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FEATURES OF LATTICE DYNAMICS IN LAYERED CRYSTALS GaS AT ION IMPLANTATION OF HYDROGEN WITH ENERGY OF 140 keV

[1,2]R.S. Madatov, [1]A.I. Najafov, [3]F.F. Komarov, [1]Y.M. Mustafayev, [1]F.I. Ahmadov, [1]N.I. Huseynov, [1]M.A. Mammadov, [1]M.M. Jahangirov

[1]Institute of Radiation Problems of ANAS,
[2]Azerbaijan National Aviation Academy,
[3]ETCC «Nanotechnology and physical electronics» Belarusian State University
msrahim@mail. ru

Abstract: It has been studied the degree of structural disorder of layered crystals GaS before and after implantation by hydrogen (H_2+) with energy of 140 keV by Raman scattering method. From Raman spectra of layered crystals GaS it is established that at hydrogen implantation up to dose below $5x10^{15}cm^{-2}$ the position and intensity of the bands are kept, which is connected with stability of crystal lattice, but at $5x10^{15}cm^{-2}$ dose the intensity of the bands decreases due to the increase in degree of the structural disorder.

Keywords: single crystal, Rutherford scattering, Raman scattering, amorphization dose, ion implantation.

1. Introduction

Modification of semiconductor materials, i.e. directional change of their properties, beams of light ions, is one of the most promising methods. As, ion implantation can form compounds and alloys, which essentially cannot be obtained by conventional methods [1-3]. Naturally, the interstitial atoms can enter into chemical bonds with the atoms of semiconductor under favorable conditions. These structural defects lead to a change of optical and photoelectric properties of materials. Thus, the change of nature of the chemical bonds, through the introduction of radiation defects allows a wide range to change the electrical properties of the semiconductor.

Single crystals of GaS according to [4-7], are of interest as promising materials for the formation of semiconductor detectors of elementary particles and hard electromagnetic radiation. The increased interest in these compounds is due to the fact that, they have a high photosensitivity to the visible, ultraviolet, X-ray and gamma-radiation, despite their strong defects [8-10].

Layered crystals are formed from layers containing four atomic planes. Bond has ionic-covalent nature inside layers, and the interaction is mainly carried out by van der Waals forces with a small amount of Coulomb forces, between the layers. Anions and cations are located in planes perpendicular to the crystal axis - C in sequence of S-Ga-Ga-S. The arrangement of atoms within a layer corresponds to the space group $D\_(sh)^1$[3-6]. Despite numerous studies of electrical [1], photoelectric [3] and optical [10] properties of crystals GaS, there are few research in which the effect of y-quanta and electrons studied [8], and the effect of interstitial low-energy ions on the structural properties are not studied. The obtained results indicate that, decrease in the degree of space non-homogeneity of crystals is observed under the irradiation of y-quanta and electrons. In the article [9], the characteristics of crystal structure of layered crystals GaSe with different polytypic modifications, exposed to laser irradiation are analyzed. It was found out the formation of areas with a different polytypic structure and areas of residual stress after laser irradiation. The study of the nature of restructuring of the vibrational spectrum in the solid solution systems based on A^3B^6 type compounds provides useful information about the structural phase transitions. Features of the phonon spectra of highly anisotropic crystals are well known [14]: all vibrations can be divided into two groups- low-frequency "interlayer" and high-frequency "intralayer". "Interlayer" vibrations should be characterized by large (~ 10) values of multimode Grüneisen parameters: but "intralayer" - relatively small (~ 1) values. Considering that, there is a correlation between the nature of the interatomic chemical bond and properties of semiconductor, then the studies of radiation effects in layered semiconductors, in particular of GaS, are promising from practical point for prediction of durability of the materials under ionizing radiation influence.

In the article it is shown the results of diagnostic of changes in the degree of structural disorder before and after implantation by hydrogen ions by Raman scattering method.

2. Studied samples and experimental technique

The studied single crystals p-GaS were grown by Bridgman technique in the Institute of Radiation Problems of ANAS. When growing GaS it was used excess sulfur (1,5%) in order to determine the possibility of filling vacancies with sulfur atoms. Resistivity of the obtained samples was -2-10^9 Ohm-cm at room temperature. Ion implantation of hydrogen was carried out on Van de Graaff accelerator (type ESA-2) with the energy of 140 and 500 keV, ion current density - 0,15 mkA/cm^2 and the dose was 10^{15} - 10^{16} ion/cm^2.

Raman spectra were studied on micro Raman spectrometer Nanofinder in backscattering geometry at laser excitation with X= 473 nm. Scattered light was collected under right angle towards exciting radiation that fell on the face of natural crystal, perpendicular to C axis. All measurements were carried out at room temperature.

3. Experimental Results and Discussion

Spectral dependences of Raman signal in layered crystals GaS implanted by hydrogen ions with the energy of 140 keV at spectral range from 500 to 50 cm^{-1} are depicted in Figure 1. As it is seen from figure 1, curve 1 there are three intense bands at 188; 295 and 360 cm^{-1} in Raman spectrum of the original single crystal GaS. The following table shows the results of the experimental oscillation frequency, type of oscillation and data published in literature [1, 7] for atomic plane, constituing the layers of the crystal GaS.

After irradiation of the crystals GaS by multimode ruby laser radiation pulses (HN=1.78 eV) with power density below the damage threshold of sample surface for stoichiometric composition and within deviation from stoichiometry the intensity of the bands 60 cm^{-1} changes as in the annealed samples.

In Raman spectra of GaS the intensity of the bands 215 cm^{-1} increases, herewith the intensity of the bands 211 cm^{-1} does not change substantially after irradiation by hydrogen ions at dose 1x10^{15}ion/cm^2 (fig.1.curve 2). The intensity of the bands 249 cm^{-1} grows which exceeds the intensity of the bands 254 cm^{-1} after irradiation (fig. 2a, b, curves 1-3).

In Raman spectra of single crystals Ga1.o5Seo.95 the intensity of the bands 215 cm^{-1} does not change after irradiation but the intensity of the bands 211cm^{-1} decreases considerably, herewith notable changes are not observed in the spectral region 247—254 cm^{-1} (fig. 2, c, curves 1-3).

As the Raman bands 293 cm^{-1} and 360 cm^{-1} identified as modes E1g2 and Ä1g2 respectively, of which frequency can only be measured within the propagation of phonons along the corresponding axes of symmetry, that the proton irradiation at dose within the range of Ы0^{15} ~ 2,2-10^{15} ion/cm^2 and from 6-10^{15} to 7,3-10^{15} ion/cm^2 in initial section of dose dependence for the bands 293 cm^{-1} and 360 cm^{-1} leads to initial violation of structure periodicity in modified layer undergoing changes contributing more intense propagation of phonons along the symmetry axes. Characteristic feature of phonon spectrum of layered crystals is the existence of low- frequency modes, corresponding to displacement of layers relative to each other, entirely. For

GaS these are acoustic modes ^2 $_u$, EМ and optical , $B2_b$ (modes E - GaS symmetry -

doubly degenerated). For atoms disposed in the layer at oscillations they are not shifted relative to each other and characterized by three types of low-frequency modes, corresponding to interlayer vibrations, two of them are conditioned by reciprocal movement of layers in plane parallel to the layers $E^{\wedge}_u$ shifted to oscillation and one E2g conditioned by displacement of layers in plane perpendicular to plane, along the hexagonal axis C (compression oscillation).

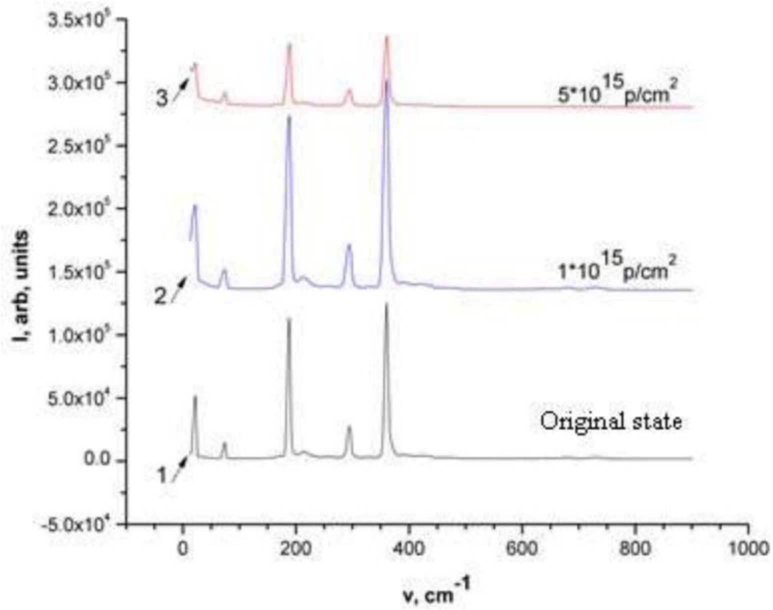

Fig.1. Raman spectra of GaS samples, implanted by hydrogen ions for dose range 1x1015 - 1x1016 ion/cm2 and ion energy of 140 keV

Experimental oscillation frequency ν, ρμ-1	Literary data ν, cm^{-1}	Oscillation type
188,4	187,9	$^{A}1\ g\ ^{1}$
293,2	295.0	$E1g^2$
360,2	360,2	$A1g^2$

The analysis of dose dependence of Raman spectra change of GaS samples (fig.2) showed that decrease and slight increase in relative intensity of Raman bands in layered space of GaS from ion implantation dose within the range 10^{15}-10^{16} ion/cm^2, for oscillation type E1g and Ai $_g{}^2$ corresponding to wave vector 293,2 cm^{-1} and 360,2 cm^{-1} may be associated with the growth and redistribution of vacancy created as sulfur atoms and gallium atoms in modified layer.

Decrease and slight increase in relative intensity of Raman bands in layered space of GaS from ion implantation dose within the range 10^{15}^10^{16} ion/cm^2, for oscillation type E $_{1g}{}^2$ and $A_1\ _g{}^2$ corresponding to wave vector 293,2 cm^{-1} and 360,2 cm^{-1} may be associated with the growth and redistribution of vacancies.

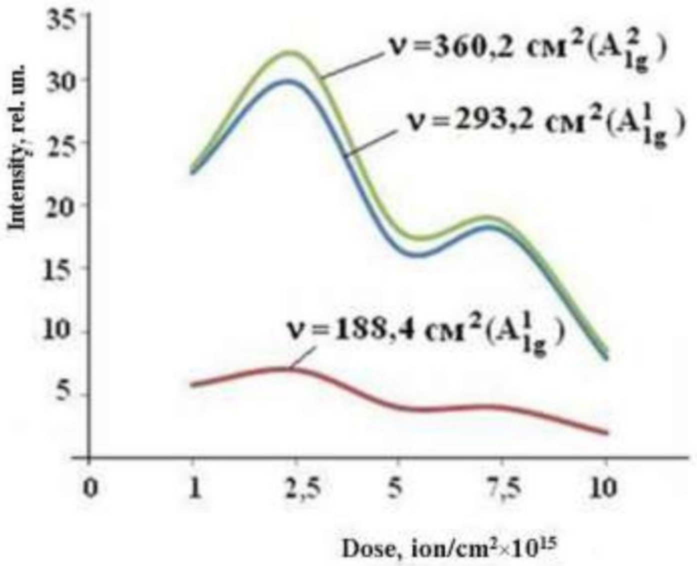

Fig.2. Dose dependence of relative intensity of Raman bands in layered space of GaS within 10^{15}-10^{16} ion/cm^2

As the Raman bands 293,2 cm^{-1} and 360,2 cm^{-1} identified as modes E_{1g}^2 and A_{1g}^2 respectively, of which frequency can only be measured within the propagation of phonons along the corresponding symmetry axes, that the proton irradiation at dose within the range of 1-10^{15} ~ 2,2-10^{15} ion/cm^2 and from 6-10^{15} to 7,3-10^{15} ion/cm^2 in initial section of dose dependence for the bands 293,2 cm^{-1} and 360,2 cm^{-1} leads to initial violation of structure periodicity in modified layer undergoing changes contributing more intense propagation of phonons along the symmetry axes. Decline in relative intensity for dose ranges is due to violation of selection rules by creating a large number of stacking faults along the axis C.

Study of vibration spectrum of layered semiconductor compounds is of considerable interest, because as a result of such research it becomes possible to determine the value of force coefficient of interaction between atoms, establish the nature of chemical bond, improve the structure of the studied compound and define the areas of structural phase transitions. As it is shown in [7,13], the presence of a large amount of stacking faults in layered crystals, as well as formation of complex radiation defects under radiation influence in layers and interlayers leads to violation of the structure periodicity and interaction within the layers and interlayers [10-16]. Interlayer vibrations are always of single-mode nature of adjustment, while the adjustment nature for inside of layered vibrations can be both single-mode and dual-mode. Determination of the values of interlayer frequencies enabled to compare the interlayer interaction with the forces binding the atoms inside the layers. Since quasi-two-dimensional character of vibrational states in composites becomes apparent in properties of the materials determined by phonon subsystem, the ion introduction into the area containing three and more atomic planes in the state on the short-range order modifies this layer. So, the atomic plane of layer can be divided into nanoplane, nano-wire and even quantum dots by amorphous sections at high-dose implantation. Such capacity of the ion implantation allows obtaining semiconductor materials with unique physical properties. Therefore, the works carried out in this area are relevant and may be of considerable practical interest.

Thus, the degree of structural disorder of layered crystals GaS before and after implantation by hydrogen (H2+) with the energy of 140 keV was studied by Raman scattering and Rutherford method. It is shown that redistribution of the crystal components is in depth uniformly and stoichiometric composition of compounding ingredient is observed up to dose 5-10^{15}cm^{-2}.

Experimental value of critical dose of breaking of amorphization makes up about $5x10^{15}cm^{-2}$ and is in accordance with the calculated value. The results obtained by Raman scattering method, confirm the preservation of crystallinity of the structure and beginning of the amorphization process.

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ОСОБЕННОСТИ ДИНАМИКИ РЕЩЕТКИ В СЛОИСТЫХ КРИСТАЛЛАХ GaS ПРИ ИМПЛАНТАЦИИ ИОНАМИ ВОДОРОДА С ЭНЕРГИЕЙ 140 кэВ

Р.С. Мадатов, А.И. Наджафов, Ф.Ф. Комаров, Ю.М. Мустафаев, Ф.И. Ахмедов, Н.И. Гусейнов, М.А. Мамедов, М.М. Джахангиров

Резюме: Методом КРС исследована степень структурного беспорядка слоистых кристаллов GaS до и после имплантация водородом (H 2 +) с энергией 140 кэВ. Из спектров КРС слоистых кристаллов GaS установлено, что при имплантации водорода до доз ниже 5x10 см-2 положение и интенсивность полос сохраняется, что связанно с устойчивостью кристаллической решетки, а при дозе 5x1015см-2 наблюдается уменьшение интенсивности полос, что обусловлено увеличением степени структурного беспорядка.

Ключевые слова: Монокристалл, Резерфордовское рассеяние, Рамановское рассеяние, доза аморфизации.

140 keV ENERJİ ILƏ HIDROGEN ION IMPLANTASIYASI ZAMANI GaS LAYLI KRİSTALLARINDA QƏFƏS DİNAMİKASININ XÜSUSİYYƏTLƏRİ

R.S. Mədətov, A.I. Nəcəfov, F.F. Komarov, Y.M. Mustafayev, F.I. Əhmədov, N.I. Hüseynov, M.A. Məmmədov, M.M. Cahangirov

Xülasə: GaS laylı kristallarının struktur nizamsızlıq dərəcəsi Raman metodunun köməyi ilə 140 keV enerji ilə hidrogen (H2+) implantasiyasından əvvəl və sonra öyrənilmişdir. GaS laylı kristallarının Raman spektrlərindən müəyyən olunmuşdur ki, $5x10^{15}sm^{-2}$-dan aşağı dozaya qədər hidrogen implantasiyası zamanı zolaqların vəziyyəti və intensivliyi qorunub saxlanılır, hansı ki bu hal kristal qəfəsin möhkəmliyi ilə əlaqəlidir, ancaq $5x10^{15}sm^{-2}$ dozada zolaqların intensivliyində azalma müşahidə olunur ki, buna da səbəb kimi struktur nizamsızlıq dərəcəsinin artması göstərilir.

Açar sözlər: monokristal, Rezerford Əks Səpilmə, Raman səpilməsi, amorflaşma dozası, ion implantasiyası.