

Optical Absorption Spectrum of a Thin CuFeS_2 Film

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Thin CuFeS_2 films were prepared by means of the close-spacing chemical vapor deposition technique, and the optical absorption spectra of the films were measured. Distinctive feature of the spectrum is the existence of an absorption edge at 3.7 eV in addition to a broad band located between 0.6 eV and 3.7 eV with a maximum around 2 eV. One can conclude from this observation that the absorption edge (0.6 eV) of CuFeS_2 reported previously is the foot of the 'charge transfer' transition and that the extra absorption edge (3.7 eV) found in the present work corresponds to the fundamental absorption edge of the nonmagnetic analogs.

The optical absorption edge of the chalcopyrite (CuFeS_2) has been known to be located around 0.6 eV.^{1,2)} The energy value is remarkably small compared with the corresponding I-III-VI₂ chalcopyrite compounds.

In our previous report on the $\text{CuAl}_{1-x}\text{Fe}_x\text{S}_2$ system,³⁾ we proposed that the absorption edge of CuFeS_2 does not correspond to the transition from the valence band to the 4s, 4p-conduction band but to the 'charge transfer' type transition from the valence band mainly composed of the sulfur 3p-orbitals to the empty band mainly of the iron 3d-orbitals. (Hereafter the former transition will be referred to as the 'band to band' transition and the latter as the 'charge transfer' transition.) Theoretical calculation based on the molecular orbital treatment also favors this model, although the strong covalent mixing of 3p and 3d orbitals makes the case complicated.⁴⁾

However, since the previous observation was limited to only the foot part of the 'charge transfer' band, it has been hoped to observe the peaks of the band directly and also an additional absorption edge corresponding to the 'band to band' transition. We, therefore, planned to make thin films of CuFeS_2 in order to extend the absorption measurement to higher energy region than the previous study.

Thin films have been prepared by means of the close-spacing chemical vapor deposition technique, which is essentially the same method as used for an epitaxial growth of GaAs on Ge etc. by Nicoll *et al.*⁵⁾ As shown in Fig. 1, a source tablet (a) was placed in a hollow of a graphite plate (c), which was covered by a

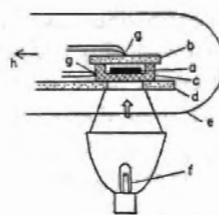


Fig. 1. A schematic diagram of the deposition system. (a—source tablet, b—silica substrate, c—hollowed graphite plate, d—silica supporter, e—silica reaction chamber, f—1 kW infrared lamp, g—thermocouples, h—vacuum pump).

fused silica substrate (b). These were placed on a silica supporter (d) and set in a transparent reaction chamber (e) made of fused silica. The graphite plate was heated by an 1 kW infrared lamp (f). Temperatures at the graphite plate and the substrate were sensed using Pt-PtRh thermocouples (g). The source tablet was composed of the CuFeS_2 powder made from constituent elements by the solid state reaction, and of a small amount of the CuBr powder;* the latter being the transporting agent. The mixture was pressed in a metal mold with the pressure of 200 kg/cm² to be formed into a tablet with 12 mm diameter and 1 mm thickness.

Films of good quality have been obtained under the following conditions:

* CuCl_2 and CuI were also tried as transporting agents. Deposition with CuCl_2 required relatively higher source temperature, and the X-ray diffraction pattern of obtained films often contained some lines which could not be identified. No transport was found with CuI .

(1) Temperature at the surface of the graphite plate is about 320°C (450°C at the source tablet), and that at the upper surface of the substrate is about 260°C.

(2) Content of the CuBr powder is 2.5 wt% of the CuFeS₂ powder.

(3) Vacuum of the reaction chamber is 10⁻⁸ mmHg. (Transport have been observed even in the Ar atmosphere with the pressure up to 10⁻¹ mmHg.)

(4) Heating duration is 3–10 minutes.

The films obtained have metallic faces with golden luster, and are transparent with greyish violet color. Their structures were analyzed by means of the X-ray diffractometer. The diffraction pattern of thickly deposited samples was just like that of the polycrystalline powder of CuFeS₂. No extra line was detected. Some of the samples showed only the (112) diffraction line with the intensity more than one order of magnitude greater than that of the polycrystalline powder. This fact suggests that a preferential orientation of (112) plane occurs parallel to the surface of the substrate.

The optical absorption spectra of the films were measured between 220 and 2200 nm employing a Cary 14 spectro-photometer at room temperature. A typical example of the spectra is shown in Fig. 2(a). The absorption coefficient was calculated using the sample thickness of 300 Å which was measured with an interferometric microscope.

It should be noted that this spectrum extends to much higher absorption coefficient (10⁹ cm⁻¹) than our previous data on a vacuum evaporated film (10⁸ cm⁻¹). The distinctive feature of the spectrum is that there exists an extra absorption edge at 3.7 eV in addition to a broad absorption band with a maximum at 2 eV.

The broad absorption band in a region between 0.6 and 3.7 eV has a shoulder (a) at 1.1 eV and a broad peak (b) around 2 eV. The total oscillator strength of this band is estimated to be 2 × 10⁻¹ assuming that the refractive index is 4.

Figure 2(b) shows an absorption spectrum of CuAlS₂:Fe_{0.008} described in ref. 2. A broad band can be seen which has two peaks (A) and (B) at 1.3 eV and 1.9 eV, respectively, in the low energy side of the fundamental absorption edge of the CuAlS₂; the total oscillator strength

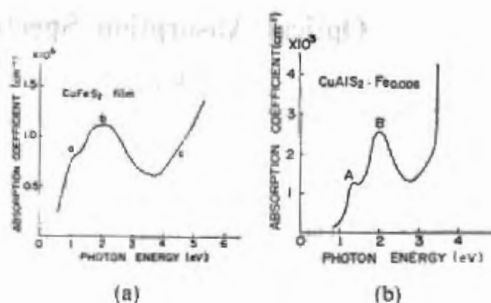


Fig. 2. (a) An absorption spectrum of the CuFeS₂. The sample thickness is 300 Å. (b) An absorption spectrum of the CuAlS₂:Fe_{0.008}.

of the band was estimated to be 7.5×10^{-2} .⁽²⁾ These peaks have been assigned to the 'charge transfer' transition from the 3p-orbitals of the ligands to the 3d-orbitals of the impurity center. The peak position, the shape and the value of the oscillator strength of this band are quite similar to those of the broad band of CuFeS₂ found in the present study. Therefore we can assign the latter band to the transition with the 'charge transfer' nature.

An extra absorption edge is found at 3.7 eV. This can be assigned to the onset of the 'band to band' transition, because the energy value is comparable to those of the fundamental absorption edge of nonmagnetic chalcopyrite crystals; e.g. CuAlS₂—3.4 eV, and CuGaS₂—2.5 eV.

In summary, we have obtained thin films of CuFeS₂ by means of the close-spacing chemical vapor deposition method, have measured optical absorption spectra and have concluded that the 0.6 eV absorption edge of CuFeS₂ is the foot of the 'charge transfer' type transition and the 3.7 eV edge found in the present work is the onset of the 'band to band' transition.

For detailed optical studies of CuFeS₂ it is essential to obtain single crystalline films on single crystalline substrates. The preparation of such films is now in progress.

References

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