OPTICAL PROPERTIES OF CdIn$_2$S$_4$ SINGLE CRYSTALS
H. Nakanishi, S. Endo, T. Irie

To cite this version:
H. Nakanishi, S. Endo, T. Irie. OPTICAL PROPERTIES OF CdIn$_2$S$_4$ SINGLE CRYSTALS. Journal de Physique Colloques, 1975, 36 (C3), pp.C3-163-C3-168. <10.1051/jphyscol:1975330>. <jpa-00216300>

HAL Id: jpa-00216300
https://hal.archives-ouvertes.fr/jpa-00216300
Submitted on 1 Jan 1975

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
OPTICAL PROPERTIES OF CdIn$_2$S$_4$ SINGLE CRYSTALS

H. NAKANISHI, S. ENDO (*) and T. IRIE (*)

Department of Electrical Engineering, Faculty of Science and Technology
Science University of Tokyo, Noda, Chiba-ken, Japan

Introduction. — Recently the ternary compound CdIn$_2$S$_4$ is attracting increasing attention. One of the reasons for this interest is the fact that CdIn$_2$S$_4$ is a photosensitive semiconductor and has a possibility of use as photocatalyst in the visible region of the spectrum. The optical absorption, reflection, the photocatalytic property and the photoluminescence have been measured by several workers [1]-[9]. However, the results obtained by these authors were not always in agreement. We have succeeded in growing homogeneous single crystals of CdIn$_2$S$_4$ and have measured several transport and optical properties [10]-[13]. The work presented here is the result of the more detailed optical measurements of the optical properties of CdIn$_2$S$_4$ than have been made previously. The result of the study on the low frequency oscillations of the photocurrent in CdIn$_2$S$_4$ will also be presented.

(*) Department of Electrical Engineering, Faculty of Engineering, Tokyo University of Science, Shinjuku-ku, Tokyo, Japan.

1. Experimental procedure. — The samples were cut out of the single crystal grown from a melt with excess sulphur. Electrical resistivity of the samples in the dark is about $10^5$ Ω·cm. Samples for the optical measurements were thin slices with their surfaces polished by emery paper and diamond paste. A Nihon Bunko SS-50 grating monochrometer was employed. The absorption coefficient $a$ and the sample thickness $t$ are connected by the following equation neglecting multiple reflections,

$$I = I_0 (1 - R)^2 \exp(-at)$$

(1)

where $I_0$ and $I$ are the incident and the transmitted light intensity, respectively and $R$ is the reflectivity of the sample. A plot of the ln $(I/I_0)$ vs $t$ should give a straight line, the slope of which gives $a$ if $R$ is constant throughout the measurement. The absorption coefficient was determined from such a plot of the relative transmittance of the sample having various thicknesses ranging from 0.03 mm to 0.2 mm. Measu-
rements below room temperature were made using a cryostat having quartz windows.

The photocurrent was recorded as potential drop across the series resistance which was selected to be low enough to insure constant voltage across the sample.

2. Experimental results and analysis. — The absorption coefficient $\alpha$ was measured at several temperatures in the spectral range from 0.4 to 0.8 $\mu$. For the shorter wave length than 0.4 $\mu$ the apparatus was not sensitive enough to detect the weak transmitted light. In order to determine the energy gap for the direct transition, $\alpha^2$ is plotted as a function of the photon energy in figure 1. Extrapolating a linear por-

![Fig. 1. Square of the absorption coefficient of CdIn$_2$S$_4$ single crystal at various temperatures as a function of photon energy.](image1)

tion to $\alpha^2 = 0$, the allowed direct energy gap $\Delta E$ at respective temperatures can be obtained as shown in figure 2. It can be seen that $\Delta E$ varies with temperature $T$ as

$$\Delta E = \Delta E(0) - 9.5 \times 10^{-4} T$$  \hspace{1cm} (2)

with $\Delta E(0) = 2.7$ eV in the temperature range studied. This result yields the indirect energy gap of about 2.5 eV at 0 K.

Figure 3 shows the photocurrent as a function of the temperature for various light intensities when the sample is illuminated by the light from a mercury lamp. It is clear from the figure that thermal quenching is above a temperature near 200 K. From a temperature dependence of the photocurrent corresponding to the knee on the photocurrent-temperature curve, the energy level of the recombination centers (sensitizing centers) was found to be about 0.7 eV above the valence band edge.

Thermally stimulated current (T. S. C.) was also measured in order to obtain information on the electron traps. The T. S. C. was measured by heating the

![Fig. 2. The direct energy gap of CdIn$_2$S$_4$ as a function of temperature.](image2)

![Fig. 3. Photocurrent in a single crystal of CdIn$_2$S$_4$ as a function of temperature for various illumination intensities.](image3)
sample at constant rate from 80 K after illuminating the sample by the light from a mercury lamp for 15 seconds. The current showed two broad maxima. In order to determine the energy levels of the individual trap states, the decayed T. S. C. [14] was measured. This method consists of heating in the dark the sample, previously illuminated, until the measured current $i$ reaches a maximum, then the sample being cooled down immediately and, without illumination, reheated to obtain another current curve. The process is repeated several times and for each heating the ln $i$ is plotted against $1/T$. Well-defined straight lines are obtained with slopes corresponding to some activation energies. The result is shown in figure 4. From this figure the three kinds of trap levels were found at 0.1, 0.2 and 0.5 eV below the conduction band. The trap depth of 0.2 and 0.5 eV are in good agreement with the activation energies of the donor levels determined from the Hall measurement. The density of the traps of 0.1 and 0.2 eV depth were estimated from the area of the T. S. C. curve both to be about $3 \times 10^{15}$ cm$^{-3}$.

The current-voltage characteristics were studied on the sample immersing in the liquid nitrogen and illuminating with the light from a mercury lamp. Figure 5 shows the photocurrent vs electric field intensity for several illumination levels. Above some critical field, negative differential conductance region appeared. In this region low frequency (0.05 Hz-10 Hz) oscillations of the current were observed. The region of the electric field in which oscillations are observed depends on the illumination level. Two types of the oscillations were observed corresponding to two different conditions. One of the types is pulse type and another is sinusoidal one. In some cases the two types are observed alternately. Figures 6 and 7 show oscillograms of the pulse type and the sinusoidal type oscillations, respectively. For both types of the oscillations the frequencies depend on the applied field and the illumination level. Figures 8 and 9 show the frequency as a function of the applied field intensity and of the relative light intensity, respectively for the pulse type oscillations. Figures 10 and 11 are the similar plots as those in figures 8 and 9, respectively for the sinusoidal oscillations.

In order to study a dependence of the oscillation characteristic on the sample dimension, the oscillations were observed for the various thicknesses along the direction perpendicular to the current flow of a sample. The sample thicknesses examined were 1.7 mm, 1.5 mm, 1.0 mm and 0.6 mm. For the thickness of 1.7 mm the sinusoidal oscillations were observed but the wave forms were irregular. For the thickness of 1.5 mm stationary sinusoidal oscillations were observed. When the thickness was reduced to 1.0 mm, the pulse type oscillations were observed. For the thickness of 0.6 mm breakdown occurred before oscillations were observed and hereafter the sample was no longer photosensitive. It is noted that as the sample thickness is reduced the oscillation wave form changes from sinusoidal to pulse type. For a critical sample size corresponding to the transition from sinusoidal to pulse type oscillations, the both types of the oscillations were often observed alternately.
From the facts described above, it may be concluded that the mechanism of the oscillations is essentially the same as those of the oscillations observed in CdS and CdSe [15], [16] and that of the oscillations recently observed in CdIn$_2$S$_4$ by Allakhverdiev et al. [17]. The sinusoidal oscillations are repetition of the current peak due to the exhaustion of the electron traps by avalanche-type process caused by the Joule heat and the successive recombination. The pulse type oscillations are, in addition, thought to be concerned with the thermal quenching because the current decreases to the value lower than the stationary one. This interpretation is supported by the experiment on the size dependence of the oscillation characteristic above-stated, that is, as the sample size is reduced...
the temperature rise in the sample becomes rapid and large, leading easily to the thermal quenching.

V. L. Vinetskii et al. [15] derived a condition for the instability as follows:

$$M \lambda^2 e \mu E^2 (e_M/kT) > T Q_m \rho C_V,$$

(3)

where $M$ is the trap concentration, $\lambda$ the generation rate of the conduction electrons, $\tau$ the free electron life time, $e$ the electronic charge, $\mu$ the electron mobility $E$ the electric field, $e_M$ the trap depth, $k$ the Boltzmann constant, $Q_m = Q \exp(-e_M/kT)$ ($Q$ is the density of states at the edge of the conduction band), $\rho$ the density and $C_V$ is the specific heat of the sample. Typical values of the parameters in the case of CdIn$_2$S$_4$ ($M = 10^{15}$ cm$^{-3}$, $\tau = 10^{-3}$ s, $e_M = 0.1$ eV, $\rho = 5.3$ g/cm$^3$, $C_V = 0.18$ J/g. deg) results in the value of the threshold field for instability, $E_{th} \approx 10^3$ V/cm. This value agrees in order of magnitude with the observed values.

When a sample was subjected to additional illumination at 6 000 Å, the oscillations, both of the sinusoidal type and the pulse type, were stopped. The additional illumination was removed, then the oscillations again started. The photon energy corresponding to 6 000 Å is about 2.06 eV and is approximately equal to the energy difference between the conduction band and the sensitizing level or that between the trap level and the valence band.

3. Conclusions. — The interband gap for the direct allowed transition of CdIn$_2$S$_4$ single crystal was found from the optical absorption measurement to have a temperature coefficient of $-9.5 \times 10^{-4}$ eV/deg between 100 K and 300 K and to have a value of 2.7 eV when extrapolated to 0 K. The absorption edge was found to have low energy tail. If we attribute this tail to the indirect transition, we obtain the indirect gap as about 2.5 eV at 0 K. This value is nearly the same as that obtained by the electrical measurement.

The low frequency oscillations of photocurrent in CdIn$_2$S$_4$ are closely connected with the electron traps the energy levels of which are 0, 0.1, 0.2 and 0.5 eV below the conduction band and the sensitizing centers the level of which is 0.7 eV above the valence band. Figure 12 is the energy level diagram of these electron traps and these sensitizing centers. The mechanism of the oscillations is essentially the same as those of the oscillations observed in CdS and CdSe.

Acknowledgment. — The authors are much indebted to Mr. T. Komiya for help with the experiments.

References