YU ISSN 0015—3206
FZKAAA 17 (1) 7 (1985)

ON THE INFLUENCE OF ELECTRON AND γ-IRRADIATION ON ABSORPTION AND PHOTOCONDUCTIVITY OF $ZnIn_2S_4$ SINGLE CRYSTALS

ALEKSANDRA TURKOVIĆ, BOJAN PETROVIĆ, BOŽIDAR ETLINGER, NATKO B. URLI, SERGEI I. RADAUTSAN**, VASILE F. ZHITAR**, IVAN M. TIGINYANU** and ANATOLII I. MACHUGA**

»Ruđer Bošković« Institute, 41000 Zagreb, Yugoslavia

***Institute of Applied Physics, AS MSSR, Kishinev, USSR*

Received 30 September 1983

Revised manuscipt received 11 June 1984

UDC 537.311.33

Original scientific paper

Effects of electron and Co^{60} γ-irradiation on optical absorption and photoconductivity of $ZnIn_2S_4$ in the range of 400 nm to 600 nm have been studied. A tail in the absorption spectra is observed, which changes itself during the irradiation. This type of changes indicates, that the radiation reduces microstresses inherent to the growth of samples. The study of photoconductivity spectra demonstrates that the perfection of $ZnIn_2S_4$ single crystals improves after irradiation.

1. Introduction

$ZnIn_2S_4$ belongs to the group of ternary compounds generally represented by formula AB_2X_4 (where A is Zn, Cd or Hg, B is Al, Ga or In, and X is S, Se or Te). In most of these compounds, a large number of vacancies (1/4 of the cation sites) is present in stoichiometric conditions[1], $ZnIn_2S_4$ is a layer semiconductor and it posseses a rhombohedral structure with the space group C_{3v}^{5}[2]. It exhibits a large number of polytypes[3]. The three-packet polytype $ZnIn_2S_4$ (III) has been investigated in this work. There are 12 extremely close-packed sulphur layers in the unit cell of $ZnIn_2S_4$(III), with strong In-S and Zn-S bonds in them and weak

S-S bonds between the layers[2]. The band gap energy E_g of $ZnIn_2S_4$(III) equals 2.86 eV at 300 K[3].

The study of photoconductivity (PC) and luminescence spectra of $ZnIn_2S_4$ crystals has been performed and a lot of localized levels as well as quasi-continuously distributed traps below the conduction band were found[3]. Apart of that, the presence of a tail in the absorption spectrum of the compound has been reported[4]. Such properties of $ZnIn_2S_4$ single crystals are associated, as was reported in Ref. 5, with some kind of intrinsic disorder. In a view of that type of disorder, $ZnIn_2S_4$ as well as other $A^{II}B_2^{III}C_4^{VI}$ compounds may be considered as intermediate structures between amorphous and crystalline semiconductors[6].

The purpose of the present work was to investigate the influence of electron and γ-irradiation on optical absorption and PC of $ZnIn_2S_4$(III) single crystals.

2. *Experimental technique*

$ZnIn_2S_4$(III) single crystals have been prepared by iodine transport technique. All samples are of n-type conductivity and they represent thin platelets with thicknesses $d \cong 10^{-5}$—10^{-4} m. Initial crystals (their resistivity equals 10^{11} Ωcm) as well as samples irradiated by electrons ($E = 100$ keV) or Co^{60} γ-rays at a dose of $2.5 \cdot 10^{16}$ γcm^{-2} have been investigated.

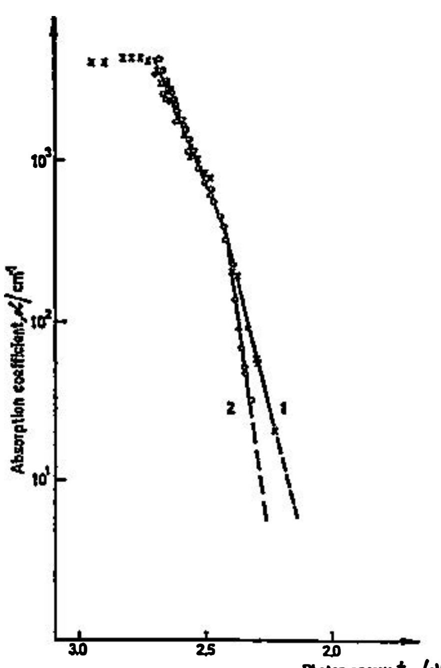

Fig. 1. The dependence of α on photon energy for $ZnIn_2S_4$(III) crystals before (curve 1) and after γ-irradiatilon (curve 2).

To measure *PC* the indium contacts were prepared on the (0001) faces of samples by virtue of vacuum deposition. The excitation spectra of *PC* were normalized by comparison with a black-body detector. The absorption coefficient was calculated from the absorption spectra making the corrections for reflection. Those corrections were taken as constant and their value was estimated according to the Moss rule[7].

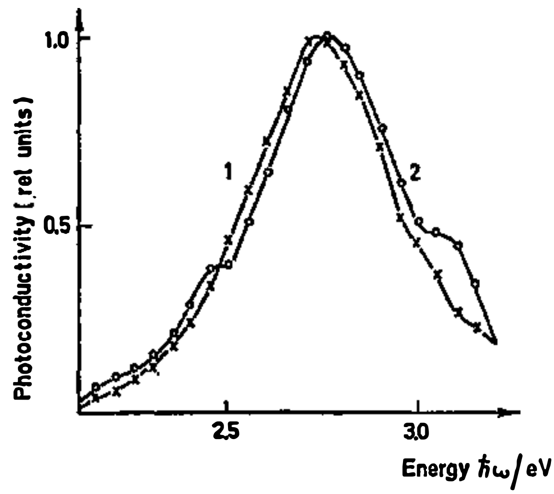

Fig. 2. *PC* curves of $ZnIn_2S_4$(III) crystals before (curve 1) and after electron irradiation (curve 2).

In our experiments *SPM*-2 monochromator (Zeiss, Jena) was used as a spectrometer. The energy position of spectral features was determined with accuracy not worse than 0.02 eV. The measurements were performed at room temperature.

3. Results

Fig. 1 presents the absorption coefficient of the $1.3 \cdot 10^{-5}$ m thick sample before (curve 1) and after irradiation (curve 2) with γ-rays. It can be seen that the absorption coefficient of initial crystals varies as an exponential function of photon energy having two slopes: $\Delta_1 = 0.25$ eV and $\Delta_2 = 0.17$ eV. The first slope practically does not change after irradiation, whereas the second one drops to the value $\Delta_2 = 0.085$ eV. As to the electron irradiation, it does not cause a visible deformation of the absorption spectrum.

The normalized *PC* spectra of $ZnIn_2S_4$ single crystals before and after electron irradiation are illustrated in Fig. 2. The spectra are similar, although the maximum of *PC* curve shifts after irradiation to higher energy and the intrinsic *PC* peak (3.05 eV) is clearly seen. The lower energy peak has been observed after γ-irradiation of the crystals, too.

4. Discussion

As it has been shown earlier[4] and confirmed by the present study, the tail appears in the absorption spectrum of $ZnIn_2S_4$ single crystals. In the tail region, the absorption coefficient exhibits an exponential dependence on photon energy. It has been suggested that the existence of microfields gives rise to optical transitions which are responsible for the absorption tail[8]. These microfields seem to be related to inclusions, vacancies and lattice deformations. The diminution of the slope Δ_2 of the absorption tail from 0.17 eV to 0.085 eV during irradiation (Fig. 1) is caused, in our opinion, by decrease of microstresses inherent to the growth of samples. The shift of the *PC* curve to higher energy and the increase in the intensity of the intrinsic *PC* peak (Fig. 2) also indicate an improvement of the perfection of crystals by irradiation.

Analysis of the obtained results shows that $ZnIn_2S_4$ single crystals possesses a high radiation stability. It is to be noted, that the radiation stability proves to be a common property of all semiconductor compounds with stoichiometric vacancies[9]. The electrical activity of centres in such semiconductors is strongly suppressed, this effect being caused by introduction of native or impurity atoms in stoichiometric vacancies[9].

Thus, electron and γ-irradiation may be employed for the purpose of improving the properties of $ZnIn_2S_4$ single crystals.

References

1) N. A. Goryunova, *Complex Diamond-like Semiconductors*, Soviet Radio, Moscow 1968;
2) F. Lappe, A. Niggli, R. Nitsche, and I. G. White, Z. Krist. **117** (1962) 146;
3) F. G. Donika, V. F. Zhitar, S. I. Radautsan, *Poluprovodniki sistemy ZnS-In₂S₃*, Shtiintsa, Kishinev 1981;
4) S. I. Radautsan, V. F. Zhitar, V. Ya. Railjan, FTP **9** (1975) 2278;
5) A. Bosacchi, B. Bosacchi, S. Franchi, and L. Hernandez, Solid State Commun. **13** (1973) 1805;
6) S. I. Radautsan, J. Non-Cryst. Solids **4** (1970) 370;
7) T. S. Moss, *Optical Properties of Semiconductors*, Butterworth (1959) p. 48;
8) J. A. Beun, R. Nitsche, and M. Lichtensteiger, Physica **26** (1960) 647;
9) V. M. Koshkin, L. P. Galchinetski, V. N. Kulik, V. I. Minkiev, U. A. Ulmanis, Solid State Commun. **13** (1973) 1.

UTJECAJ ELEKTRONSKOG I γ-ZRAČENJA NA APSORPCIJU I FOTOVODLJIVOST U $ZnIn_2S_4$ MONOKRISTALIMA

ALEKSANDRA TURKOVIĆ, BOJAN PETROVIĆ, BOŽIDAR ETLINGER, NATKO B. URLI, SERGEJ I. RADAUTSAN**, VASILE F. ZHITAR**, IVAN M. TIGINYANU** i ANATOLIJ I. MACHUGA**

Institut »Ruđer Bošković«, 41001 Zagreb, p.p. 1016

***Institut primjenjene fizike, AN MSSR, Kišinev, SSSR*

UDK 537.311.33

Originalni znanstveni rad

Izvršena su mjerenja utjecaja elektronskog i γ-zračenja Co^{60} na fotovodljivost i apsorpciju $ZnIn_2S_4$ u području od 400 do 600 nm. Nakon ozračivanja došlo je do promjene u području fundamentalnog ruba apsorpcijskog spektra. Ovakva promjena pokazuje da zračenje smanjuje mikropritiske nastale prilikom rasta kristala. Ispitivanje spektra fotovodljivosti pokazuje da zračenje popravlja uređenost monokristala $ZnIn_2S_4$.