X-RAY and RAMAN INVESTIGATIONS Of LAYERED InSe AND GaSe SINGLE CRYSTALS IRRADIATED WITH HIGH-ENERGY GAMMA-QUANTA

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ABSTRACT

In the present paper regularities of the effect of high-energy γ-quanta on the defects system of layered InSe and GaSe semiconductors is investigated by means of X-ray diffraction analysis and Raman scattering. It is established that the absorbed dose of γ-radiations in 140 kGy does not lead to changes of the crystal structure and a considerable modification of the lattices parametres of III-VI crystals that testifies to preservation of their structural perfection. This fact makes layered compounds attractive from the point of view of radiation resistance. The radiation influence comes to the appearance of point vacancy defects.

Key words: layered crystals, InSe, GaSe, high-energy irradiation, radiation hardness, Raman spectra, X-Ray diffraction

INTRODUCTION

Wide application of high-energy radiations in science, many technological processes, medicine, the safety in atomic power engineering demand a search of radiation-resistant materials and working out of electronic equipments capable to operate at high radiation levels.

A use of the semiconductors of modern electronics (silicon, gallium arsenide, and germanium) and dielectric layers of their intrinsic oxides shows insufficient radiation stability of based on them devices [1]. As the alternative to them one can consider anisotropic III-VI crystals with a layered crystalline structure, in particular InSe and GaSe [2]. The presence of weak Van-der-Waals bonds between the layers enabbles easily to gain substrates with atomically smooth surfaces that in a combination with simple production techniques (oxidation, Van-der-Waals contact) gives a possibility to create high-efficiency

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photoconverters [3-5]. A considerable quantity of intrinsic defects in layered crystals allows to apply them under conditions of large radiation doses.

At present there is a great number of papers devoted to radiation physics of the classical semiconductors but researches of the influence of high-energy radiation on III-VI crystals is not less important.

METHODS OF SAMPLE MANUFACTURING AND IRRADIATION

InSe and GaSe single crystals were grown by the vertical Bridgman method. Intentionally undoped InSe had *n*-type conductivity with a concentration of uncompensated donors of 10^{14} – 10^{15} cm^{-3} and a Hall mobility along the layers $\mu_n \sim 10^3$ $cm^2V^{-1}s^{-1}$ at 300 K. For obtaining *p*-type conductivity InSe was doped with 0.2 wt.% Cd what leads to the following parameters: $p = 10^{13}$ cm^{-3} and $\mu_p \sim 10^2$ $cm^2/V{\cdot}s$. In order to increase the electrical conductivity of GaSe, we doped this semiconductor with dysprosium in an amount of 0.1 wt %. At room temperature, the concentration and mobility of charge carriers were $\sim 5{\cdot}10^{14}$ cm^{-3} and 35–50 $cm^2/V{\cdot}s$, respectively.

Investigated samples have a form of plane-parallel plates with average sizes 8×8 mm and about of 2 mm thick.

The samples have been irradiated bremsstrahlung γ-photon in the energy range of 0.5-11.5 MeV with a maximum at 3 MeV at a linear electron accelerator KUT-10. The flux of γ-photon was about 2×10^{11} $cm^{-2}s^{-1}$, and the irradiation time was chosen so that to give the total γ-fluence 2×10^{16} cm^{-2} that corresponds to the absorbed dose 140 kGy.

X-ray diffraction (XRD) investigations of the samples were made in monochromatic CuKα-radiation with a DRON-UM1 diffractometer. Raman spectra of the crystals were excited by an argon laser with a wavelength of 514.5 nm and registered by a spectrometer DFS-24. All measurements were carried out at room temperature.

RESULTS AND DISCUSSION

The carried out analysis of the X-ray diffraction patterns of the initial InSe and InSe:Cd crystals before (*Fig. 1a* and *Fig. 2a*) and after (*Fig. 1b* and *Fig. 2b*) irradiation with fluence 10^{16} γcm^{-2} enables to conclude that in all the states these crystals are single phase InSe of the 3R structure. The measurements of the unit cell parameters by using the Bond method at 110 and 0027 reflections indicate on the γ-polytype of InSe (the space group $R\overline{3}m$). A typical feature of the X-ray diffraction patterns for the samples under investigation is the presence of diffusion maxima nearby the 009, 00.12, and 00.18 peaks of the 3R structure. These peaks are situated from the side of smaller angles and can be interpreted as caused by the stacking faults in the 3R structure, which lead to stacking of the layers typical for the 2H structure of InSe ($P6_{-3}/mc$). Similar results are received for *p*-GaSe crystals (*Fig. 3a* and *Fig. 3b*) with the 4H structure (the space group $P6_3/mc$). As one can see from Figs. 1-3, there are no essential changes in the crystals after irradiation with γ-quanta except for a small decrease (in the case of InSe) or increase (for GaSe) of the lattice parameters.

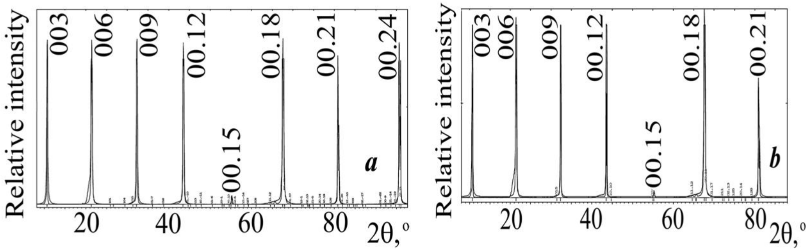

Fig. 1. - XRD spectra of the initial *n*-InSe crystal (*a*) and irradiated (*b*).

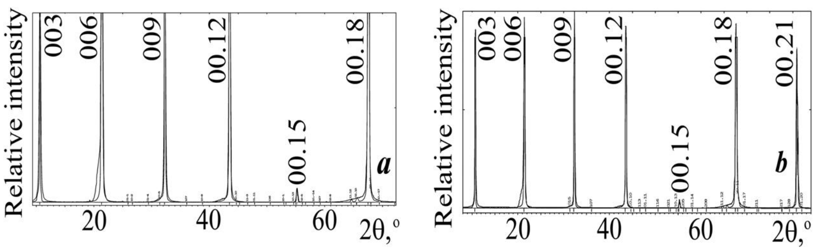

Fig. 2. - XRD spectra of the initial *p*-InSe crystal (*a*) and irradiated (*b*).

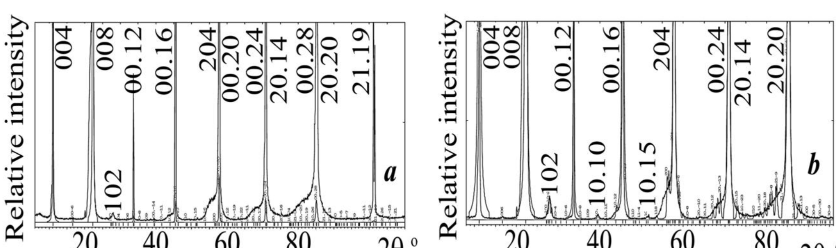

Fig. 3. - XRD spectra of the initial *p*-GaSe crystal (*a*) and irradiated (*b*).

The Raman spectra of *n*-InSe and *p*-InSe crystals in the initial state (*Fig. 4a*, curves *1* and *2*, respectively) are very similar each other, except for a small transferring intensity between the two bands in the range of 215 and 230 cm^{-1}. Note that in the *p*-InSe sample the band at 215 cm^{-1}, which is caused by the presence of Cd atoms, is more well expressed. The Raman spectra of the irradiated *n*-InSe and *p*-InSe crystals contain the bands at frequencies 120.8, 184.8, 205.7, 218.0, 231.8, 409.3, and 430.3 cm^{-1} (*Fig. 4a*, curves *3* and *4*, respectively). These bands correspond to those known from the literature Raman spectra of InSe [6]. Only insignificant transferring relative intensities between the bands in the spectra of different samples was observed. It is caused by different defect concentrations in these samples after their irradiation. Other peculiarities related to a change of atoms coordination were not found.

The Raman spectrum of the *p*-GaSe sample (Fig. 4*b*, curves *1*) sharply differs from that of InSe. It does not contain the doublet band at 410-420 cm^{-1} but has intensive bands at frequencies 260 and 215 cm^{-1} and as well as the intensive band at 175 cm^{-1} what is typical for GaSe crystals [7]. The Raman spectra of irradiated GaSe crystals (Fig. 4*b*, curves *2*) contain narrow lines at frequencies 138.7, 216.6 and 313.5 cm^{-1}. One can also see some redistribution between the relative intensities of the lines above. Other features related to changes of the atom coordination have not been observed.

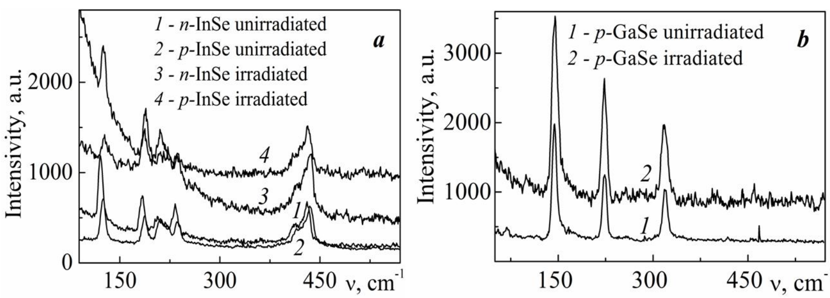

Fig. 4. - Raman spectra of InSe (*a*) and GaSe (*b*) crystals.

Thus, one can conclude that irradiation of the layered crystals has not led to qualitative changes in the investigated Raman spectra which are extremely sensitive to variation of the coordination of Raman scattering centres. The conclusion about insignificant influence of irradiation with γ-quanta at fluences up to $5 \cdot 10^{15}$ cm^{-2} on a change of the vacancy and impurity subsystems in layered crystals is indirectly confirmed by the authors of [8].

CONCLUSIONS

Thus, irradiation of layered crystals does not result in qualitative changes of the investigated spectra, including Raman one, which is extremely sensitive to changes in the coordination of Raman scattering centres. It is possible to say about saving structural perfection of these semiconductors against the background of radiation-induced defects.

The obtained results prove the resistibility of III-VI crystals lattice for γ-radiation that is especially important for the case of the mixed bonding in them:

strong ionic-covalent bonding within the layers and weak Van-der-Waals between neighboring layers.

It is possible to put forward a preliminary hypothesis that Cd atoms in InSe and Dy atoms in GaSe act as centres of the localization of radiation vacancies, whereas in the intentionally undoped compounds the vacancies are localized in the sublattices In or Ga.

REFERENCES

[1] Radiation Effects in Semiconductors (Eds. V.S. Vavilov, N.P. Kekelidze, L.S. Smirnov) Nauka, Moscow, 1988.
[2] J.S.J.M. Terhell, Prog. Cryst. Growth and Charact., 1983, Vol. 7, P. 55-110.
[3] J. Martinez-Pastor, A. Segura, J.L. Valdes, A. Chevy, J. Appl. Phys., 1987, Vol. 62, No4, P. 1477-1483.
[4] Z.D. Kovalyuk, V.M. Katerynchuk, A.I. Savchuk, O.M. Sydor, Mater. Sci. Eng. B, 2004, Vol. 109, P. 252-255.
[5] S. Shigetomi, T. Ikari, J. Appl. Phys., 2000, Vol. 88, No3, P. 1520-1524.
[6] N. Kuroda, Y. Nishina, Sol. State Commun., 1979, Vol. 30, No2, P. 95-98.
[7] N.M. Gasanly, A. Aydinli, H. Özkan, C. Kocaba, Materials Research Bulletin, 2002, Vol. 37, No1, P. 169-176.
[8] T.D. Ibragimov, E.A. Dzhafarova, Z.B. Safarov, Semiconductors, 2002, Vol. 36, P. 805-810.