ANOMALOUS CONDUCTIVITY IN ZnSe SINGLE CRYSTALS BY X-RAY IRRADIATION

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PACS 29.40.Wk; 61.80.Cb; 61.82.Fk; 72.80.Ey

We study experimentally the ability of ZnSe to be detectors in the mode of direct conversion of the ionizing radiation energy in that of an electric signal. We have established that, for a monocrystalline ZnSe-sample of the n-type ($E_d = 0.26$ eV) with the specific resistance $\rho \sim 10^9$ Ohm·cm at room temperature, a reduction of the conductivity under the action of X-ray radiation is observed, unlike the high-resistance single crystals with $\rho > 10^{12}$ Ohm·cm. We have discovered that the current-voltage characteristic (CVC) of such samples for the dark conductivity lies over the CVC with the X-ray conductivity, and the shapes of these CVC curves differ significantly. Obviously, the character of the X-ray-induced conductivity of ZnSe, under which free carriers of both signs are generated, differs substantially from that of the dark conductivity, when a sample contains only free electrons. Respectively, we have obtained a decreasing lux-ampere characteristic (LAC) for the X-ray-induced conductivity current. Till now, the scientific and technical literature sources contained no indications of such nontypical behavior of the mentioned physical quantities and characteristics. We assume that such anomalous phenomenon can be caused by the heterogeneous recharge of deep centers near electric contacts and, therefore, by the appearance of volume charges reducing the X-ray conductivity of monocrystalline ZnSe.

1. Introduction

Zinc selenide (ZnSe) belongs to the most promising wide-band materials of type A^2B^6, is quite well studied [1–3], and has found the numerous applications to the development of devices of semiconductor electronics and the information display systems [4]. It is known that polycrystalline zinc selenide is a material for the production of optical lenses, windows, prisms, mirrors, *etc.*, which are able to operate in the visible and infrared spectral regions (0.55–22 μm) in special optical systems and CO_2-lasers.

For the last decade, one more promising direction, where ZnSe (single-crystal) is used in detectors of ionizing radiation (scintillators) [5] and in devices of the direct transformation of the energy of high-energy particles to that of the electric current [6, 7,] has been developed. By the totality of its electrophysical, physico-chemical, and luminescence properties and by its resistance to radiation, zinc selenide doped with tellurium ZnSe(Te) is now one of the most efficient scintillators used in detectors of the "scintillator–photodiode" type [5].

The application of nondoped ZnSe as a semiconductor detector became possible only after the development of the technology of growing of quite qualitative single crystals with small concentrations of noncontrolled impurities and a high specific resistance of the material on the level of $\rho \sim 10^{10}$ Ohm·cm. It is worth noting that the rather large values of the effective atomic number $Z_{\text{ef}} = 32$ and the energy gap $E_g = 2.7$ eV (at 300 K) make zinc selenide to be a suitable material for the fabrication of X-ray detectors, which do not require to be cooled [6]. Therefore, the experimental studies of the X-ray conductivity of ZnSe single crystals at room temperature became the priority direction for us.

We have also studied the kinetics of the X-ray luminescence (XRL) and the X-ray conductivity (XRC) at the successive switching-on of X-ray radiation and the supply of an electric voltage to the contacts and in the opposite way. It is of interest to compare the curves of buildup and decay of the XRL intensity and the XRC current in various specimens of ZnSe, as well as to compare them with the kinetics of buildup and decay of the dark conductivity. These studies yield original results, which are presented in this article.

2. Experiment and the Results

We studied the luminescence and the conductivity of single-crystal ZnSe under the action X-ray quanta. The ZnSe crystals were grown in a preliminarily purified powdery blend and were not doped during their growth. These measures ensured the possibility to produce specimens with minimum concentration of point-like defects and with maximum specific resistance ($\rho \geq 10^{12}$ Ohm·cm). It is commonly known that the increase of

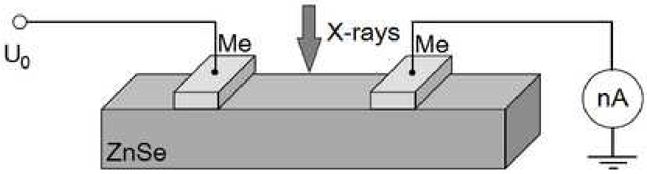

Fig. 1. Scheme of measurements of the X-ray conductivity

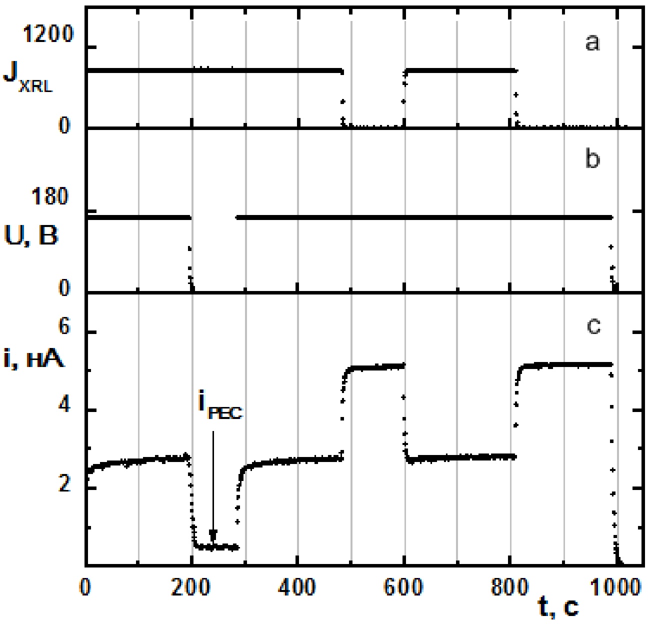

Fig. 2. Time dependence of the intensity of the X-ray luminescence band at 630 nm (a), supplied voltage U_0 = 165 V (b), and the conductivity current (c) for a ZnSe specimen at room temperature

the intensity of the external irradiation of a semiconductor crystal causes a rise of both the number of free charge carriers and, respectively, the conductivity current in it. But our studies of the X-ray conductivity yield the opposite result. A specific feature of the experiment consists in that this anomaly was observed only in specimens with comparatively low specific resistance ($\rho \sim 10^9$ Ohm·cm), for which the dark current was several times (rather than by several orders) less than the XRC current in high-resistance specimens. To study the conductivity, we sprayed metallic electric contacts on the crystal surface by the resistance method and soldered copper conductors to them. The distance between the electrodes was 5 mm. The voltage U_0 was supplied only onto one electrode. Another one was grounded through a nanoamperemeter. The studies of the conductivity current were carried out in vacuum ($P<$ 1 Pa). For all values of the conductivity current, the following necessary condition was satisfied: the input impedance of a nanoamperemeter was by several orders less than the electric resistance of a ZnSe specimen. The scheme of the experiment and the geometry of the specimen are shown in Fig. 1. The optical axis of the luminescence registration system passes through the middle of the specimen between the electric contacts.

The measurement was executed at room temperature (295 K), The excitation of XRL and XRC was made with the integral emission of an X-ray tube BKhV-7 (operation mode: Re, 20 kV, 5–25 mA, L = 120 mm) through a Be window in a cryostat. The X-ray intensity was varied by means of the regulation of the anodic current of the X-ray tube at a constant voltage. In this case, the shape of the emission spectrum of the tube was invariable, and the intensity was proportional to the current of the tube. By the method of thermo-emf, we have established that the specimens under study possess the conductivity of the n-type. By the temperature dependence of the dark conductivity, we determined the depth of the donor level E_d =0.26 eV, which ensures the dark conductivity at room temperature. In addition, we have measured CVC of the dark and X-ray conductivities, as well as the lux-voltage characteristics of XRC and XRL. The dominant emission band in the XRL spectrum was the well-known red band with a maximum at a wavelength of 630 nm. his band was observed practically in all specimens of ZnSe [4–7]. With the help of the registration of the X-ray luminescence, we made the continuous control over the irradiation of a specimen. As was found experimentally for some specimens of single-crystal ZnSe, the conductivity current decreases under the X-ray irradiation, and, the intense X-ray luminescence was simultaneously observed (Fig. 2).

The kinetics of variation of the current at the switching-on/out of the voltage and X-ray radiation becomes equilibrium for several tens of seconds. For several tens of minutes, no tendencies to changes are observed. We note that, under the X-ray irradiation of a specimen in vacuum and the zero voltage on the contacts, the X-ray emission current ($i_{\rm xrec}$) of tens of picoamperes is observed. This current is caused by the emission of high-energy electrons from the specimen during the absorption of X-ray quanta in the near-surface layer. In this case, the emitted electrons fall into the grounded case of a cryostat and return through a current to the ZnSe specimen. As is seen from Fig. 3, CVC of the dark conductivity exceeds CVC of the X-ray conductivity and has a different behavior.

We pay attention to the fact that, at small strengths of the external electric field (up to 100 V/cm), the XRC current is practically the same as the dark current, which

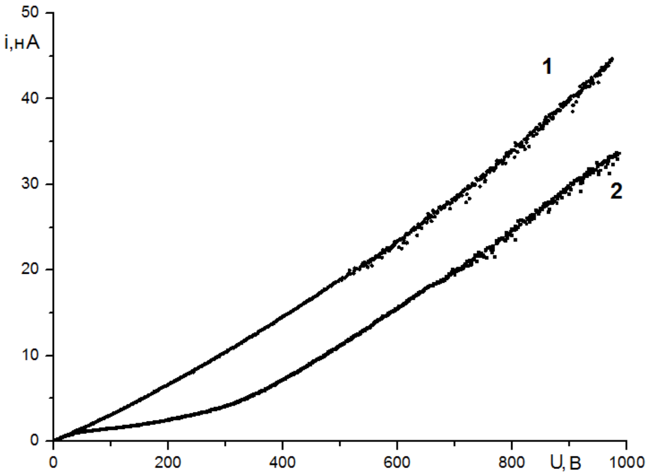

Fig. 3. Current-voltage dependences of the dark (*1*) and X-ray conductivities (*2*) of a single-crystal ZnSe specimen at room temperature

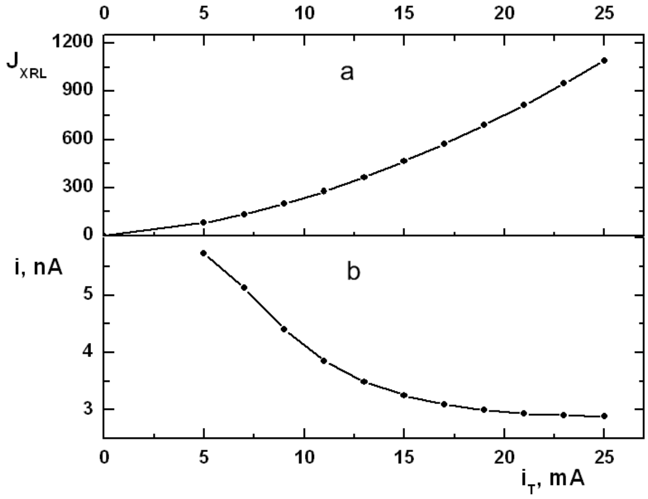

Fig. 4. Dependences of the XRL intensity (*a*) and the XRC current (*b*) on the X-ray radiation intensity (values of anodic current of an X-ray tube) at $U_0 = 165$ V

can testify to a small variation of the concentration of free charge carriers. The same X-ray irradiation of high-resistance crystals of ZnSe causes currents equal to microamperes. In other words, this specimen is characterized by the extremely short lifetime of carriers in the free state and a high concentration of donors. At fields higher than 500 V/cm, the curves of CVCs are practically parallel with a constant shift of 350 V/cm. This can be explained by the stationary generation of bulk charges near the electric contacts of the specimen, which create the field directed contrarily to the applied external field.

The measured LVC for XRC and XRL, which are given in Fig. 4, are consistent with the other results presented in this work. The XRL intensity (the band with the maximum at 630 nm) varies, as was expected, practically linearly with the intensity of X-ray radiation. In this case, the XRC current decreases monotonically with the radiation intensity. Such a dependence of LVC for the XRC current is anomalous and has no explanation in the frame of the classical theory of photoconductivity. As is known, the increase of the conductivity with the concentration of free carriers is always observed experimentally, or the conductivity is not changed (like that in metals), if the concentrations of generated free carriers remain much less than the dark concentrations of charge carriers.

The decrease of the conductivity under the growth of the intensity of generation of charge carriers is an anomaly, since the probability of the absorption of X-ray quanta is independent of their number. Up to now, the literature has contained no indications of such anomalous behavior of the conductivity in wide-band semiconductor single crystals of the A^2B^6 type under X-ray or γ-irradiation. At the same time, some researchers have obtained the nonlinear LVC for the photo- and X-ray conductivities [8–11].

3. Conclusions

Thus, for a single-crystal of ZnSe of the n-type with a certain value of intrinsic conductivity (specific resistance $\rho \sim 10^9$ Ohm·cm), we have observed the anomalous behavior of the X-ray conductivity, namely: at a constant voltage on the contacts, the conductivity current decreases sharply almost twice during the X-ray irradiation. At the same time, such an effect does not hold in high-resistance specimens. It is established that CVC of the dark conductivity exceeds CVC of the X-ray conductivity by magnitude. Moreover, CVC of the dark conductivity is almost linear, whereas CVC of the X-ray conductivity is noticeably nonlinear. In other words, the different physical processes affect the dark and X-ray conductivities. The weak nonlinearity of the dark conductivity is probably caused by the Poole–Frenkel effect [12]. The strong nonlinearity of the X-ray conductivity, when free carriers of both signs are generated, is possibly related to the creation of bulk charges in the near-contact parts of a specimen, which changes basically the resulting value of electric field inside the crystal. We have established experimentally the following very significant fact: for the certain values of parameters of a single-crystal zinc selenide (e.g., not too high specific resistance), the conductivity of a semiconductor material decreases under the action of X-ray radiation, which is equivalent to to the amplitude of a friendly signal from a detector. In order that single-crystal ZnSe be suitable for applications in solid-state detectors with direct transformation of the incident flow of ionizing radiation, it is necessary to use only a high-resistance material with specific resistance of at least 10^{12} Ohm·cm.

The authors are sincerely grateful to Academician M.S. Brodyn for the fruitful discussion of results of the work, their interpretation, and valuable remarks.

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Received 27.07.12.
Translated from Ukrainian by V.V. Kukhtin

АНОМАЛЬНА ПРОВІДНІСТЬ У МОНОКРИСТАЛАХ СЕЛЕНІДУ ЦИНКУ ПІД РЕНТҐЕНІВСЬКИМ ОПРОМІНЕННЯМ

В.Я. Дегода, В.Т. Весна, Б.В. Кожушко, Г.П. Подуст

Р е з ю м е

Експериментально досліджено здатність монокристалів селеніду цинку забезпечити роботу напівпровідникового детектора в режимі прямого перетворення енергії іонізуючого випромінювання на електричний сигнал. Встановлено, що для зразка ZnSe n-типу ($E_d = 0,26$ eB) з питомим опором $\rho \sim 10^9$ Ом·см за кімнатної температури спостерігається зменшення провідності під дією рентґенівського опромінення, на відміну від високоомних монокристалів з $\rho > 10^{12}$ Ом·см. Виявлено, що вольт-амперна характеристика (ВАХ) таких зразків для темнової провідності вища за ВАХ рентґенопровідності, при цьому форми цих кривих помітно відрізняються. Очевидно, що характер рентґенопровідності ZnSe, за якої генеруються вільні носії обох знаків, суттєво відрізняється від характеру темнової провідності, коли в зразку є лише вільні електрони. Відповідно, для струму рентґенопровідності одержано спадаючу люкс-амперну характеристику. Досі згадок про таку нетипову поведінку зазначених вище фізичних величин і характеристик у науково-технічній літературі не було. Це аномальне явище може бути зумовлене неоднорідною перезарядкою глибоких центрів біля електричних контактів і, відповідно, появою об'ємних зарядів, які зменшують рентґенопровідність монокристалічного ZnSe.