PHOTOELECTRICAL PROPERTIES AND THE STABILITY AT RADIATION FOR MONOCRYSTALS $ZNIN_2S^4$

Professor, Efim ARAMA, University of Medicine and Pharmacy "Nicolae Testemitanu"
Professor, Eugeniu GHEORGHITA, Tiraspol State University
Senior Lecturer, Valentina PINTEA, Technical University of Moldova
Assoc. Prof., PhD, Anatol MACIUGA, Technical University of Moldova

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 ($30 \div 75\,keV$) and the respective doses ($10^{14} \div 10^{20}\,cm^{-2}$). It considers the possibilities to manufacture accelerated electron detectors and assesses their parameters. Considering that the energy values of the order $10^2\,keV$ are near the threshold of structural defects of intensive formation, the influence of this phenomenon on the detector parameters is subject to the analysis.

Key words: *photoelectric properties, ternary combinations, Irradiation conductivity, electron beam, irradiation stability, crystals' surface, binary semiconductors*

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 with 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 characteristics stability of microelectronic devices and prevention of degradation processes on 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 100 keV on physical properties of semiconductors. To highlight the changes that occur in optical, photoelectric and irradiation properties, investigations were carried out on optical absorption spectra, photo-conductibility for non-irradiated samples and for those irradiated with different doses of electrons at certain energies. Depending on the doping element, the impurity concentration is in the range of $(1,2\cdot10^{19} \div 2\cdot10^{20})\ cm^{-3}$. Growth technology of $ZnIn_2S_4$ is described in detail in [1-2].

Experimental results on irradiation conductivity

This paper describes the experimental results regarding the change of photoelectric properties and irradiation under the influence of electron beam accelerated in ternary combinations of the 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 quality optical thickness from $0,20$ to $1,0\,mm$, obtained from gas phase using iodine as a carrier agent.

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

Based on the dependence of the relative resistance change R/R_0 and the current density of the electron beam, the three samples of $ZnIn_2S_4$ at $40\,keV$ (figure 1), one may observe that this dependence for all 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, figure 2), the resistance decreases slightly, in a narrow range of variation of the irradiation dose. At the electron beam energy $40\,keV$ (curve 2) this passage is observed to be very slow, which is approximately linear, and at the energy of $30\,keV$ the dependence on the dose is a linear function in the studied range.

For all measurements described above, a constant conductivity of the samples in the dark was observed, that of $(10^7 \div 10^9)\,\Omega$. 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 monocrystal (at least to the depth of penetration of the electrons $\approx 5\,\mu m$).

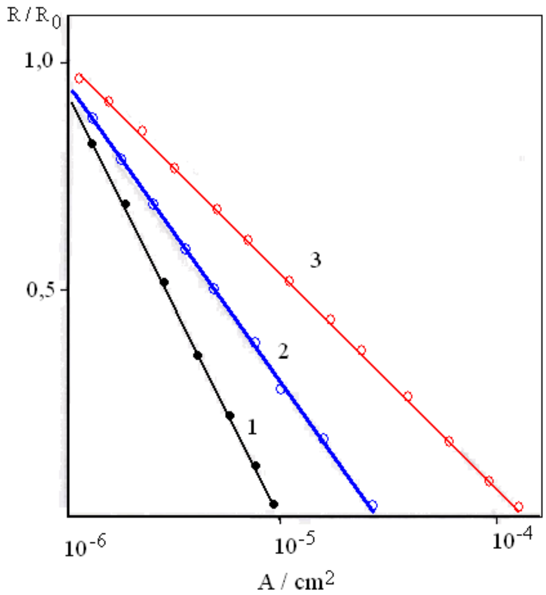

Figure 1. Dependence of relative resistance R/R_0 upon the size of the electron beam current for the samples of $ZnIn_2S_4$, sample thickness: 1 -$0,20\,mm$, 2 -$0,5\,mm$, 3 -$1,0\,mm$.

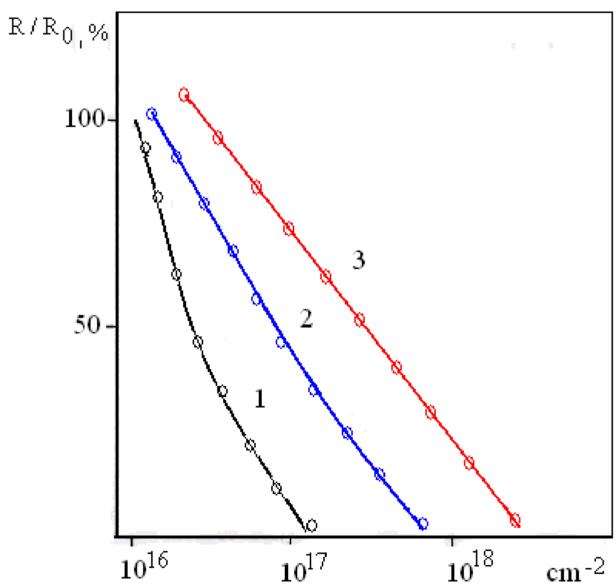

Figure 2. Dependence of relative resistance R/R_0 and radiation dose at different values of the electron beam energy: 1-75, 2-40, 3-30 keV.

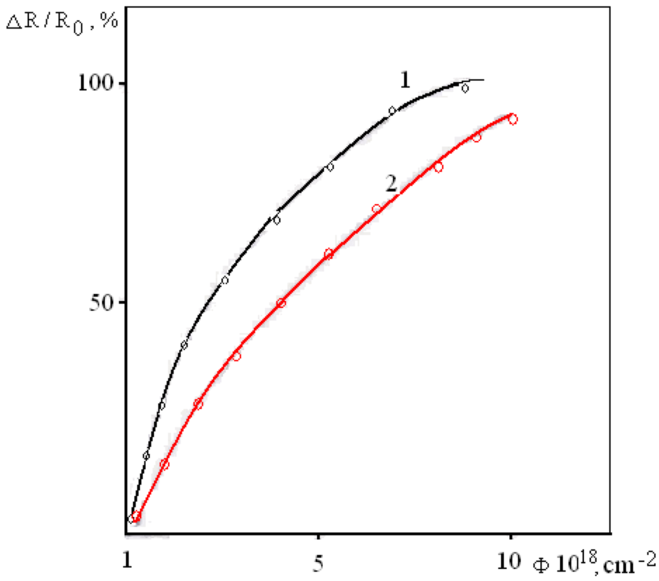

Figure 3. The dependence $\Delta R/R_0$ of single crystals $ZnIn_2S_4$ according to the dose of irradiation, T = 296K, 1 - $50\,keV$ **, 2 -** $100\,keV$

In figure 3, it is shown the dependence $\Delta R/R_0$ according to the dose of irradiation, wherein $\Delta R = R_0 - R$, R is dark resistance of the sample after irradiation dose of $(10^{18} \div 10^{20})\,cm^{-2}$. According to this dependency one may conclude that, at a radiation dose of $10^{20}\,cm^{-2}$, the resistance in the dark becomes very small, it is approximately $10^2\,\Omega$.

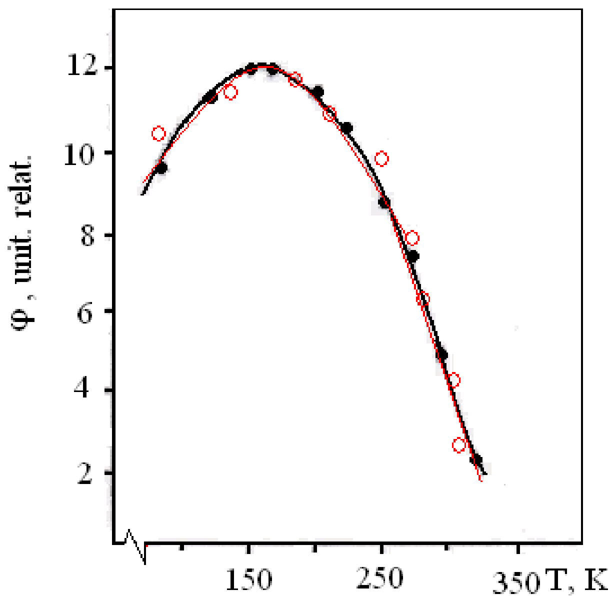

Figure 4. The temperature dependence of the parameter φ for accelerated electrons:

1. - 50 keV; 2. - 100 keV; $5\cdot10^{18}$ cm^{-2}

Figure 4 represents the temperature dependence of the parameter φ for accelerated electrons with energy: 1 - $50\,keV$, and 2 - $100\,keV$ at the radiation dose $5\cdot10^{18}\,cm^{-2}$, wherein $[\varphi] = \Delta R / R_0 \Phi = cm^{-2}$. Following the above it can be mentioned that the activation energy of the conductivity decreases along with the decrease of sample resistance.

Based on the experimental results concerning the cathode conductivity of single crystals $Zn\,In_2S_4$, it can be concluded that the conductivity type of the single crystals in this case 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 the increase in dose leads to reduction of activation energy. For example, for the dose $5 \cdot 10^{18}\ cm^{-2}$, the activation energy was $0,006\ eV$, that is comparable to the ionization energy of Zn atoms between nodes Zn_i for the network ZnO according to the data [4]. So 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 exploitation parameters of electron detectors with energies up to $50\,keV$ made on the basis of $ZnIn_2S_4$. For electrons with $50\,keV$ energies 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 calculated contact voltage of $(5 \div 20)\,V$, reaches the value of $\approx 10^3$ [5], which is obviously lower in comparison to 10^8 for the binary compounds. Being experimentally determined, the detector's power reached the value of $4\ W \cdot cm^{-2}$, as for the detectors based on $Cd\,S$ and $Cd\,Se$, it is $10^{-3}\ W \cdot cm^{-2}$ [6].

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.

Experimental results of 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 (figure 5 the curve 1) and irradiated with different doses of accelerated electrons $10^{18}\ cm^{-2}$, $10^{20}\ cm^{-2}$ with the energy $60\ keV$ (curves 2 and 3, figure 5). From the comparison of these curves, it is observed that after irradiation with the dose $10^{18}\ cm^{-2}$, highest spectrum is moving towards the area of low energies located at $2,68\,eV$ (curve 2, figure 5). On the high-energy wing of the spectrum, it is clearly perceived a platform feature at $2,85\,eV$. It should be noticed that at the radiation dose $10^{18}\,cm^{-2}$, 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 mono-crystals $ZnIn_2S_4$ undergoes radical changes by increasing the dose of irradiation (curve 3, figure 5). At the irradiation of $ZnIn_2S_4$ with accelerated electron of $10^{20}\ cm^{-2}$ dose, 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 $10^{20}\ cm^{-2}$, the samples' resistance to the dark decreases irreversibly up to $10^2\ \Omega cm$ and photosensitivity decreases accordingly. Similar studies have been carried out on the crystals $CdGa_2S_4$ that have demonstrated that at their irradiation with $D \approx 10^{20} cm^{-2}$ dose, significant changes occur in optical and radiation properties.

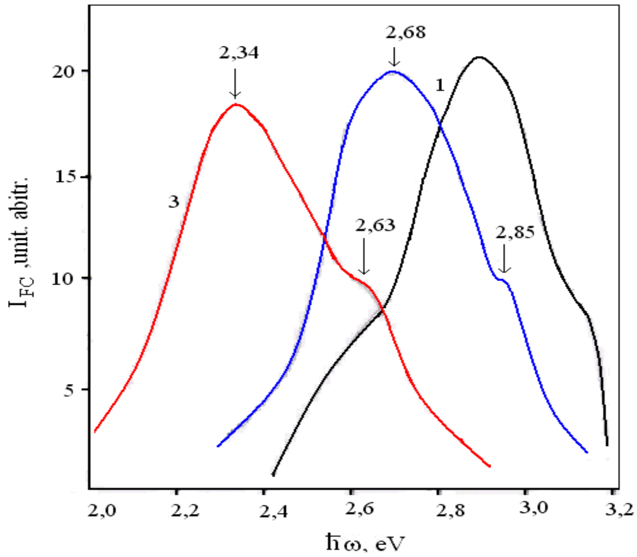

Figure 5. Photo-conductivity spectra of ternary compounds $ZnIn_2S_4$: original sample (curve 1) and irradiated with different doses of accelerated electrons $D \approx 10^{18}\ cm^{-2}$, $D \approx 10^{20}\ cm^{-2}$ (curves 2and 3), with energy $60\ \ keV$.

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 energy 50, and respectively $100\ keV$, at a density of electron beam $1{,}5 \cdot 10^{-2}\ A \cdot cm^{-2}$ and at the temperature of $296\,K$ (Figure 6). Exponential sector of the absorption spectrum can be explained by 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 of the properties of elementary or binary semiconductors $[7]$ at their irradiation with the electrons of energies up to $100\,keV$ occur starting by the doses $\left(10^{14} \div 10^{16}\right) cm^{-2}$ and in the case of compounds $ZnIn_2S_4$ and $CdGa_2S_4$ essential changes in optical properties occur starting by doses higher than $10^{19}\,cm^{-2}$. In the case of ternary semiconductor compounds, which have a forbidden energy band, higher than $3\,eV$, while radiating them with dose $\approx 10^{14}\,cm^{-2}$, it shows a reduction of optical absorption in the ultraviolet diapason of spectrum, which is called - the effect of low doses.

These results correlate with the data presented in $[8]$. The absorption increase is recorded at doses higher than $10^{15}\,cm^{-2}$. The results we obtained and presented in this work concerning the nature of clear structure of the spectrum FC of single crystals $ZnIn_2S_4$ irradiated at dose $10^{18}\,cm^{-2}$ are consequences of state improvement of crystals' surface at the initial stage of irradiation, which we suppose, influences the recombination of free charge carriers at the sample's surface.

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

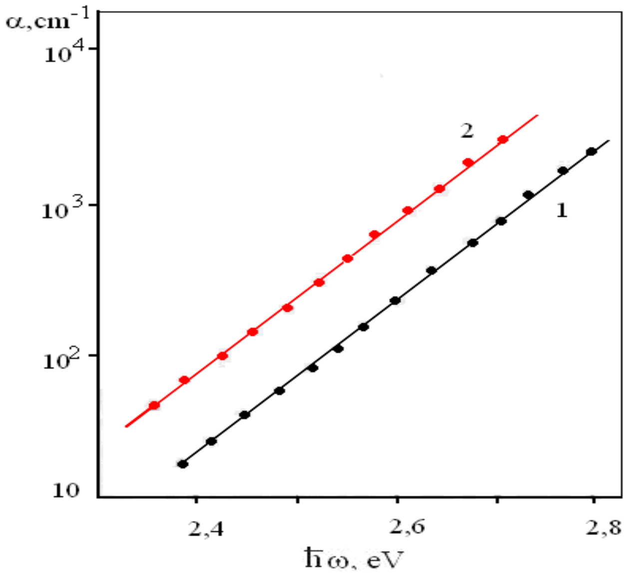

Figure 6. Optical absorption for single crystals $ZnIn_2S_4$ irradiated with accelerated electrons: 1-$50\,keV$ **; 2-**$100\,keV$ **;** $j = 1,5 \cdot 10^{-2}\ A \cdot cm^{-2}$ **;** $T = 296\,K$ **.**

Bibliography:

1. GHEORGHIŢĂ E., MACIUGA A., RADU R., PÎNTEA V.,. *Luminescenţa compuşilor tripli* $A^{II}B_2^{III}C_4^{VI}$ *la nivel înalt de excitare//* Culegere de lucrări ştiinţifice. Tehnologii moderne, calitate, restructurare. UTM. Chişinău, mai 2005, Vol.2, pag. 137-141.
2. JOSHI N. V., RODRIGNEZ C.E., VINCENT A.B., *Photoconductivity and photosensitivity of a* $CdIn_2S_4$ *monocrystal*// Nuovocim, 1983, 02, Nr.6: Int. Conf. Ternary and Multinary Compound, Cagliari, sept. 14-16, 1982, p.1906-1910.
3. АТАБЕКЯН Р. Р., ВИПЕЦКИЙ В.Л., ГЕВОРКЯН В.А., и др.б *Оптический эффект малых доз в радиационной физике твердого тела*// Письма в ЖЭТФ, 1983, т.9, в.23, с.1448.
4. ЖИТАРЬ В. Ф., АРАМЭ Е. Д., МАЧУГА А .И. и др.,*Влияние специфики и кристаллической структуры* $ZnIn_2S_4$ *на оптические поглощение*// Воронеж, 1989, с.8.
5. ВАВИЛОВ В.С., КИВ А.Е., НИЯЗОВ О.Р., *Механизмы образования и миграции дефектов в полупроводниках*// Наука, Москва, 1981, стр.40.
6. ЖИТАРЬ В.Ф., АРАМЭ Е. Д., РАДАУЦАН С. И., и др., *Получение, структура и люминесценция* $ZnIn_2S_4$ // Материалы VIII Всес. Конф. по росту кристаллов. Харьков. 1992, т.1, стр.275.
7. КОМАШЕНКО В. Н., МАМОК Н.Ф., ФЕДОРУС Г.А., и др., *Детекторы электромагнитного и корпускулярного излучения на основе гетероперехода* $p{-}Cu_2S_2{-}n{-}CdS$. *Полупроводниковая техника и микроэлектроника//*, 1973, вып.13, стр.33-34.
8. МИХАЙЛОВ М. М., *Изменение энергии активации поверхностной проводимости поликристаллической окиси цинка при облучении электронами//* Известия ВУЗ-зов Физика, 1984, в.7, стр.94-97.