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# The effect of intrinsic defects on the hole transport in $\text{Cu}_2\text{O}$

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Structural and electrical properties of  $\text{Cu}_2\text{O}$  bulk samples are characterized by X-Ray diffraction (XRD) and Hall effect measurements. The variation of the carrier concentration with temperature is explained in terms of the thermal activation energy of an acceptor level originating from intrinsic defects. An acceptor energy level of 0.22 eV above the edge of the valance band has been obtained. A high compensation ratio has been estimated as 0.49 by using an expression valid for a compensated material. The strong compensation of donors in  $\text{Cu}_2\text{O}$  samples is predicted due to a high density of native acceptor defects. The temperature dependence of the mobility is interpreted in terms of Seto's model which was proposed for polycrystalline materials. Utilizing Seto's model, various electrical parameters of the present samples such as grain boundary potential, surface densities of trap states, the average size of the crystallites and Debye screening length have been determined.

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*Keywords:* Cuprous oxide, Hole transport, Compensation ratio, Grain boundary model, Grain boundary potential, Surface densities of trap states, Debye screening length

## 1. Introduction

Cuprous oxide ( $\text{Cu}_2\text{O}$ ) has attracted a great deal of attention due to its potential of device applications such as humidity sensors and phototransistors [1, 2].  $\text{Cu}_2\text{O}$  has brown color with a direct band gap of around 2 eV [3]. With this band gap energy,  $\text{Cu}_2\text{O}$  is used as an absorber layer for heterojunction solar cells [4]. However, solar cells with efficiency around 2%, prepared with  $\text{Cu}_2\text{O}$ , have been reported [5]. This low efficiency arises due to the difficulty in improving its electrical properties.

$\text{Cu}_2\text{O}$  usually exhibits considerable amounts of deviation from stoichiometry due to the presence of the intrinsic defects such as copper and oxygen vacancies [6]. So, the electrical properties of  $\text{Cu}_2\text{O}$  are mainly controlled by these intrinsic defects [4]. These defects lead to degrade the conductivity and  $\text{Cu}_2\text{O}$  samples with good quality could not be generally obtained [7-9].  $\text{Cu}_2\text{O}$  is known to have p-type conductivity and the mobility of the material has always been found to be very low.

In order to account for transport properties of semiconductors, a detailed temperature-dependent mobility study of samples is essential. The measured carrier mobility depends on the predominant scattering mechanisms which are related to structural perfection of the crystal, and temperature. Therefore, we are interested to investigate the effects of the nature of the defects on the structural perfection and properties of  $\text{Cu}_2\text{O}$  by analyzing their transport properties.

In this study, we have carried out the XRD and Hall effect measurements for the  $\text{Cu}_2\text{O}$  bulk samples. Various electrical parameters of the present samples are extracted from the temperature dependence of the carrier concentration and Hall mobility data.

## 2. Experimental

The pieces of copper sheet (purity: 99.99%, thickness; 200  $\mu\text{m}$ , dimensions: 10 mmx10mm) were chemically cleaned by means of deionized water, acetone ( $\text{CH}_3\text{COCH}_3$ ) and a mixture of deionized water and nitric acid (50% $\text{H}_2\text{O}$ +50%  $\text{HNO}_3$ ). In order to obtain very clean copper surfaces they were placed in a furnace at temperature 973 K for 10 minutes [8]. In this period the dried hydrogen gas was passed over the samples. As the samples were let to cool to room temperature the very thin copper layer (consisting of oxides and chemical complexes as impurities, thickness 1-2  $\mu\text{m}$ ) were spontaneously cleaved from the surfaces by the help of hydrogen exposure. In order to grow cuprous oxide samples, cleaved copper metal were hang by a platinum wire in a furnace at the temperature 1313 K for 15 minutes and copper pieces were completely oxidized. At the end of this period they were let to cool to room temperature. The samples were annealed in a furnace at temperature 873 K for five minutes [9].

In order to realize electrical measurements, cuprous oxide  $\text{Cu}_2\text{O}$  sample, having  $51\ \mu\text{m}$  thickness, was also cut into the  $4.5\ \text{mm} \times 4.5\ \text{mm}$  dimensions and then it was placed on fiber holder by means of araldite as shown in Fig. 1 and the copper ohmic contacts with  $0.20\ \text{cm}^2$  area were applied on surfaces of  $\text{Cu}_2\text{O}$  layer under a vacuum of  $1 \times 10^{-7}$  Torr and finally a  $\text{Cu}/\text{Cu}_2\text{O}/\text{Cu}$  sandwich structure was obtained. In order to eliminate the effect of the light and the electrical noise on the current-voltage measurements of  $\text{Cu}/\text{Cu}_2\text{O}/\text{Cu}$  structure, the sample was placed in a sealed, screened, closed and darkened metal box. All the measurements were carried out at temperature range of  $273 - 363\ \text{K}$ . It was observed that the current passing through the  $\text{Cu}/\text{Cu}_2\text{O}/\text{Cu}$  sandwich structure was depended on temperature.

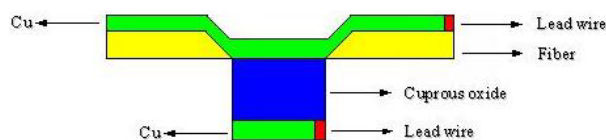


Fig. 1. The sandwich structure of  $\text{Cu}/\text{Cu}_2\text{O}/\text{Cu}$  developed for Hall measurements.

In order to determine hole mobility of  $\text{Cu}_2\text{O}$  polycrystal, it was utilized from the Hall measurement.  $\text{Cu}_2\text{O}$  piece having  $51\ \mu\text{m}$  thicknesses, in the dimension of  $12\ \text{mm} \times 4\ \text{mm}$  was placed on a glass substrate by means of araldite. The hole mobility of  $\text{Cu}_2\text{O}$  was measured by Hall experiment in the temperature range of  $273 - 363\ \text{K}$  by means of a similar way and similar electrical circuit used in the literature published by author [10]. It was observed that the obtained results of the hole mobility were very close to the results published in the literature [10, 11].

### 3. Results and discussion

$2\theta$  XRD examination proved that the samples grown by us are totally  $\text{Cu}_2\text{O}$ . Each of five peaks lied in  $2\theta$  XRD pattern corresponds to special orientation of single crystals of  $\text{Cu}_2\text{O}$ . These orientations are labeled by means of the Miller indexes (110), (111), (200), (211) and (220), which corresponded to the existence of  $\text{Cu}_2\text{O}$  single crystals oriented in different directions (Fig. 2). The differences in the height of the peaks are meant that with the amount of  $\text{Cu}_2\text{O}$  single crystal was the largest in case the Miller index (111) and the smallest in (110) case. In other word  $\text{Cu}_2\text{O}$  samples used in this study are polycrystals and it consisted of random distribution of  $\text{Cu}_2\text{O}$  single crystal and the amount of the single crystal oriented in (111) Miller index was effectively dominant.

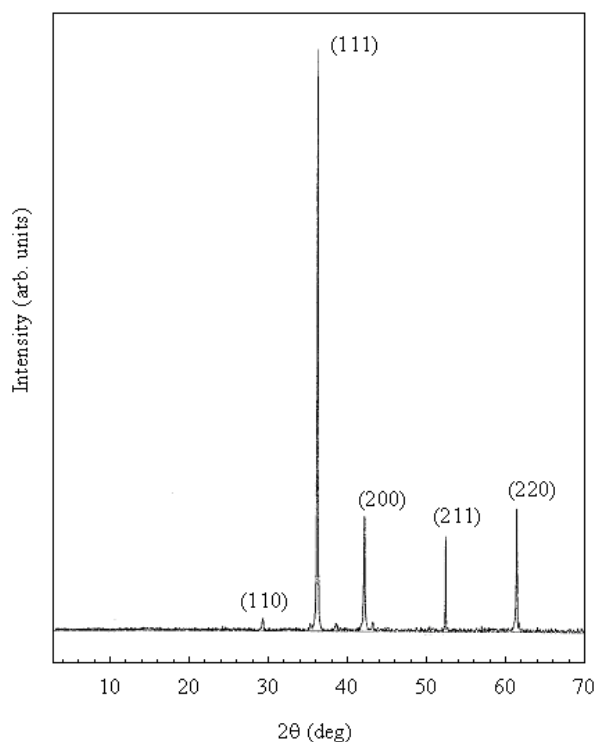


Fig. 2.  $2\theta$  x-ray diffraction of  $\text{Cu}_2\text{O}$  polycrystal.

Fig. 3 shows the temperature dependence of the carrier concentration for the investigated samples in a temperature range of  $273-363\ \text{K}$ . The unintentionally doped  $\text{Cu}_2\text{O}$  samples exhibit  $p$ -type conductivity, which may be due to the presence of copper vacancies. In the present case, we find that  $\text{Cu}_2\text{O}$  have carrier concentrations at room temperature which are about three orders of magnitude smaller than those reported one [13].

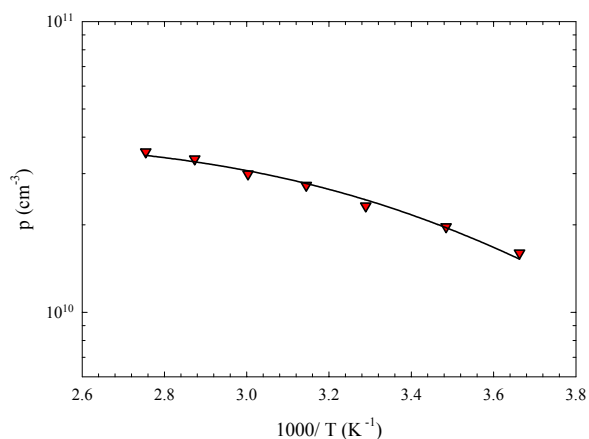


Fig. 3. Plots of  $p$  vs  $1000/T$  of the  $\text{Cu}_2\text{O}$  in a temperature range of  $273-363\ \text{K}$ . Solid triangles show the experimental points, solid line is the least squares fit of Eq. (1) to the experimental data.

However, no appreciable difference in the magnitude of the hole mobility has been observed. One can expect that stoichiometric crystals of  $\text{Cu}_2\text{O}$  have higher carrier concentrations than samples which are prepared with non-stoichiometric compositions. It is observed that the hole mobility of the samples varies between 17 and 56  $\text{cm}^2/\text{Vs}$  at whole temperature range (Fig. 4). Similar results have also been reported earlier [6, 12, 13].

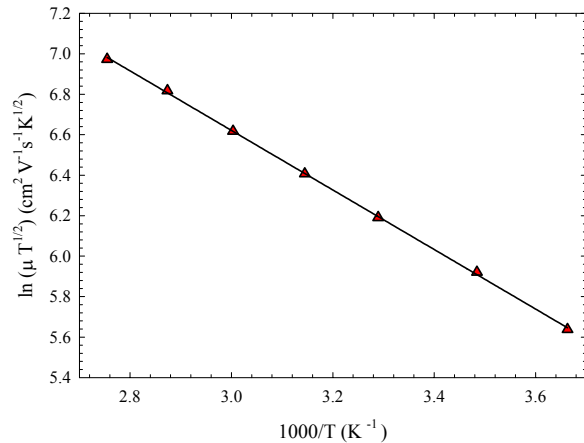


Fig. 4. Plots of  $\ln(\mu T^{1/2})$  vs  $1000/T$  of the  $\text{Cu}_2\text{O}$  in a temperature range of 273–363 K. Solid triangles show the experimental points, solid line is the least squares fit of Eq. (3) to the experimental data.

The low carrier concentration in the doped  $\text{Cu}_2\text{O}$  may be also associated with the low acceptor concentration and the large degree of compensation due to the high concentration of donors.  $\text{Cu}_2\text{O}$  is a compensated material and it is well known that the acceptors and donors are the negatively charged copper vacancies and the positively charged oxygen vacancies, respectively.

To obtain information on the acceptors, least-squares fittings to experimental carrier concentration at whole temperature range have been performed using an expression valid for a compensated material [14]

$$p = -\frac{1}{2} \left( N_D + \frac{N_V}{\exp(E_a/k_B T)} \right) + \frac{1}{2} \sqrt{\left( N_D + \frac{N_V}{\exp(E_a/k_B T)} \right)^2 + 4 \left( \frac{N_V}{\exp(E_a/k_B T)} \right) (N_A - N_D)} \quad (1)$$

where  $N_V$  is the effective density of states in the valance band which is given by,

$$N_V = 2 \left( \frac{2\pi m^* k_B T}{h^2} \right)^{3/2} \quad (2)$$

here,  $N_A$ ,  $N_D$ ,  $m^*$ ,  $k_B$  and  $h$  are the acceptor density, donor density, effective hole mass, Boltzmann's constant and Planck's constant, respectively. The value of the  $m^*$  is taken to be  $0.58 m_0$  [15]. Calculated hole concentration as a function of temperature is indicated in Fig. 3 by the solid line. From the fitting, the values of  $E_a$ ,  $N_A$ ,  $N_D$  and

compensation ratio  $N_A/N_D$  are estimated to be 0.22 eV,  $7.8 \times 10^{10} \text{ cm}^{-3}$ ,  $3.8 \times 10^{10} \text{ cm}^{-3}$  and 0.49, respectively. There is a well agreement with the activation energy value reported in previous works [6, 7]. For undoped  $\text{Cu}_2\text{O}$ ,  $E_a$  reported in literature varied widely from 0.12 to 0.45 eV [3, 7, 12]. These values are attributed as activation energy of native acceptors in  $\text{Cu}_2\text{O}$ . The energy of 0.22 eV obtained for our sample is within this range. The compensation ratio is rather large in investigated samples, because of the high concentration of ionized donors. Therefore, the strong compensation of donors in  $\text{Cu}_2\text{O}$  seems to be due, for the most part, to a high density of native acceptor defects. The relatively low carrier mobility in the  $\text{Cu}_2\text{O}$  is due to the strong scattering of charge carriers by ionized defect centers, because of their high density, and additional scattering by non-uniformly distributed process-induced defects.

In order to achieve a deeper understanding of the electrical transport in  $\text{Cu}_2\text{O}$ , the temperature dependence of Hall mobility is studied. Fig. 4 shows the temperature dependence of the Hall mobility for the  $\text{Cu}_2\text{O}$  in a temperature range of 273–363 K. The  $\text{Cu}_2\text{O}$  has a highest mobility of 56  $\text{cm}^2/\text{Vs}$  at 363 K. A high compensation ratio of 0.49 reduces the mobility calculated for material of a given low electron concentration. Such a sustained high level of compensation appears unlikely in a system having high mobility; we therefore now consider grain boundary scattering which is to be expected in polycrystalline samples. In polycrystalline samples the transport properties are strongly influenced by boundaries between ordered grains, mainly if lateral transport occurs. Potential barriers exist at grain boundaries which act as traps of free carriers. The temperature dependence of Hall mobility is found to obey Seto's relation [16];

$$\mu = \mu_0 T^{-1/2} \exp\left(-\frac{E_b}{k_B T}\right) \quad (3)$$

$$\mu_0 = \frac{L e}{(2\pi m^* k_B)^{1/2}} \quad (4)$$

where  $e$  is the electron charge,  $E_b$  is the grain boundary potential and  $L$  is the average size of the crystallites. Fig. 4 shows the plots of  $\ln(\mu T^{1/2})$  vs  $1000/T$  for the investigated samples. The solid triangles in Fig. 4 are the experimental data and the solid line is the best fitted values. The  $r^2 = 0.999$  ( $r$  = correlation coefficient) is obtained, which indicates a satisfactory fit. The linearity of the plots reveals that the grain boundary scattering of the charge carriers is more predominant in the investigated samples. The values of  $L$  and  $E_b$  are calculated from the plots of Fig. 4 as 262 nm and 127 meV, respectively.

In polycrystalline materials, high densities of defects are expected at the grain boundaries which are often charged with majority carriers. The charged states at the grain boundaries create depleted regions and the potential barriers which provide a resistance for the passage of carriers [16, 17]. Trapping states are capable of trapping free carriers and, as a consequence, more free carriers become immobilized as trapping states increases. Now,

the surface densities of trap states ( $Q_i$ ) in the films can be estimated using the relation [16],

$$Q_i = \frac{(8\epsilon\epsilon_0 N_A E_b)^{1/2}}{e} \quad (5)$$

where  $\epsilon_0$  is the permittivity of vacuum and  $\epsilon$  is the static dielectric constant of material which equals 10.5 for Cu<sub>2</sub>O [18]. Substituting the values of  $N_A$  and  $E_b$  into Eq. (5), the value of  $Q_i$  is found to be as  $6.78 \times 10^8 \text{ cm}^{-2}$ , which is in reasonable agreement with the reported values for polycrystalline materials [17].

Applicability of grain boundary model involves many grain boundaries. This effect is examined by evaluation of the Debye screening length ( $L_D$ ) in comparison with the average grain size ( $L$ ). The Debye screening length can be calculated from a hydrogenic model of the possible acceptor centers. The pertinent expression is [19]

$$\frac{1}{L_D^2} = \frac{4p^{1/3}}{a_B^*} \quad (6)$$

where  $p$  is the carrier concentration and  $a_B^*$  is the Bohr radius for the acceptor centers, given by

$$a_B^* = 4\pi\epsilon_0 \epsilon \hbar^2 / m^* e^2 \quad (7)$$

from Eq (6) and (7), we obtain

$$L_D = \left( \frac{\hbar}{2e} \right) \left( \frac{\epsilon\epsilon_0}{\pi m^* p^{1/3}} \right)^{1/2} \quad (8)$$

if  $L_D < L/2$ , potential barriers exist in grain boundary region due to interface trap states [17]. If, however,  $L_D$  is larger than  $L/2$ , the conduction band becomes flat without the potential barrier [17], and the electrons are transported without grain boundary scattering. The value of  $L_D$  is obtained from Eq. (8) as 29 nm. It can be noticed that the condition  $L_D < L/2$ , appropriate for a grain boundary model is obeyed here for the investigated samples.

#### 4. Conclusions

Cu<sub>2</sub>O is a stoichiometry defect type of semiconductor, the deviation from stoichiometry reflected in the electrical properties of Cu<sub>2</sub>O. Compensation ratio of acceptors is expectedly high in the present samples. The formation of a highly compensation has been predicted due to the presence of copper vacancies. These vacancies create an acceptor energy level of 0.22 eV above the edge of the valance band. We have found that the electrical properties of Cu<sub>2</sub>O are mainly controlled by the intrinsic defects such as copper vacancies. The high compensation accounts for the observed low mobilities in these materials. We have obtained that the low Hall mobility commonly observed in undoped Cu<sub>2</sub>O is mainly due to grain boundaries which was proposed for polycrystalline materials. In the light of

Seto's model, important physical parameters of present samples has been determined.

#### References

- [1] T. C. Richardson, J. L. Slack, M. D. Rubin, *Electrochim. Acta* **46**, 2281 (2001).
- [2] C. Fernando, L. Silva, R. Mehra, K. Takahashi, *Semicond. Sci. Technol.* **16**, 433 (2001)
- [3] R. A. Ismail, I. Ramadhan, A. Mustafa, *Chin. Phys. Lett.* **22**, 2977 (2005).
- [4] G. P. Pollack, D. Trivich, *J. Appl. Phys.* **46**, 163 (1975).
- [5] B. P. Rai, *Sol. Cells* **25**, 265 (1988).
- [6] N. Kikuchi, K. Tonooka, *Thin Solid Films* **486**, 33 (2005).
- [7] N. Serin, T. Serin, Ş. Horzum, Y. Çelik, *Semicond. Sci. Technol.* **20**, 398 (2005).
- [8] N. Serin, T. Serin, B. Ünal, *Semicond. Sci. Technol.* **15**, 112 (2002).
- [9] N. Serin, T. Serin, S. Karadeniz, *Semicond. Sci. Technol.* **17**, 60 (2002).
- [10] S. Gürçan, Ph. D. Thesis, Gazi University Science Institute, Ankara, 1988.
- [11] R. A. Smith, *Semiconductors*, Cambridge: Cambridge University Press, London, 1968.
- [12] K. Akimoto, S. Ishizuka, M. Yanagita, Y. Nawa, G. K. Paul, T. Sakurai, *Sol. Energy* **80**, 715 (2006).
- [13] B. S. Li, K. Akimoto, A. Shen, *J. Cryst. Growth* **311**, 1102 (2009).
- [14] W. H. Brattain, *Rev. Mod. Phys.* **23**, 203 (1951).
- [15] J. W. Hodby, T. E. Jenkins, C. Schwab, H. Tamura, D. Trivich, *J. Phys. C* **9**, 1429 (1976).
- [16] J. Y. W. Seto, *J. Appl. Phys.* **46**, 5247 (1975).
- [17] J. W. Orton, M. J. Powel, *Rep. Prog. Phys.* **43**, 1263 (1980).
- [18] J. Bloem, *Philips Res. Rep.* **13**, 167 (1958).
- [19] C. Kittel, *Introduction to Solid State Physics*, Wiley, Singapur, 1995.

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