

ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

**FREQUENCY DEPENDENT IN  $Zn(In_2S_3)_S$  SEMICONDUCTOR FILMS**

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**ABSTRACT**

$Zn(In_2S_3)_S$  films have been deposited with decreasing amount of the  $In_2S_3$  contents by the spray pyrolysis technique. The metal-semiconductor-metal systems have been produced in planar form. On the ac measurements, the conductivities were measured with respect to the frequency and it was observed that conductivities depend on the frequency in the form of  $\omega^s$  where  $s$  is 0.7. This variation of the ac conductivity is attributed to the hopping of charge carriers between the localized states. In the conductivity vs frequency characteristic of  $Zn(InS_{1.5})_S$ , on the otherhand, showed that  $s \sim 1.5$  at higher frequencies.

**Key Words:** AC conductivity, Hopping conduction, Semiconductor compounds,  $Zn(In_2S_3)_S$  films, Spray pyrolysis.

**$Zn(In_2S_3)_S$  YARIİLETKEN FİLMLERİNİN FREKANS BAĞLI İLETKENLİĞİ**

**ÖZ**

$Zn(In_2S_3)_S$  yarıiletken filmleri, yapıdaki  $In_2S_3$  miktarı azaltılarak, spray pyrolysis tekniği ile elde edilmiştir. Elektriksel ölçümler, düzlemsel formda oluşturulan metal-yarıiletken-metal yapılarda elde edilmiştir. Ac elektriksel ölçümlerle; iletkenliğin  $\omega^s$  modeline uyduğu gözlenmiş ve  $s$  değerinin 0,7 olduğu hesaplanmıştır. İletkenliğin frekansa üssel bağıllığı, iletimin serbest yükler tarafından lokalize durumlar arasında hopping iletim ile sağlandığının bir sonucudur.  $Zn(InS_{1.5})_S$  filmindeki iletkenlik-frekans bağımlılığı yüksek frekanslarda ise  $s \sim 1.5$  olarak gözlenmiştir.

**Anahtar Kelimeler:** AC iletkenlik, Hopping iletim, Yarıiletken bileşikler,  $Zn(In_2S_3)_S$  yarıiletken filmler, Spray pyrolysis.

**1. INTRODUCTION**

Studies on the electrical and the optical properties of  $Zn(In_2S_3)_S$  semiconductors have shown that defects present in these semiconductors, so that  $Zn(In_2S_3)_S$  semiconductors can be considered as having a structure intermediate between amorphous and crystalline semiconductors (Mott and Davis, 1971; Serpi, 1976; Grilli and Guzzi, 1977; Cinngolani et al., 1974; Giorgianni et al., 1978; Romeo et al., 1972; Anagnostopoulos et al., 1984; Unger et al., 1978; Kao and Hwang, 1978; Zor M. et al., 1997). These defects distributed in the energy

gap are called localized states (Mott and Davis, 1971). The localized states have the effects on the electrical conductivity of compound semiconductors in such a way that the carriers in these states contribute to the conduction by means of the hopping processes. There are three mechanisms of charge transport in the ac conduction of semiconductors. These are (i) the transport by carriers excited to the extended states near the conduction or valance band, (ii) the transport by carriers excited into the localized states near to the edges of the conduction or valance band, and (iii) hopping transport by the carriers via the states near the Fermi level.

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In this work we studied the ac conductivity of the Zn(In<sub>2</sub>S<sub>3</sub>)S semiconductor compounds produced by the spray pyrolysis method (SP). SP method is a straightforward technique to obtain compound semiconductors with varying anion-cation concentrations. It is also useful to produce varying band gap materials during the deposition process.

## 2. EXPERIMENTAL DETAILS

The aqueous solutions of the compounds that contain the required elements of the relevant concentrations of the desired material, sprayed onto the hot glass substrates to produce Zn(In<sub>2</sub>S<sub>3</sub>)S films. Zn(In<sub>2</sub>S<sub>3</sub>)S films and others which produced with decreasing amount of In<sub>2</sub>S<sub>3</sub> in the structure were deposited onto the glass substrates at 250°C. X-ray diffraction patterns of all the films showed that they are in polycrystalline structure. We have obtained that the energy gaps of the films are direct and having values between 2.65 and 3.00 eV at room temperature and all samples were found to be n-type characteristics. Other workers on the electrical and optical properties of Zn(In<sub>2</sub>S<sub>3</sub>)S films have reported that the energy gap of the Zn(In<sub>2</sub>S<sub>3</sub>)S is varied between 2.73 and 3.00 eV and obtained direct transition (Serpi, 1976; Grilli and Guzzi, 1977; Cinngolani et al., 1974; Giorgianni et al., 1978; Romeo et al., 1972; Anagnostopoulos et al., 1984; Unger et al., 1978).

The planar structures of the metal semiconductor-metal systems have been produced by vacuum deposition of gold electrodes onto the semiconductors by Leybold Heraus 300 Univex system. The electrical measurements for the ac characteristics of the structure were carried out at room temperature in the frequency range between 5Hz and 13 MHz in dark, by using Hewlett Packard LF Impedance Analyzer 4192A.

## 3. RESULT and DISCUSSION

In a semiconductor, electrons in a conduction band and holes in a valance band are responsible for dc conduction mechanism. On the other hand, charge carriers in the localized states also contribute to the electric current. A localized electron is bound to its site, and lies within its potential well, separated from the neighbours by potential barriers. It can move from one site to a neighbouring one only if it is energetically excited above the potential barrier. This process is known as hopping conduction (Mott and Davis, 1971). In hopping conduction, an electron jumps over the potential barrier from one localized state to another that has a different energy. This hopping energy between states is provided by the phonon. An electron exchanges energy

with a phonon at every jump (Mott and Davis, 1971; Kao and Hwang, 1978; Brodsky, 1979). So an electron can move through the solid via hopping between atomic sites and can contribute to the electric current.

The electrical conductivity,  $\sigma(\omega)$ , as a function of the frequency  $\omega$  of an alternating electric field can be written as,

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac}(\omega) \quad (1)$$

where  $\sigma_{dc}$  and  $\sigma_{ac}(\omega)$  are the dc and ac conductivities, respectively. There are three mechanisms of charge transport that can contribute to the ac conductivity as follows:

- a) Transport by carriers excited to the extended states near the conduction and the valance bands. This result is given by a formula of the Drude type (Mott and Davis, 1971);

$$\sigma(\omega) = \frac{\sigma_{dc}}{(1 + \omega^2\tau^2)} \quad (2)$$

Where  $\tau$  is the relaxation time, since it is so small that a change in conductivity of this kind is not expected until a frequency  $10^{15}$ Hz.

- b) Transport by carriers excited into the localized states at the edges of valance or conduction band. The carriers in these localized states can take part in the electric charge transport only by hopping. It is expected that conductivity increases with frequency and it is given by (Mott and Davis, 1971; Kao and Hwang, 1978; Brodsky, 1979),

$$\omega \left[ \ln \left( \frac{v_{ph}}{\omega} \right) \right]^4 \quad (3)$$

where  $v_{ph}$  is the phonon frequency. It is expected that the conductivity would increase with frequency as  $\omega^{0.8}$  when  $\omega \ll v_{ph}$ .

- c) Hopping transport by carriers with energies near the Fermi level. This will also cause an increase in conductivity with frequency in the same manner as for process (b). The ac conductivity in this case is given by (Mott and Davis, 1971, Kao and Hwang, 1978, Brodsky, 1979),

$$\sigma_{ac}(\omega) = \frac{1}{3} \pi e^2 kT [N(E_F)]^2 \sigma^{-5} \omega \left[ \ln \left( \frac{v_{ph}}{\omega} \right) \right]^4 \quad (4)$$

where  $T$  is temperature,  $N(E_F)$  density of states and  $\alpha$  absorption coefficient. Here also the conductivity is expected to increase with  $\omega^{0.8}$  when ac conduction dominates dc conduction. Hopping conduction equation can be approximated by an expression of the form (Mott and Davis, 1971),

$$\sigma_{ac}(\omega) A \omega^8 \quad (5)$$

where  $s$  is not a constant for all substances, but is a function of the temperature, approaching unity at low temperatures and decreasing to 0.5 or less at high temperatures (Mott and Davis, 1971; Brodsky, 1979; Kao and Hwang, 1984).

Figure 1 shows the frequency dependencies of conductivity. It is seen that the ac conductivity takes over from dc conductivity at a frequency of about  $10^3$  Hz. At higher frequencies, the ac conductivity showed a variation with frequency as  $\omega^{0.7}$ . Whereas in Figure 2, a rather different type of frequency dependent conductivity has been observed, such as  $\omega^{1.5}$ . However, this variation could be attributed to the decreased amount of the  $\text{In}_2\text{S}_3$  in the structure, but the lossy mechanism could not be discarded since it shows itself with nearly  $\omega^2$  variation. Comparing exponents  $s$  of  $w$  in these two figures, it is expected that at higher frequencies a lossy mechanism had played a role in the conductivity in Au-Zn( $\text{InS}_{1.5}$ )S-Au structure (Figure 2).

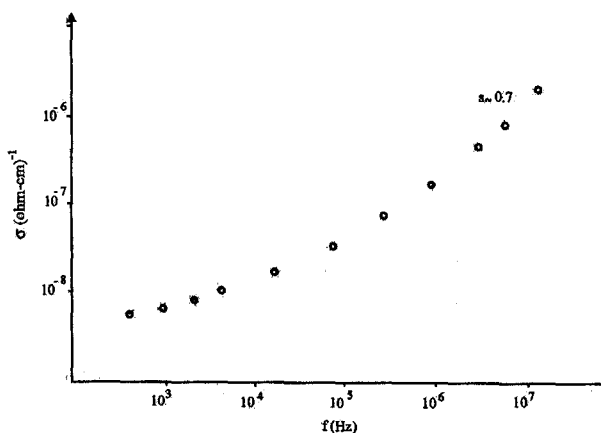


Figure 1. The Loss and Conductivity of Au-Zn( $\text{In}_2\text{S}_3$ )S-Au Film as Function of the Frequency.

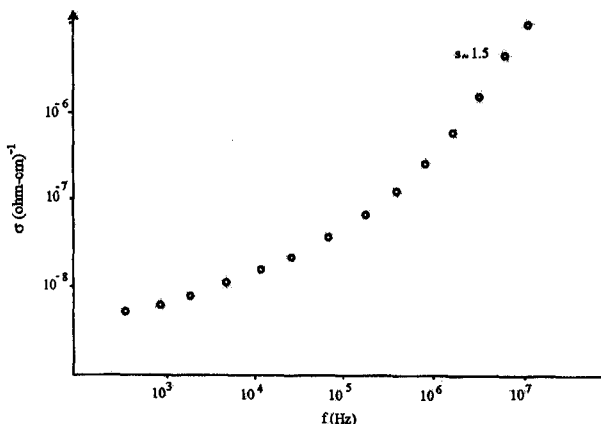


Figure 2. The Loss and Conductivity of Au-Zn( $\text{InS}_{1.5}$ )S-Au Film as Function of the Frequency.

## REFERENCES

- Anagnostopoulos, A.N., Kambas, K. and Ploss, B. (1984). Optical measurements and temperature dependence of energy gap in  $\text{ZnIn}_2\text{S}_4$  layered compound. *Phys. Stat. Sol. (b)* 123, K155-159.
- Brodsky, M.H. (1979). *Amorphous Semiconductors* Springer Verlag, 337p.
- Cingolani, A., Ferra, M., Minafra, A. and Aducci, F., Tantalò, P. (1974). Photoelectronic properties of  $\text{ZnIn}_2\text{S}_4$ . *Phys. Stat. Sol. (a)* 23, 367-375.
- Giorgianni, U., Grasso, V., Mondio, G., and Saitta, G. (1978). Optical properties of the layered semiconductor. *Physics Letters* 68A, 247-248.
- Grilli, E. and Guzzi, M. (1977). Recombination process of photoexcited carriers in  $\text{ZnIn}_2\text{S}_4$ . *Phys. Stat. Sol.(a)* 40, 69-74.
- Kao, K.C. and Hwang, W. (1979). *Electrical transport in solids*, Pergamon Press, 663p.
- Mott, N.F. and Davis, E.A. (1971), *Electronic processes in non-crystalline materials*, Clarendon Press, London, 437p.
- Romeo, N. and Dallaturca, A. (1973), Charge storage in  $\text{ZnIn}_2\text{S}_4$ , single crystals. *Appl. Phys. Lett.* 22, 21-22.
- Serpi, A. (1976). Trap distribution in from photoconductivity analysis, *Jphys. D.: Appl. Phys.* 9, 1881-1892.
- Unger, W.K., Meuth, H., Irwin, J.C. and Pink, H. (1978). Photoluminescence and resonant raman scattering in  $\text{CdIn}_2\text{S}_4$  and  $\text{ZnIn}_2\text{S}_4$ , *Phys. Stat. Sol (a)* 46, 81-87.
- Zor, M., Aksay, S., Kul, M. and Aybek, A.Ş. (1997). DC and AC properties of the compound semiconductors prepared by spray pyrolysis, *Proc. Suppl. Balkan Physics Letter.*, 5, 1132-1135.



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