synthesized by the ion implantation and studied by the Raman scattering, show the behavior characterizing the two-mode semiconductors.

Thus, the complicated system $Ga_{1-x}Al_xP$ synthesized by the high temperature ion implantation and thermal treating, is characterized by a defective structure. The concentration of defects is considerably less in case of implanting with low fluencies. To obtain the more perfect crystalline structure it is necessary to continue the experiments.

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