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BAND GAP OF $AgGaTe_2$ SEMICONDUCTOR

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Summary

Chalcopyrite semiconducting compounds of the I-III-VI_2 group are of interest in their potential application in electro-optical devices. Some basic physical properties of the compounds are still in controversy. The band gap of $AgGaTe_2$ was reported to be 1.1 and 1.32 eV by Pamplin et al. *(Pamplin, B.K., Kiyosawa, T. and Masumoto, K. (1979)* Prog. Crystal Growth Charact, 1, *331-387) and by Shewchun* et al. *(Shewchun, J., Loferski, J.J., Beaulieu, R., Chapman, G.H. and Garside, B.K. (1979)* J. Appl. Phys. 50, *6978-6985) respectively. Optical absorption study of polycrystalline sample from present investigation yields a direct band gap of 1.21$_1$ eV.*

Introduction

The two most important semiconducting elements, Si and Ge crystallize in diamond structure of the cubic family. Their commercial interest can be traced back to this fact. The four electrons per site rule[1,2] can account for their semiconducting and doping properties. The rule can also be used to predict semiconductivity in vast families of diamond structure compounds which are called adamantine or diamond-like family. These are the zinc blende, wurtzite and the chalcopyrite structures. Most of the binary compounds of the groups III-V and II-VI crystallize into either zinc blende or wurtzite structure. However, two of the more interesting ternary compounds of the groups I-III-VI_2 and II-IV-V_2 usually have the chalcopyrite structure. More than fifty of such compounds are now known. Their properties and promising application have been reviewed by Shay and Wernick[1] and by Pamplin *et al.*[2]. Alloys from different I-III-VI_2 compounds have also been studied by many investigators. These materials are of interest because of their potential application in electro-optical devices such as solar calls[3,4]. Most of the I-III-VI_2 compounds have been studied by more than one technique. Some results using different techniques are not in agreement with each other. The band gap of $AgGaTe_2$ has been reported to be 1.1 eV by Pamplin *et al.*[2] and 1.32 eV by Shewchun *et al.*[3]. The purpose of the present study is to determine the band gap of this compound by the optical absorption technique using polycrystalline sample.

Theory

The fundamental absorption edge of semiconductors corresponds to the threshold for electron transitions between the highest nearly filled band and the lowest nearly empty band. The absorption is very small for photon energies much less than that of the energy gap and increases significantly for higher photon energies. The study of fundamental absorption provides information about the electron states near the band extreme as well as the band gap.

The basic theory relating optical properties of semiconductors and their band structures has been given elsewhere[5,6]. Only a brief summary will be given here. The intensity of an optical wave passing through a solid is attenuated by electronic absorption of the photon energy. The absorption coefficient which determine the energy absorption in solid is given by

$$\alpha = \frac{4\pi\kappa}{\lambda} \tag{1}$$

Where λ is the wavelength, and κ is the extinction coefficient. Experimentally, one can observe the intensity of the wave reflected from the surface and the wave transmitted through the sample. The reflectivity R and the transmittivity T for normal incidence are the two quantities generally measured. They are given by

$$R = \frac{I_r}{I_o} = \frac{(n-1)^2 - \kappa^2}{(n+1)^2 + \kappa^2} \tag{2a}$$

$$T = \frac{I_t}{I_o} = \frac{(1-R)^2 \exp(-\alpha x)}{1 - R^2 \exp(-2\alpha x)} \tag{2b}$$

where I_o, I_r and I_t are the incident, reflected and transmitted intensities respectively, n is the normal refractive index and x is the thickness of the sample.

From the viewpoint of the electron band structure, we are interested in the probability that, under the influence of the radiation field, an electron will make a transition between energy levels which give rise to the energy absorption. This is given by w, the number of transitions per unit volume per unit time. For one photon process, this is equal to the number of photon absorbed per unit volume per unit time. The corresponding energy absorbed is obviously $wh\nu$. By considering the energy flow of the optical wave and the energy absorbed, the absorption coefficient and the transition probability can be related. The relationship is

$$\alpha = 2\pi ch^2 \frac{1}{nh\nu} \frac{w}{A_o^2} \tag{3}$$

where A_o is the amplitude of the potential vector. In the presence of a radiation field, the transition probability of an electron from ground state o to excited states n is given by the Golden rule:

$$\frac{w}{A_o^2} = \frac{2\pi}{h} \sum_n \left\{ \frac{|H_{no}|^2}{A_o^2} \rho_n(k) \right\} \delta \left[h\nu - \varepsilon_n(k) \right] \tag{4}$$

thus the absorption coefficient can be written in the form

$$\alpha h\nu = \frac{4\pi^2 hc}{n} \sum_n \left\{ \frac{|H_{no}|^2}{A_o^2} \rho_n(k) \right\} \delta \left[h\nu - \varepsilon_n(k) \right] \quad (5)$$

where H_{no} is the optical matrix element and ρ_n (k) is the density of final states. Details of the electron band structure and the type of transition by which the absorption occurs are included in this two quantities. Even in the absence of specific band model, detail consideration of the electron wave functions gives rise to a simple expression

$$\alpha h\nu \; \alpha \; (h\nu - Eg)^{\gamma} \quad (6)$$

where Eg is the band gap, and γ is a constant which equals 1/2 and 3/2 for allowed direct transition and forbidden direct transition respectively. It is equal to 2 for direct transition where phonon processes must be incorporated. By measuring the absorption coefficient as a function of photon energy, one can distinguish, using Eqn. 6 between direct and indirect transitions as well as the energy gap.

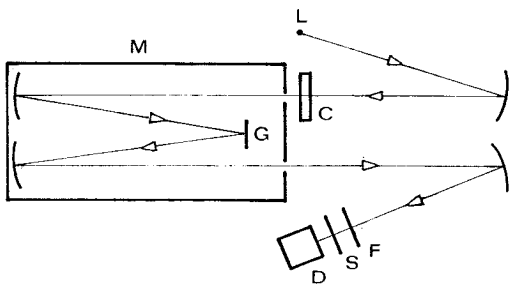
Materials and Methods

Sample preparation

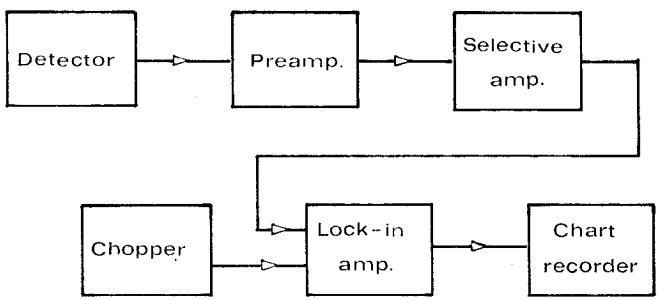
The $AgGaTe_2$ polycrystalline ingot was obtained from direct melting stoichiometric proportion of high purity Ag, Ga and Te in a 6 mm bore quartz tube sealed under vacuum of 10^{-5} torr. During one hour of melting at 1200°C, the sample was shaken intermittently in order to ensure a good mixing among the elements. After being cooled to room temperature, the sample was transfered to an annealing furnace and was kept at 500°C for one week. X-ray powder photograph showed sharp lines of the chalcopyrite structure. The sample was then cut into slices of approximatily 1 mm thick using thin carborundum disc cutter. Careful polishing of the slice using 5 μm alumina polishing powder, thin slice of about 100 μm thick was obtained for optical absorption study.

Experimental procedure

Monochromatic light for optical absorption study was obtained for a Czerny-Turner scanning spectrometer. The whole spectrum to be used was calibrated using mercury lamp. Since the band gap of $AgGaTe_2$ is in the infrared (IR) region, a tungsten light source and PbS IR detector was employed. Schematic diagram of the experiment and the detection system are shown in Fig. 1 (a) and (b). The signal from the detector was amplified by a preamplifier. A selective amplifier which was tuned to the frequency of the light chopper was used to eliminate noise signal other than the chopper frequency. Large signal from the selective amplifier was detected by a Lock-in amplifier which was locked to the frequency of the light chopper. The output was recorded by a chart recorder.



(a)



(b)

Fig. 1. (a) Schematic diagram for optical absorption measurement. M; monochromator, L; Light source, C; light Chopper, G; grating, D; detector, S; Sample and F; filter.

(b) Detection system.

The transmitted intensity of the IR light was measured by mounting the thin slice sample behind a circular hole cut through a sample holder which was placed in front of the IR transmitted. An IR transmitted filter was also used to absorb second order visible light at long wavelength infrared. The intensity of incident IR light was measured after the whole spectrum of the transmitted intensity near the absorption edge had been taken. Thickness of the sample was also measured after the transmission measurement.

Results and Discussion

For sample thickness much greater than α^{-1}, the interference effects due to internal reflections as well as the reflectivity at normal incidence are negligible, and Eqn. 2b can be approximated by

$$I_t = I_0 e^{-\alpha x} \tag{7}$$

Using Eqn. 7, the value of α at various photon energy can be obtained. This is shown in Fig. 2. The background absorption coefficient α_0 at low photon energy due to crystal defects in the sample was fitted to an appropriate curve. For the present experimental data, a straight line was fitted using a Hewlett–Packard calculator. The absorption coefficient due to transition near the fundamental edge, $\alpha-\alpha_0$, was then taken. The best fit of the data to Eqn. 6 can be obtained by assuming γ equal 1/2. This suggests a direct allowed transition which is commonly found in this group of semiconducting compounds. To obtained the band gap, the variation of $[h\nu(\alpha-\alpha_0)]^2$ with photon energy is plotted. This is also shown in Fig. 2. An extrapolation of the straight line portion of the curve intersects the energy axis to give the energy band gap of 1.21_1 eV.

The data of optical absorption in polycrystalline $AgGaTe_2$ indicate that this material is a direct band gap semiconductor with a band gap of 1.21_1 eV at room temperature. The present result is in between the values quoted by previous authors of 1.1 and 1.32 eV. It is usually found that the results using different samples and different methods do not agree very well. The disagreement can be accounted for from the degree and types of defects present in the sample as well as from the method by which the band gap is determined. It is suggested that a more accurate method such as electroreflectance or thermoreflectance and a single crystal sample should be employed in order to gain more reliable band gap for this compound.

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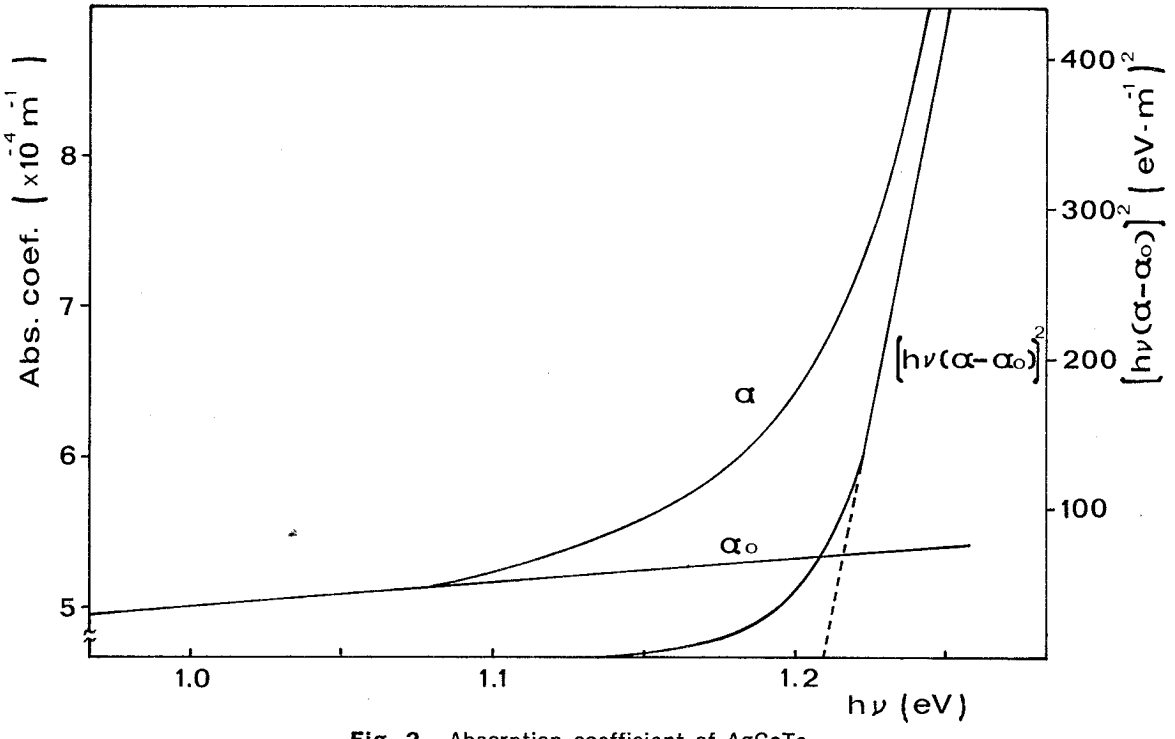

Fig. 2. Absorption coefficient of $AgGaTe_2$

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บทคัดย่อ

สารประกอบกึ่งตัวนำที่มีโครงสร้างผลึกแบบชาลโคไพไรท์ (chalcopyrite) โดยเฉพาะในกลุ่มซึ่งมีสูตร I-III-VI_2 เป็นสารที่ได้รับความสนใจและมีการศึกษากันมาก ทั้งนี้เนื่องจากเป็นสารที่มีแนวโน้มที่จะสามารถนำไปใช้งานทางด้านอุปกรณ์เปลี่ยนรูปพลังงานไฟฟ้าและแสง (electro-optical devices) ได้ แต่ทว่าคุณสมบัติพื้นฐานทางฟิสิกส์บางประการของสารกึ่งตัวนำในกลุ่มนี้หลายชนิด จากรายงานต่าง ๆ ยังขัดแย้งกันอยู่ เช่น ขนาดช่วงพลังงานระหว่างแถบของสารประกอบ $AgGaTe_2$ จากรายงานของ Pamplin (Pamplin, B.K., Kiyosawa, T. and Masumoto, K. (1979) Prog. Crystal Growth Charact. 1, 331–387) มีขนาด 1.1 eV แต่จากรายงานของ Shewchun (Shewchun, J., Loferski, J.J., Beaulieu, R., Chapman, G.H. and Gaside, B.K. (1979) J. Appl. Phys. 50, 6978–6985) มีขนาด 1.32 eV จากการศึกษาด้วยวิธีการดูดกลืนแสงของรายงานฉบับนี้ได้ขนาดช่วงพลังงานระหว่างแถบ 1.21_1 eV และมีลักษณะแถบพลังงานเป็นแบบตรง