USE OF LASER RAMAN SPECTROSCOPY FOR STUDY OF SURFACE PROPERTIES OF SOME SEMICONDUCTORS OF A^3B^5 TYPE

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<u>ABSTRACT.</u> Laser Raman spectroscopy is used to study optical properties of surface thin layers of semiconductors. Use of various wavelengths of exciting laser enabled us to alter at request the skin values of penetration of laser radiation in films under observation. Through proper selection of film thicknesses, absorption coefficients and skin-values, we achieved absolute exclusion of interfering LO and TO phonons of substrate from Raman spectra of various films of $Ga_xAl_{1-x}P$ under observation.

That enabled us to fix LO_1, LO_2, TO_2 vibrations of optical phonon branches for GaP- and AlP-like sublattices to a high accuracy and plot more accurate graphs characterizing two-mode crystal. On the basis of this technique we were able to estimate thicknesses of films and the first to study resonance Raman scattering in system $Ga_xAl_{1-x}P$. With the aid of laser Raman spectroscopy surface thin layers modified by P and Al ion implantation of substrates of GaAs and GaP, respectively, has been studied. Varying technological conditions of ion implantation we obtained amorphous ternary thin films α-GaAsP, α-GaAlP of substrate.

Their identification for various depths has been done with laser Raman spectroscopy.

As is well known, the main tendency of modern semiconductor microelectronic instrument-making industry is miniaturization of devices. This, on its part, is based on use of semiconductor material's surfaces rather than bulk crystals. An obvious example of this is epitaxial films' use for that purpose. These films may be received both by usual chemical (liquid-phase, molecular, organo-metallic epitaxy and their different modifications) methods, and various physical extremal methods (ion implantation, radiation-laser, electron beam and etc.). Utilization of those methods implies both thin surfaces' reception and preliminary modification of existing substrates' properties for goal achievement. Dimension of such layers may be changed from nanosizes to microsizes. Naturally, the problem of testing such thin layers and objects of small sizes arises. Most likely, there are mainly two problems to be taken into consideration. The first one, physical, consists in the following: 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 phonons' propagation is expressed by plane waves and in the first order Raman scattering the q = 0 selection rule is observed. 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 $\mathbf{\Delta k \approx L^{-1}}$. Just when studying a microcrystalline semiconductor Si, Richter introduced the so-called "phonon confinement" conception, according to which shift of phonons' frequencies and asymmetric broadening of halfwidths take place in microcrystalline materials.

Here a concrete example is given for Raman scattering on phonons, but the fact that almost all properties of spatial crystal differ from physico-chemical properties of nanomaterials and thin layers, is already admitted generally. This first basic physical difference gives rise to the second, "geometrical" problem, as we call it - testing methods for small dimension materials are to be selected in such a way that they correspond to experimental fixing of their different properties and manifestation of peculiarities. For example, by usual spectroscopic methods it is difficult or impossible to carry out univocal measurements for thin films, micro or nano materials, and out-of-the-way places. There is no theoretical possibility of this sometimes, because it is impossible for incoherent and great classical radiation source emission to be focused on micro or less sizes, and it is almost impossible to direct this radiation concentrically. Multicolored directions of laser spectroscopy based on various physical principles are irreplaceable for this objective. In the present article the possibilities of only one of the basic directions of laser spectroscopy-laser Raman spectroscopy will be discussed. Naturally, the universally recognized physical methods, as various analytical methods based on ion, *X*-Ray and electronic beam sondes will not be touched.

In 1976 first in Georgia we constructed several laser Raman spectrometers of various types, carried out investigations in different directions, and thus most likely grounded development of laser Raman spectroscopy direction in Georgia. The analogues of the laser Raman systems we have constructed are very expensive at international markets. Perhaps, that is why this very important scientific direction has not found corresponding propagation in Georgia as yet. It is a pity, because this direction's potential is very high and practical almost in all spheres of science from fundamental as well as applied, analytical, industrial points of view.

One of the aims of the work presented here is just the popularization of the mentioned direction among scientists from the point of its wide utilization. We shall try to realize this purpose on the basis of the experiments we have made. This time, all these experiments show monitoring of semiconductor surfaces by laser Raman spectroscopy.

When studying surfaces by laser methods, peculiarity and advantage in comparison with classic, ordinary optic spectroscopy mainly consists in use laser as a radiation source. Laser's advantage is expressed with its radiation coherence, radiation unidirectionality, narrowness of its radiation spectral band; it has property of summing its radiation with the aid of lenses in focal point of very small size (of nano dimensions). A lot of types of lasers of the day enable to change discreetly their radiation from ultraviolet of optical spectrum to near infrared area; according to spectral task, if necessary, this area may be overlapped continuously (with the aid of dye lasers, semiconductor heterolasers, nonlinear laser optics and other lather techniques). Geometric mobility of laser beam is of great importance, also - it may penetrate out of the way places and analyze and interact with matter even from the aggressive medium (from separating surface of heterosurfaces, the phase buried in crystal matrix, various inclusions in minerals, active zone of reactor, high temperature and acid volumes and many others).

We are presenting our experimental material and discussing two different themes concerning semiconductor surfaces we have studied by laser Raman spectroscopy.

1. RESONANCE RAMAN-SPECTROSCOPY OF MIXED SEMICONDUCTORS GA$_X$AL$_X$P AND ESTIMATION OF FILMS' THICKNESS

The mixed Ga$_x$Al$_{1-x}$P crystal is an interesting material though less studied for semiconductor electronics. Particular interest in this material is caused by the fact that because of its wide band-gap it could be used for making light-emitting devices in visible region of spectrum. For example, semiconductor heterostructural Raman-lasers were made on its ground [1]. Optical properties of this compound have been less studied while Crystal lattice vibrational dynamics is discussed in works [2-5].

With Raman-spectroscopy we routinely study semiconductors modified by ion implantation, especially complex semiconductors synthesized by ion implantation. Simultaneously, we receive standards for qualitative identification of ion synthesized films and their quantitative estimation as the result of Raman scattering studies of the same semiconductors synthesized by ordinary chemical methods, for example, by liquid phase epitaxy.

The above-mentioned work serves just the purpose. On the other hand, identification of phonons in Ga$_x$Al$_{1-x}$P and studies of mode structure of this compound is needed for interpretation of Raman-spectra of quaternary (Al$_x$Ga$_{1-x}$)$_{0.5}$In$_{0.5}$P, a necessary semiconductor at present. This is connected to the fact that this compound consists of components Ga$_x$Al$_{1-x}$P and Ga$_x$In$_{1-x}$P. The above mentioned quaternary semiconductor grown epitaxially on GaAs substrate is widely used nowadays in the visible region of spectrum for producing light-emitting microelectronic devices, as it has wide forbidden zone.

In the present work Raman scattering has been studied in a lot of *n*- and *p*-type Ga$_x$Al$_{1-x}$P epitaxial films. We studied undoped films as well. The mentioned films were grown by liquid-phase epitaxy on GaP substrates with (001) orientation. The film thickness was in the range of 5-18 mmk.

The Raman-spectra were recorded on the home-made laser Raman-spectrometer constructed on the base of double monochromator DFC-24. Argon laser emission of 514.5, 488.0, 457.9 nm and excitation source helium-cadmium laser emission of 441.6 nm wavelengths respectively served as excitation source. The Raman system experimental equipment is described in details in [6].

Fig.1 shows Raman-spectra for $Ga_{0.3}Al_{0.7}P$ composition when exciting by various wavelengths of laser. It is clear from the picture that when we use short waves to get spectrum, the intensity of LO phonon of GaP substrate at 402 cm^{-1} diminishes gradually and when carrying out excitation with helium-cadmium laser radiation with 441.6 nm wavelength, the peak characterizing LO phonon vanishes at all. Simultaneously increases the intensity of LO phonon at 487 cm^{-1}, which characterizes vibration of a sublattice similar to AlP in $Ga_{0.3}Al_{0.7}P$ system. Thus, with shortening the exciting laser's wavelength, manifestation of interfering spectrum of substrate gradually decreases, and in boundary conditions we are absolutely free from it.

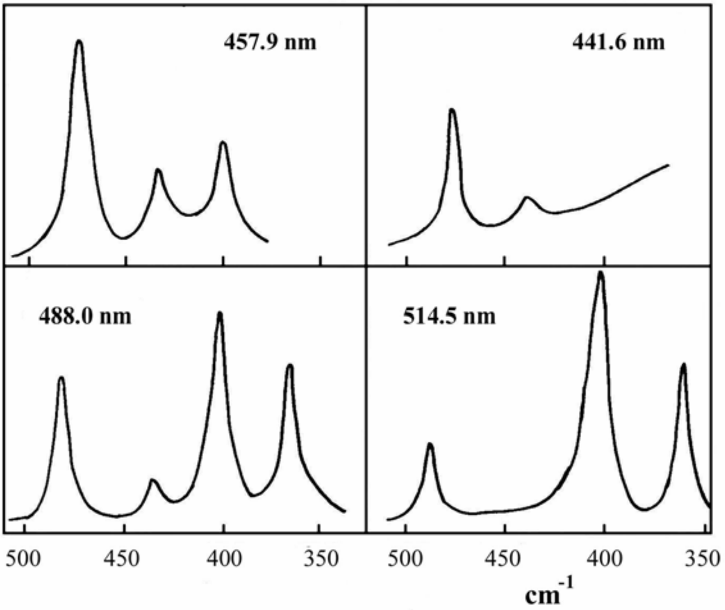

Fig.1. Raman spectra for $Ga_{0.3}Al_{0.7}P$ excited with various wavelengths of the laser.

Fig.2 shows the dependence of ratio of LO phonons intensities at 487 cm^{-1} and 402 cm^{-1} frequencies respectively upon energy of exciting photons.

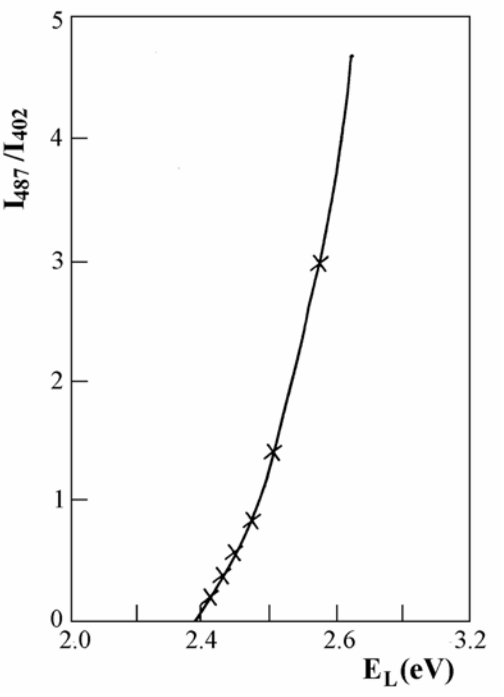

Fig.2. Dependence of ratio of intensity of LO phonon at frequency 487 cm^{-1} to intensity of LO phonon 402 cm^{-1}.

The direct band-gap E_0 of system $Ga_{0.3}Al_{0.7}P$ is 3.5 eV [7]. Fig.2 shows that when the exciting quantum energy approaches to the amount of direct band of $Ga_{0.3}Al_{0.7}P$, weak resonance is observed. The mentioned does not give completely the picture of resonance Raman-scattering because exciting quanta energies are sufficiently far from direct band width. We shall have the complete picture if we are able to use laser shorter wavelengths for excitation. Besides it would be more correct if we take the ratio of LO_{487} to phonon vibration intensity of standard crystal CaF_2.

The fact that we study the system-GaP substrate with $Ga_xAl_{1-x}P$ film-by various wavelength of laser emission, gives us the possibility to estimate epitaxial layers` rough thickness by Raman-spectroscopy.

According to [8] Raman-scattering intensity

$$I = (I_oR/2\alpha)(1\text{-}\exp 2\alpha d), \quad (1)$$

where I_0 is intensity of impinged radiation, R_0 - scattering cross-section, α - absorption coefficient, d - film thickness.

If we assume that the film $Ga_xAl_{1-x}P$ is grown on GaP substrate with steep front, then it is possible to assume, that the scattering intensity equals to substrate and film Raman scattering intensities sum.

$$I_{Total} = I_f + I_{subst} \exp(-2\alpha_f d) \quad (2)$$

$$I_f = (I_0 R_f / 2\alpha_f)[1 - \exp(-2\alpha_f d)] \quad (3)$$

$$I_{\text{substr}} = (I_0 R_{substr} / 2\alpha_{substr}) \exp(-2\alpha_f d) \quad (4)$$

If we take the ratio of intensities, it would be possible to calculate the film thickness.

$$I_{substr}/I_f = (R_{substr}\alpha_f / R_f \alpha_{substr})[exp(\text{-}2\alpha_f d)]/[1 \text{-} exp(\text{-}2\alpha_f d)] \quad (5)$$

By above mentioned method we estimated the thickness of $Ga_{0.3}Al_{0.7}P$ composition film thickness and got d = 12.5 mmk. The same film thickness measured by ordinary microscopic method gives d = 12 mmk. In this case comparatively thick epitaxial film has been estimated. In a same manner may be estimated much thinner films, for instance, nano dimensional films formed by ion implantation, only if corresponding conditions are selected.

Scanning of focal point on the surface of the film under investigation was carried out after sharp focusing of laser beam. Raman spectra were fixed from all points, afterwards there were compared spectral lines intensities, halfwidths. This enabled to estimate films' quality along the surface, their homogeneity.

Fig.3 shows graphs plotted after recording Raman spectra of epitaxial films of different composition. They show dependence of vibration frequency of LO phonons of GaP- and AlP-like sublattices upon films' compositions. According to these graphs the system $Ga_{1-x}Al_xP$ is attributed to two-mode behavior crystals. By means of these calibration curves the compositions of nanodimensional films $Ga_{1-x}Al_xP$ synthesized by us with two different doses ($2.8\cdot10^{16}$ and $2.5\cdot10^{17}$ ion/cm^2) of ion implantation, have been defined. It turned out that $x_1 = 0.12$ when implanting with $2.8\cdot10^{16}$Al ion/cm^2 and the concentration of synthesized ternary compound $x_2 = 0.24$ at dosage of $2.5\cdot10^{17}$ Al ion/cm^2.

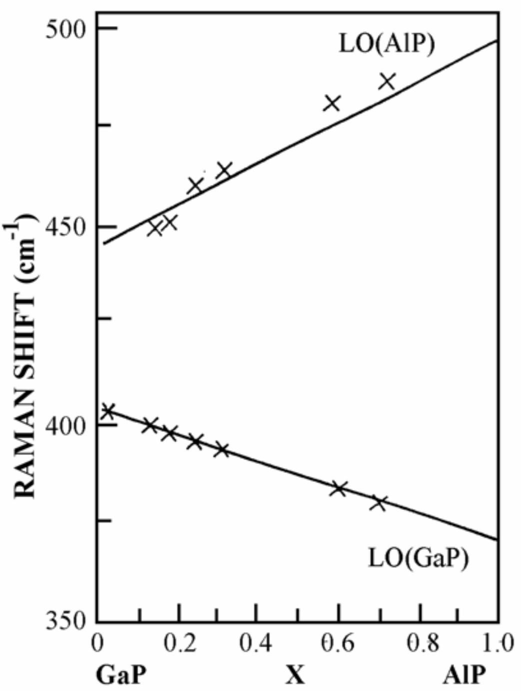

Fig.3. Dependence of the frequency of LO phonons on the composition.

2. MONITORING OF SEMICONDUCTORS GaAs AND GaP MODIFIED BY ION IMPLANTATION

Accelerated ions' penetration depth in substrates at ion implantation is determined by their energies, masses, charge values and substrate parameters. Implantation of substrates GaAs and AlP was carried out by means of charged ions of Ar, B, N, O, As, P, Al. These ions' energies varied in various cases and substrates formed by ions with 40, 60, 70, 100, 110 keV energies were mainly investigated. We had also substrates doped with so-called "distributed dose". In this case in the same substrate the implantation of the same ion with certain dose occurred, energies being changed in the great range. In these cases ion distribution function in substrates sharply differs from distribution function formed at implantation by energy with the same value. As a rule, in this case the layer buried in substrate is thicker, near surface and spreads at comparatively longer distance. It should be noted, that this is not a rule, but depends on choice of energy distribution function. It should be added, that ion implantation technique in semiconductor microelectronics is attractive just because, unlike chemical technologies, it is possible to vary strictly at request and control to a high accuracy all the parameters of substrate modification. Thus, it is possible to obtain layers of certain thickness and expansion with implantation energy change. On conducting our experiments implantation was carried out at substrate temperatures being about room temperatures, 400^0 and 450^0 C.

With the aid of laser spectroscopy one can carry out sounding of the modified substrate in the depth as well as in any surface direction. Such spatial dispersion is possible only in case of being at experimenter's disposal exciting lasers with a wide variety of wavelengths. In that case substrate skin-layer of laser radiation is proportional to absorption coefficients of the substrate and to modified-layer; if skin-layer is equal to or smaller than the modified-layer, only then occurs sounding of the modified layer and the experimental results show only the layer characteristics. Another approach is also possible: to alter ion implantation energies at fixed Raman spectra exciting wavelengths to obtain modified layers of various thicknesses. The both means are at our disposal; only the second variant will be discussed in the present work.

To receive amorphous films we were dealing with ion implantation of monocrystalline GaP and GaAs targets by Ar, B, N, P, Al, As ions. The target surfaces were of two kinds: (111) and (001) orientations. Ion energies varied from 40 to 110 keV and because of this we dealt with amorphous films of various thickness in different depths from the crystalline surface. Implantation was fulfilled with different doses at room tremperature as well as at high 400^0 and 450^0 C temperatures. For Raman-spectra recording home-made Raman-spectrometer constructed on the basis of double monochromator DFS-12 was used. Argon laser emission wavelengths 514.5 nm, 448.0 nm, 457.9 nm and Helium-Cadmiumn laser emission wavelength 441.6 nm were used for spectra exciting. The mentioned emission wavelengths were chosen so that we should be able to conduct probing in different depths of target surfaces implanted with various energies.

As is known at Raman scattering in crystal compounds optical phonon is absorbed or illuminated at about $k = 0$. When crystal structure is crushed and because of disappearing far order, the periodicity is lost, then $k = 0$ selection rule loses its sense and in the first order Raman scattering phonons with big k are participating. Such state is originated in amorphous semiconductors, when all vibrational modes are allowed and take part in Raman scattering process. Thus, we conclude that in amorphous semiconductors the first order Raman spectra reflect the general form of distribution of one-phonon density vibrational state. Vibrational state density of amorphous compounds in the first approximation seems to express the extended variant of the proper crystal lattice vibrational state density and A^3B^5 group semiconductor Raman spectra as well as IV group have the whole spectrum characteristic structure rather than the narrow bands, which correspond to the zero wave vector phonons which are active in Raman scattering.

Crystalline GaP and GaAs are of cubic symmetry with point group symmetry T_d. Therefore, on the basis of the group theory analyses according to the selection rules, when exciting (001) surface by laser emission, in Raman spectrum only LO phonon is observed, as for the (111) surface, here both LO and TO phonons are observed. For GaP LO=402 cm^{-1}, TO = 365 cm^{-1}; for GaAs LO = 290 cm^{-1}, TO=268 cm^{-1}.

Fig.4 shows Raman-spectrum, which reflects the picture created by phosphorous ion implantation in GaAs. The implantation occured at the room temperature the implantation dosage being 10^{17} ion/cm^2. Two wide bands at about 275 cm^{-1} and 375 cm^{-1} proximity are distinctly seen in the Raman-spectrum. These bands are sharply shifted from a-GaAs and a-GaP characteristic spectra. Their ion syntheses and identification by Raman has been done in our work [9]. Thus the Raman-spectra in Fig.4 characterizes a new compound a-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.

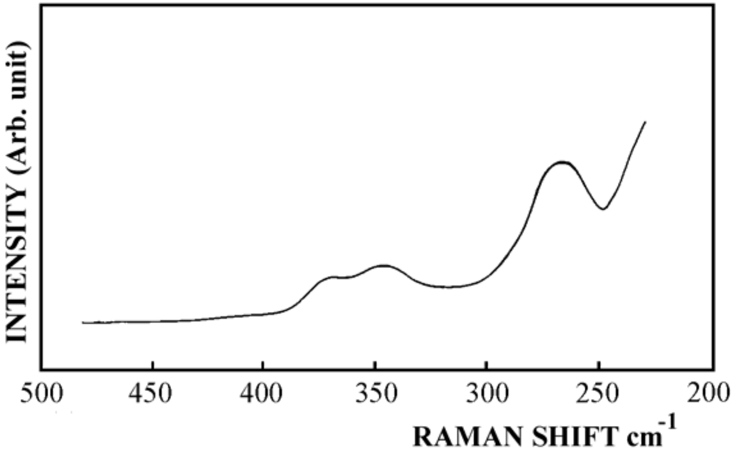

Fig.4. Raman-spectra of α-GaAsP synthesized by ion implantation at room temperature.

During the high temperature (400^{0}C) synthesis, amorphous ternary compound α-GaPAs is obtained; 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. That is shown in Fig.5.

When implanting GaP with 70 keV energetic arsenicum ion with 10^{17} ion/cm^2 dose, identification of ternary compound GaPAs had not been managed, neither ternary compound GaPN had been identified when implanting nytrogen ion in GaP with 10^{17} ion/cm^2 dose. That can be explained by energetically adverse conditions for these compounds to be synthesized according the mentioned scheme. Though in the latest period, works, in which ternary compounds GaPN and GaAsN has been synthesized by nitrogen ion implantation in GaP and GaAs and identified, appear [10,11].

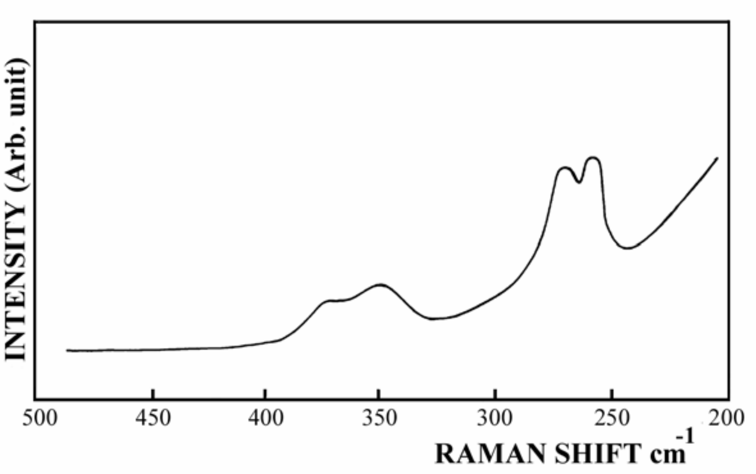

Fig.5. Raman-spectra of α-GaAsP synthesized by ion implantation at 400^0 C.

To synthesize GaPAl in (001) and (111) oriented GaP we introduced aluminum ions by ion implantation with doses $2.8\cdot10^{16}$, $2.5\cdot10^{17}$ ion/cm^2 with 100 and 110 keV energies respectively. Implantation was carried out at 400^0 C. Ion implantation was carried out also by 60 keV energy aluminum ions with $8.7\cdot10^{16}$ ion/cm^2 dose at 450^0 C.

In all three cases at the GaP surface single-phase ternary compound GaAlP is formed in the amorphous state. The mentioned are proved by two wide spectral bands in RS: one in the 450 cm^{-1} region which corresponds to Al-P pair vibration and the second, which is in the 400-350 cm^{-1} region and reflects the Ga-P pair vibration. That is shown in Fig.6 and Fig.7 respectively.

Fig.6 shows Raman spectra of a-AlGaP, when it is synthesized by bombardment GaP substrate with comparatively high-energy, 100

KeV, aluminum ions. Fig.7 shows the characteristic spectrum of α-AlGaP; it was fixed when bombarding GaP substrate with low-energy, 60 KeV, aluminum ions. The spectra presented in Figs.4, 5, 6, 7 have been recorded with the same wavelength 514.5 nm excitation. 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 is about 100 nm, whereas for synthesized amorphous layer the absorption coefficient increases still more. So, in that case only nanodimensional amorphous layer is being studied with 514.4nm excitation; therefore only the characteristic layer of amorphous layer without substrate spectrum is manifested in Raman spectrum. The same situation is in Fig.5 and 6. In this case too the picture of monitoring shows only conditions of synthesized layers. It is interesting to analyze the spectra presented in Fig.6 and 7, showing amorphous layers formed by implanting with 100 and 60 KeV aluminum ions in GaP respectively. At implantation with 100 KeV aluminum ions in GaP ion path is about 500 nm, and at implantation with 60 KeV, about 300 nm. At 514.5 nm wavelength absorption coefficient is lower for GaP and the skin-layer for this wavelength is almost 20 mmk. Synthesizing of a-AlGaP causes sharp increase of absorption coefficient. 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 being entirely absorbed in amorphous layer. Because of this the Raman spectrum is only characteristic of layer as is shown in Fig.6. At implantation with 60 KeV aluminum *αd* is not of such magnitude to absorb radiation 514.5 nm entirely; it passes through the substrate and stimulates its excitation. As a result, in Raman spectrum both, two wide bands, characteristics of α-AlGaP and a narrow band of LO phonon of substrare GaP, are fixed simultaneously. These are shown in Fig.7. In this case the narrow band of LO phonon is a very good reference point for measuring precisely the frequency shift as well as for estimating thickness of amorphous layer.

In that way, resonance Raman scattering of ternary mixed crystal AlGaP synthesized by liquid-phase epitaxy has been studied. That enables to study fundamental physical properties of thin layers and estimate their thickness. Besides, laser Raman-assisted qualitative and quantitative analyses of nanodimensional layers of GaAs and GaP monocrystal substrates modified by ion implantation have been made. It has been found, that the mentioned nanolayers correspond to amorphous ternary compounds GaAsP and AlGaP.

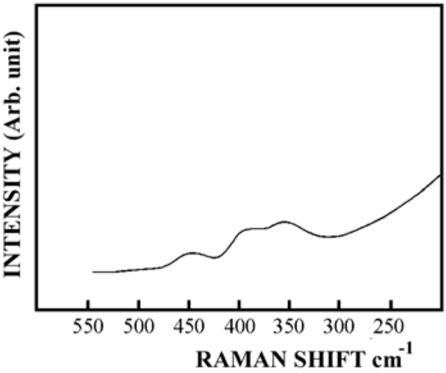

Fig.6. Raman spectra of α-AlGaP synthesized by ion implantation at 400^0 C and at energy of implantation, E = 100 KeV.

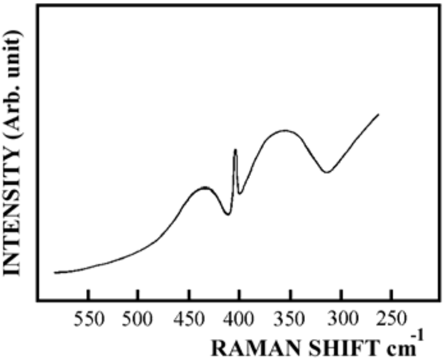

Fig.7. Raman spectra of α-AlGaP synthesized by ion implantation at 450^0 C and at energy of implantation, E = 60 KeV.

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ლაზერული რამან-სპექტროსკოპიის გამოყენება $\mathbf{A^3B^5}$ ტიპის ზოგიერთი ნახევარგამტარის ზედაპირული თვისებების შესასწავლად

დასკვნა

შრომაში ნაჩვენებია ლაზერული რამან-სპექტროსკოპიის მნიშვნელობა და განსაკუთრებულობა ნახევარგამტარების ზედაპირული ფენების შესწავლის სფეროში. კერძოდ, ეს განპირობებულია ლაზერის, როგორც რამან-სპექტრების აღმგზნებ წყაროდ გამოყენებით. მაგალითების სახით განხილულია ჩვენს მიერ სამმაგ შერეულ ნახევარგამტარ $Ga_xAl_{1-x}P$-ში რეზონანსული რამანის გაბნევა სხვადასხვა ლაზერის სხვადასხვა ტალღის სიგრძით აგზნებისას. ასეთი ტექნიკის საშუალებით შევძელით შეგვესწავლა ამ სისტემის ფუნდამენტური თვისებები და შეგვეფასებინა ფირების სისქეები.

საინტერესო და მნიშვნელოვანია ამ მეთოდით A^3B^5 ტიპის ნახევარგამტარების GaAs და GaP სხვადასხვა იონით მოდიფიცირებული ზედაპირების შესწავლა და იდენტიფყკაცია. დავადგინეთ, რომ კრისტალური GaAs და GaP ზედაპირების ფოსფორისა და ალუმინის იონებით ბომბარდირებისას შესაბამისად, მათი ზედაპირული კრისტალური ფენა ტრანსფორმირდება ამორფულ სტრუქტურაში. პირველ შემთხვევაში სარჩულის ზედაპირზე წარმოიქმნა ამორფული ერთფაზიანი სამმაგი ნაერთი GaAsP, ხოლო მეორე შემთხვევაში ამორფული GaPAl. ლაზერული ზონდირებით შეგვიძლია შევაფასოთ ამ ამორფული სტრუქტურების ზედაპირიდან გავრცელების სიდიდეები.