Absorption and photoconductivity of In₂Se₃ and Ga₂Te₃*

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Absorption measurements of two III-VI compounds In_2Se_3 and Ga_2Te_3 have been made in the temperature range of 5-300 K in the vicinity of their fundamental absorption edges. The energy positions of the absorption edge have been estimated; E_g (300 K) = 1.36 eV, E_g (80 K) = 1.52 eV and E_g (5 K) = 1.56 eV for In₂Se₃, and E_g (500 K) = 1.2 eV for Ga₂Te₃.

Spectral characteristics of photoresponses in the photocounductivity mode have been investigated in the temperature range 80-300 K, and near and above the fundamental absorption edges of both semiconductors. The shape of photoresponse characteristics, the detection parameters and possible applications of these materials in the range of infrarced and visible radiation are discussed.

1. Introduction

The ever growing demands of the electronics industry, especially in the range of optoelectronics devices, concerning better and better semiconductor materials for detecting radiation in the near infrared range as well as for conversion of solar energy has awakened the interest in the search of new semiconductor compounds.

Semiconductor materials with an energy gap of about 1.4 eV (at 300 K) and a relatively long diffusion length of excess carriers are especially desireable in the production of solar batteries. Semiconductors which have an energy gap of about 1.0 eV (at 300 K) and a short photocarrier lifetime are suitable for the production of detectors on the 1.3 μ m band for optical telecommunication using fiber transmission systems.

In the recent years, combinations of gallium and indium with tellurium and sellenium have drown our attention, especially the compounds In_2Se_3 and Ga_2Te_3 . The available information about the properties of these materials has been presented in paper [1]. These compounds have the energy gap within 1.0-1.5 eV and display a relatively high photosensitivity.

In the following paper, we report the results of some investigations of the optical and photoelectric properties of the crystals In_2Se_3 and Ga_2Te_3 prepared in the Institute of Inorganic Chemistry and Metallurgy of Rare Elements of the Technical University of Wrocław.

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2. Discussion of results for In₂Se₃

In₂Se₃ at room temperature assumes a pseudo-wurtzite structure in phase described by the P6₁ group [2]. Under these conditions, it is an *n*-type semiconductor with the electron concentration of order of 10^{20} m⁻³ and the mobility of about 3×10^{-3} m²V⁻¹ s⁻¹ [3].

2.1. Absorption measurements

The optical transmissivity of In_2Se_3 in the range of radiation wavelength varying within 0.38-2.5 μ m was investigated at the temperatures of 4.2, 80 and 300 K. To this end we used a typical measurement system with SPM-2 monochromator and applied the method described in detail in [4]. VTh-1 thermocouples or photomultipliers were used as detectors.

The qualitative plot of the absorption coefficient of this compound near the fundamental absorption edge is presented in Fig. 1. Because of the difficulty in preparing the surfaces of the samples to become suitable for reflection measurements, the latter have not been conducted and, consequently, the absorption coefficient values in the entire range of wavelengths applied in the absorption measurements have not been calculated. Only in the narrow area near the edge



Fig. 1. Absorption spectrum of In_2Se_3 near the fundamental edge



Fig. 2. Absorption coefficient of In_2Se_3 , obtained on the base of an estimated value of the reflection coefficient $B \simeq 30^0/_0$

the absorption coefficient plots were determined from the estimated value of the reflection coefficient (about $30^{\circ}/_{\circ}$). These results are shown in Fig. 2.

As can be seen in Fig. 1, the In_2Se_3 absorption edge is characterized by the appearance of two areas: a low energy one with relatively small values of a, the latter increasing relatively slowly with the increasing photon energy, and a second area in which a very rapid increase in absorption is observed. At the temperatures of 300 and 80 K, the two absorption curves run practically parallel to each other in both absorption areas. The temperature shift in the area with the essential a increase is simultaneously somewhat greater than in the low energy part. When the temperature is lowered to 4.2 K, a marked qualitative change takes place. The low energy part of the edge decays almost completely uncovering a flat absorption background of a relatively small absorption value.

The presence of low energy part of the absorption edge may be connected either with the indirect optical transitions between the top of the valence band and the bottom of the conductivity band or with the portion of transitions from the density tails of states in the valence band to the minimum of the conductivity band with the appearence of a direct gap. The character of the change of the absorption edge position due to temperature change seems to justify the second interpretation.

The fundamental absorption edge seems to be associated with the direct transitions. From the position of the fundamental edge, the transition energy can be estimated to be 1.36 eV at 300 K, 1.52 eV at 80 K, and 1.56 eV at 4.2 K. Other supplementary investigations are necessary in the case of the structure of the above mentioned fundamental edge observed in the absorption spectrum. These supplementary investigations must be carried out on very thin samples which, however, have not been available to the authors.

2.2. Photoconductivity measurements

Investigations of In_2Se_3 photoconductivity were carried out in a system with a monochromator, using the typical measurement methods described in the paper [6].

Figure 3 presents the spectral dependence of In_2Se_3 photoconductivity at a temperature of 300 K. The main maximum with the energy of about 1.4 eV is approximately twice as high as the photoresponse in the area of 1.8-3 eV. The weakly marked structure for photon energy of about 2 eV and 2.3 eV reflects the interband transmission of optical transition. The longwave photoresponse edge occurs at the energy value of about 1.24 eV.

At the temperature of about 80 K (see Fig. 4), we observe a wide photoeffect maximum which extends on the area of 1.6-1.8 eV. The longwave photoresponse edge occurs at the energy value of 1.45 eV and clearly shifts in the direction of higher energies when the temperature drops from 300 to 80 K. It should be noted that the temperature shift of the edge of the photoconductivity effect

is greater than the shift of the fundamental absorption edge, and the energy of the longwave photoresponse threshold is lower than that of direct transitions. This last fact can most probably be associated with the absorption below the fundamental absorption edge, visible in Fig. 1.

It is worth noticing that the In_2Se_3 photoresponse maximum covers the work band of detectors designed for solar radiation energy conversion.



Fig. 3. Spectral photoconductivity dependence of In_2Se_3 at 300 K



Fig. 4. Spectral photoconductivity dependence of In₂Se₃ at 80 K

3. Discussion of results for Ga₂Te₃

Ga₂Te₃ crystallizes in a sphalerite blende structure. The carrier concentration (electrons) is of about 10^{24} m⁻³, and the mobility of about $0.2 \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$. According to [5], this compound possesses an indirect energy gap with the energy of about 1.13 eV at 300 K. The direct energy gap (1.33 eV) was determined at that temperature.

3.1. Absorption measurements

Figure 5 presents the plot of the absorption coefficient of Ga_2Te_3 at the temperature of 300 K. The measurements were carried out as for In_2Se_3 . The absorption edge spreads out in the area of 1.1–1.4 eV and, at the energy of about 1.19 eV, it has a strong peak which seems to be associated with exciton transitions. Only a fragment of the absorption edge (see insert in Fig. 5) has been presented on an absolute scale, due to the reasons similar to those in the case of In_2Se_3 (lack of absolute values of reflection coefficient in the measured range of absorption coefficient changes). It should be noted that if the absorption maximum in Fig. 5 was significantly associated with the exciton*

^{*} It requires an additional measurement and through estimation,

the energy gap value of Ga_2Te_3 would be relatively accurately (with the accuracy to the energy bonding of exciton) estimated as being about 1.2 eV at 300 K.

3.2. Photoconductivity measurements

The results of the photoconductivity measurements of Ga_2Te_3 carried out at 80 and 300 K are of special interest. Because of a very high photosensitivity of this material the measurements could be conducted in as broad photoresponse



value changes as 5 orders of magnitude (see Figs. 6 and 7). The spectral dependence of photoconductivity in the measured wavelength range has the shape of sharp edges. When the temperature is lowered from 300 to 80 K the photoresponse edges shift in the direction of a higher energy. The edge structure at 300 K is richer than the structure observed at 80 K. At present an exact analysis of the shape of the obtained photoconductivity curves seems to be impossible. Nevertheless, it should pointed out that there is an agreement between the energy gap value estimated from the absorption measurements and the energy position of the edge manifesting a sharp

Fig. 5. Absorption spectrum of the Ga₂le₃ near the fundamental edge. The insert presents the absorption coefficient obtained on the base of an estimated value of the reflection coefficient $B \simeq 30^{0}/_{0}$

increase of photoconductivity (Fig. 6). On the other hand, the existence of photocarriers generating optical transitions in the vicinity of 1.0 eV energy should also be noted.

High values of sensitivity spectrum (several hundred ∇/W) and an advantageous range of photoconductivity spectrum (in the area of the maximum theoretical photoconductivity of solar radiation converters, about 1.5 eV at 300 K) predispose the use of this compound to further precise investigations of photoelectronics effects and possible application to the construction of solar batteries.

4. Final conclusions

The investigations carried out allow us to estimate the energy gap in the investigated semiconductors. The photoconductivity investigations make it possible to determine the energy position of the longwave photoresponse threshold as well as to localize the energy position and the maximum values of these photoresponses.



Fig. 6. Spectral photoconductivity dependence of Ga_2Te_3 at 300 K



It has been stated that both Ga_2Te_3 and In_2Se_3 have photoelectric properties very favourable for the construction of detector and radiation convertor in the near infrared range (0.8–0.93 μ m for In_2Se_3 at 300 K) as well as in the visible and near infrared ranges (below 1 μ m for Ga_2Te_3 at 300 K). We would like especially to point out the very high values of spectral photoresponse sensitivity of Ga_2Te_3 , located in the spectrum area characteristic of maximal (theoretical) quantum photoconductivity of solar energy converters. Acknowledgements — The authors would like to express their heart-felt gratitude to Theresa Wróbel for her brilliant help and advice without which this article would have never been written.

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Абсорбция и фотопроводимость In₂Se₃ и Ga₂Te₃

Были произведены измерения абсорбции в диапазоне температур 5-300 К вблизи основного края абсорбции. Определены энергии этого края для In₂Se₃: 1.36 eV при 300 K, 1.52 eV при 80 K и 1.56 eV при 5 K, а также для Ga₂Te: 1.2 eV при 300 K.

Спектральные характеристики фотопроводимости испытывались при температурах 80-300 К, вблизи и выше основного края абсорбции. Обсуждена форма характеристик, детективные параметры и возможные применения для обоих полупроводников.