CONDUCTIBILITY AND IRRADIATION STABILITY OF SINGLE CRYSTALS $ZnIn_2S_4$

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Abstract

This study presents the results of investigations on the conductivity and irradiation stability of single crystals $ZnIn_2S_4$ in a wide range of incident electron energies (30−75 keV) and respective doses (10^{14}–10^{20} cm^{-2}). The possibilities of manufacturing accelerated electron detectors are explored, and their parameters are estimated. Considering that the energy values on the order of 10^2 keV are near the threshold of structural defects of intensive formation, the influence of this phenomenon on the detector parameters is subject to the analysis.

1. Introduction

The materials having semiconductor properties are quite sensitive and change their essential physical properties under the action of external radiation and elementary particles bombarding them at a high energy. Usually, under the action of external radiation or different high-energy particles in crystals, following the ionization, additional scattering centers of charge carriers appear.

Experimental and theoretical study of these processes is up-to-date in terms of characteristic stability of microelectronic devices and prevention of degradation processes in different devices made of different materials with semiconductor properties. Therefore, it is quite important to perform researches related to the influence of electron beams with energies up to 100keV on the physical properties of semiconductors. To highlight the changes occurring in optical, photoelectric and irradiation properties, optical absorption spectra and photoconductibility for nonirradiated samples and for samples irradiated with different doses of electrons at certain energies were examined. Depending on the doping element, the impurity concentration is in a range of $1.2 \cdot 10^{19}$ to $2 \cdot 10^{20}$ cm^{-3}. The growth technology for $ZnIn_2S_4$ is described in detail in [1, 2].

2. Experimental results on irradiation conductivity

This paper describes the experimental results regarding the change in photoelectric properties and irradiation under the influence of an electron beam accelerated in ternary compounds of type $A^{II}B_2^{III}C_4^{VI}$, based on the example of typical ternary compound $ZnIn_2S_4$. For research, we chose perfect slabs in terms of defect density, with an outer surface that had a quality optical thickness of 0.20–1.0 mm, obtained from the gas phase using iodine as a carrier agent.

Irradiation conductivity was measured in vacuum at the temperature of 296 K, both under stationary and modulated conditions according to the method described in [3]. The current density of the electron beam was provided by the flow of 10^{16} $cm^{-2}s^{-1}$ particles; the bombardment energy was 30, 40, and 75 keV.

Based on the dependence of the relative resistance change R/R_0 and the current density of the electron beam for three samples of $ZnIn_2S_4$ at 40 keV (Fig. 1), one may observe that this dependence for all the samples is basically a linear function throughout the study period. The dependence between relative resistance (R/R_0) and irradiation dose at different levels of excitation of electron beam energy was also investigated. According to this dependence, it is observed that at 75 keV (curve *1*, Fig. 2), the resistance slightly decreases in a narrow range of variation of the irradiation dose. At an electron beam energy of 40 keV (curve *2)*, this transition is observed to be very slow and approximately linear; at an energy of 30 keV, the dependence on the dose is a linear function in the studied range.

For all the measurements described above, a constant conductivity of the samples in the dark was observed: 10^7–10^9 Ω. At high doses of radiation $(10^{18} \div 10^{20})$ cm^{-2}, irreversible changes of the resistance in the dark were observed, which indicates a sudden increase in the concentration of balanced charge carriers, in the volume of the single crystal (at least to the depth of penetration of the electrons of ≈ 5 μm).

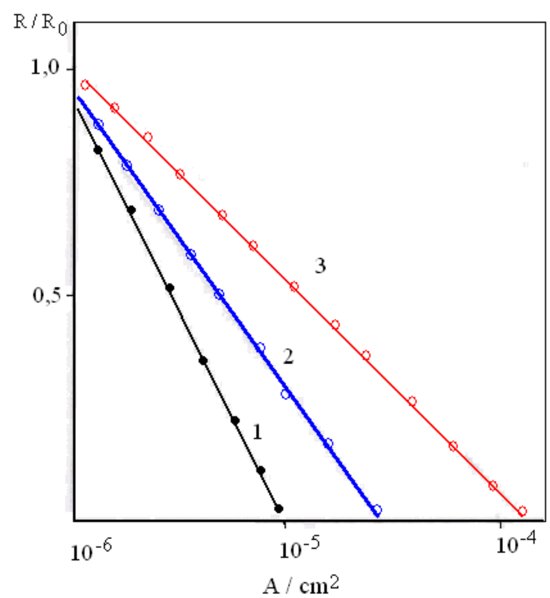

Fig. 1. Dependence of relative resistance $\Delta R/R_0$ on electron beam current for the $ZnIn_2S_4$ samples with a thickness of (*1*) 0.20, (*2*) 0.5, and (*3*) 1.0 mm.

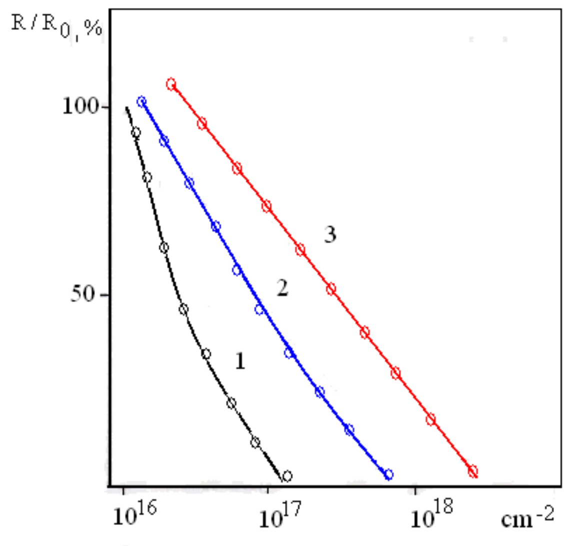

Fig. 2. Dependence of relative resistance $\Delta R/R_0$ and radiation dose at different values of the electron beam energy: (*1*) 75, (*2*) 40, and (*3*) 30 keV.

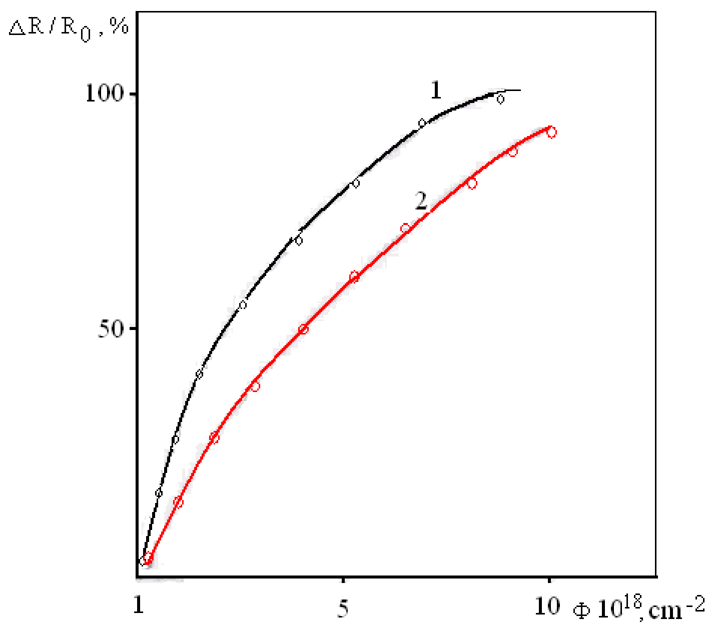

Fig. 3. Dependence $\Delta R/R_0$ of the $ZnIn_2S_4$ single crystals on the dose of irradiation, *T* = 296 K: (1) 50 and (2) 100 keV.

Figure 3 shows the dependence of $\Delta R/R_0$ on the dose of irradiation, where $\Delta R = R_0 - R$, R is the dark resistance of the sample after irradiation dose of $(10^{18} \div 10^{20})\ cm^{-2}$. This dependence suggests that, at a radiation dose of $10^{20}\ cm^{-2}$, the resistance in the dark becomes very small, it is approximately $10^2\ \Omega$.

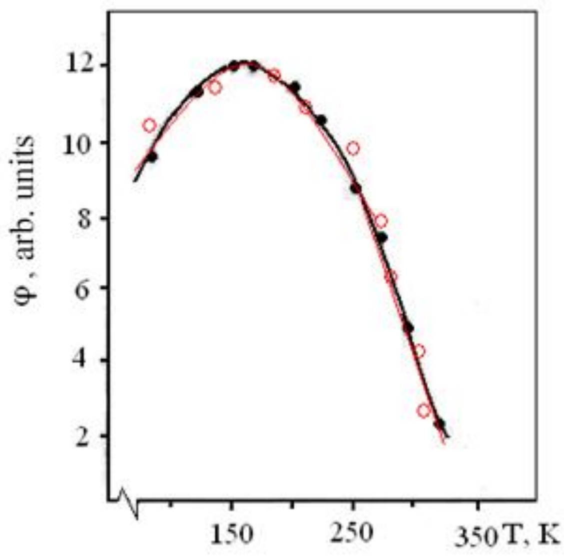

Fig. 4. Temperature dependence of the parameter φ for accelerated electrons:
1. -o-o-o- - 50 keV; 2. -•-•-•- - 100 keV; $5{\cdot}10^{18}$ cm^{-2}

Figure 4 represents the temperature dependence of the parameter φ for accelerated electrons with an energy of (*1*) 50 and (*2*) 100 keV at a radiation dose of $5{\cdot}10^{18}$ cm^{-2}, where $[\varphi] = \frac{\Delta R}{R_0 \Phi} =$ cm^{-2}. Following the above, it can be mentioned that the activation energy of the conductivity decreases with decreasing sample resistance.

The experimental results concerning the cathode conductivity of $ZnIn_2S_4$ single crystals suggest that, in this case, the conductivity type of the single crystals does not change. We assume that the concentration excess of balanced carriers occurs due to the activation of small donors, which are probably formed at an intensive irradiation. It was experimentally established that an increase in the dose leads to a decrease in the activation energy. For example, for a dose of $5{\cdot}10^{18}$ cm^{-2}, the activation energy was 0.006 eV, which is comparable to the ionization energy of Zn atoms between nodes Zn_i for the network ZnO according to the data 4 . Therefore, we could say that following the interaction of medium-energy electrons in $ZnIn_2S_4$, the zinc occurs between the nodes of crystalline network.

Based on previous results, we will examine some operation parameters of electron detectors with energies up to 50 keV made on the basis of $ZnIn_2S_4$. For electrons with energies of 50 keV having the number of excited electrons per second $\approx 10^{15}\ s^{-1}$, the lifetime of free carriers is approximately $\tau \approx 10^{-3}\ s$ and the interior propagation coefficient of carriers, at a calculated contact voltage of 5–20 V, achieves a value of $\approx 10^3$ [5, 6], which is obviously lower than 10^8 for the binary compounds. Being experimentally determined, the detector's power is up to 4 W · cm^{-2}, while for the detectors based on CdS and Cd Se, it is 10^{-3} W cm^{-2} 7 .

To develop detectors of high-energy particle and X-ray irradiation, it is necessary to take into account other advantages: simple manufacturing of detectors and their operation in steady-state and modulated conditions; high stability to the action of high energy electron beams and X-rays. Investigations on the development of new-type detectors or of their new modifications allow obtaining some performances of exploitation parameters compared to the existing ones.

Having high stability at irradiation, the investigated compounds have many practical applications including for the construction of Roentgen radiation detector. In this way, the optimum parameters make it possible to use X-ray detector in medicine, ecology as well as in agriculture.

3. Experimental results on irradiation stability

As a result of experimental investigations, there have been determined photo-conductibility spectra (FC) of layered compounds $ZnIn_2S_4$ for the initial sample (Fig. 5, curve 1) and irradiated with different doses of accelerated electrons of 10^{18} cm^{-2}, 10^{20} cm^{-2} with an energy of 60 keV (curves *2* and *3*, Fig. 5). Comparison of these curves shows that, after irradiation with a dose of 10^{18} cm^{-2}, the highest spectrum moves towards the area of low energies located at 2.68 eV (curve 2, Fig. 5). On the high-energy wing of the spectrum, it is clearly perceived a platform feature at 2.85 eV. It should be noted that at a radiation dose of 10^{18} cm^{-2}, signal intensity FC in the maximum located at 2.85 eV increases, which corresponds to the fundamental absorption.

In the research, it was found that the spectrum FC of single crystals $ZnIn_2S_4$ undergoes radical changes with increasing dose of irradiation (curve 3, Fig. 5). During the irradiation of $ZnIn_2S_4$ with accelerated electrons of a 10^{20} cm^{-2} dose, the maximum value of sensitivity is shifted even further to the area of low energies and is set at 2.34 eV. On the high-energy wing of the spectrum, an additional maximum to the energy 2.63 eV is highlighted, giving way, in terms of intensity, to initial spectrum (curve 1). At high doses of radiation of 10^{20} cm^{-2}, the samples' resistance to the dark decreases irreversibly up to $10^2 \Omega$cm and photosensitivity accordingly decreases. Similar studies were carried out on $CdGa_2S_4$ crystals and showed that, during their irradiation with a $D \approx 10^{20} cm^{-2}$ dose, significant changes in optical and radiation properties occur.

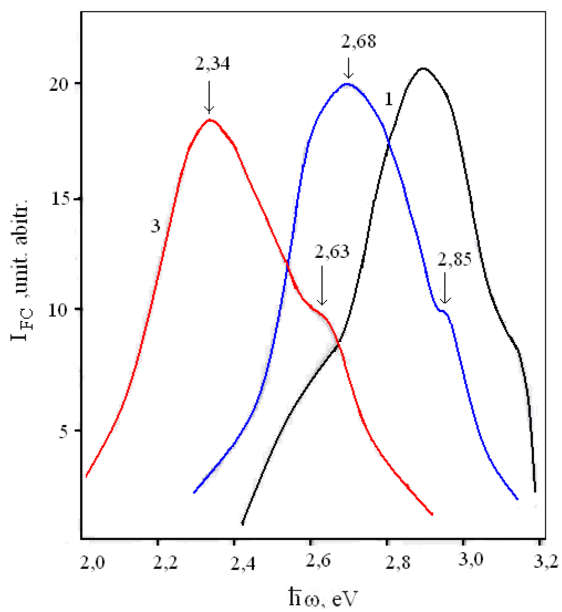

Fig. 5. Photoconductivity spectra of ternary compounds $ZnIn_2S_4$: original sample (curve 1) and samples irradiated with different doses of accelerated electrons $D \approx 10^{18} cm^{-2}$, $D \approx 10^{20} cm^{-2}$ (curves 2 and 3), with an energy of 60 keV.

4. Analysis of results

To summarize, based on these results, we could notice about high stability of optical and radiation properties of semiconductor compounds $CdGa_2S_4$ and $ZnIn_2S_4$, which is also demonstrated by the results of investigations of the optical absorption spectrum of $ZnIn_2S_4$ samples irradiated with accelerated electrons with an energy of 50 and 100 keV, respectively, at a density of electron beam of $1.5 \cdot 10^{-2}$ A $\cdot$ cm^{-2} and at a temperature of 296 K (Fig. 6). The exponential sector of the absorption spectrum can be attributed to the presence of "tails" of state densities of the conduction band conditioned by the disorder of cationic subnet. This fact is described in detail in the case of $(ZnIn_2S_4)$ 2 .

Based on the study of the bibliographic data, it can be noticed that significant changes in the properties of elementary or binary semiconductors [8] during their irradiation with electrons with energies of up to 100 keV occur starting with doses of $10^{14} \div 10^{16}$ cm^{-2}; in the case of $ZnIn_2S_4$ and $CdGa_2S_4$ compounds, essential changes in optical properties occur starting with doses higher than 10^{19} cm^{-2}. In the case of ternary semiconductor compounds, which have a energy band gap higher than 3 eV, while irradiating them with a dose of $\approx 10^{14}$ cm^{-2}, optical absorption in the ultraviolet spectrum decreases; this effect is referred to as the effect of low doses. These results correlate with the data presented in [9].

An increase in absorption is recorded at doses higher than 10^{15} cm^{-2}. The results described in this study concerning the nature of clear structure of the spectrum FC of single crystals $ZnIn_2S_4$ irradiated at a dose of 10^{18} $cm^{-2}$are consequences of the improvement of the state of crystal surface at the initial stage of irradiation, which is assumed to affect the recombination of free charge carriers at the sample surface.

At the same time, we find that the formation mechanism for threshold defects in layer compounds $ZnIn_2S_4$ is initiated at doses higher than 10^{18} cm^{-2}.

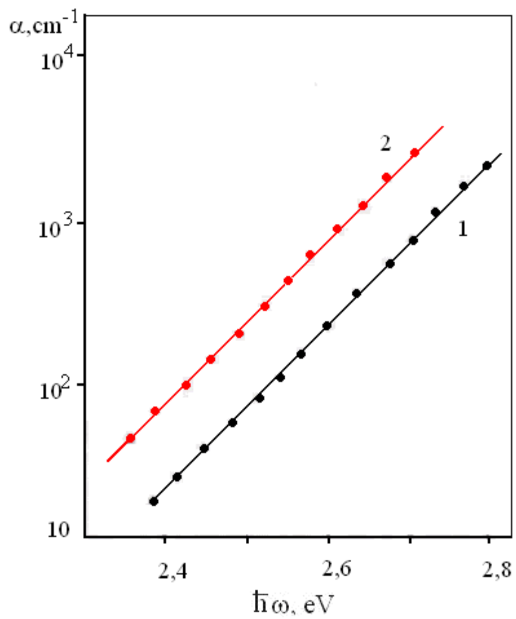

Fig. 6. Optical absorption for single crystals $ZnIn_2S_4$ irradiated with accelerated electrons: (1) 50 and (2) 200 keV, $j = 1.5 \cdot 10^{-2}$ A $\cdot$ cm^{-2}; T = 296K.

5. Conclusions

1. The experimental liniar dependence of the relative rezistence of zinc thioindate on electron beam as the stimulant has shown that manganese thioindate can be used as an active element in electron X-ray detectors. A model of an X-ray and accelerated particle detector capable of operating under both steady and modular conditions has been proposed. The coefficient of internal amplification of charge carriers at a voltage of $\approx 10^3$ has been estimated. The amplification coefficient is $\approx 10^3$.

2. The conductibility and irradiation stability of $ZnIn_2S_4$ and $CdGa_2S_4$ single crystals have been studied. The study has shown that the optical and photoelectrical properties incur significant changes only for dozes higher than 10^{19} cm^{-2}. The results suggest that the studied ternary compounds have highly stable properties.

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