Hall effect in reactively sputtered Cu_2S

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The Hall effect in thin films of reactively sputtered Cu_2S was measured at temperatures from 90 to 300°K. The hole concentration ranged from 10^{18} to 2×10^{19} cm^{-3}. The hole mobility ranged from 5.5 to 9 cm^2/V s. The predominant scattering mechanisms are ionized impurity scattering at $T < 100$°K and optical phonon scattering at $T > 100$°K.

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Cu_2S is a semiconductor of considerable interest for solar cell application, but many basic properties such as dominant scattering mechanisms are still not well understood. Findings of a study of the Hall effect in thin-film Cu_2S are presented in this letter.

Similar studies have been made, but the results are inconclusive. The first such study was conducted by Hirahara[1] in 1951. His measurements were made on polycrystalline bulk material at temperatures of – 20 to 250 °C. He reported a room-temperature hole mobility μ_h of 12 cm^2/V· s. Nonstoichiometric samples with excess sulphur had lower μ_h and higher hole concentration p than the stoichiometric ones. He therefore concluded that impurity scattering played a dominant role in free-carrier transport in Cu_2S. Abdullaev *et al.*[2] measured μ_h in single crystals of Cu_2S from 20 to 600 °C. The hole mobility was 25 cm^2/V· s at room temperature and decreased with increasing temperature, with a $T^{-3/2}$ dependence, up to 250 °C. Consequently, acoustic phonon scattering was believed to be dominant in this temperature range. Sorokin and Paradenko[3] observed the same temperature dependence in polycrystalline thick layers and thin films of Cu_2S. The mobility in thin films was about 5 cm^2/V·s, while that of bulk material was an order of magnitude larger. The great difference in mobility was explained by grain boundary scattering, which was much more prevalent in thin films. Later, Sorokin *et al.*[4] reported μ_h as high as 90 cm^2/V· s in single-crystal Cu_2S that deviated by less than 3% from stoichiometric. More recently, Bougnot *et al.*[5] reported hole mobilities of 4 cm^2/V· s in bulk Cu_2S. The μ_h is almost independent of temperature from 77 to 200 K, then decreases with increasing temperature according to $T^{-3/2}$.

The samples used in the present study were obtained by rf reactive sputtering of copper onto glass slides in an H_2S/Ar atmosphere. The photovoltaic research group at Lawrence Livermore Laboratory has demonstrated that nearly stoichiometric Cu_2S can be obtained by using this process.[6] The samples were $1\times 1\times 10^{-4}$-cm films with gold contacts evaporated onto the four corners. The magnetic field strength used was 8.6 kG. The voltage measuring system was capable of detecting signals as low as 1.0 μV. The temperature ranged from 90 to 300 °K and could be controlled to within 1 °K.

Raw data were reduced by the van der Pauw method to obtain the resistivity ρ and Hall mobility μ_H.[7] The hole concentration was then calculated from

$$p = 1/q\rho\mu_H , \tag{1}$$

where q is the electronic charge.

The Hall mobility was used in place of the drift mobility in the calculations, because for the common scattering mechanisms (ionized and neutral impurity, acoustic and optical phonon, and piezoelectric scattering) the Hall scattering factor is nearly unity. In particular, for optical phonon scattering, which dominates over most of the measured temperature range, the scattering factor is between 1.00 and 1.06.[8]

Data from a typical sample are presented in Figs. 1–3. Figure 1 is a semilog plot of hole concentration versus reciprocal temperature. The hole concentration p is related to temperature by

$$p \propto \exp[-(E_A - E_V)/2kT] , \tag{2}$$

where E_A is the energy of acceptors (eV), E_V is the valance band edge (eV), k is Boltzmann's constant, and T is temperature (°K). From the slopes of the plot there appears to be a series of close-lying states with $(E_A - E_V) = 0.013$, 0.053, 0.073, and 0.17 eV. This is consistent with the high defect concentrations present in Cu_2S.

A log-log plot of μ_h versus T is presented in Fig. 2. As a

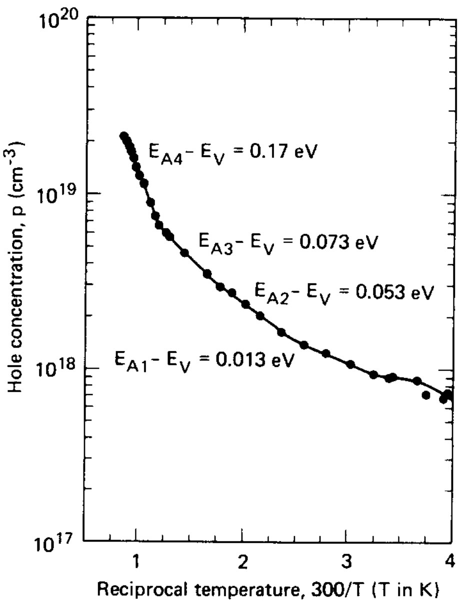

FIG. 1. Hole concentration versus reciprocal temperature.

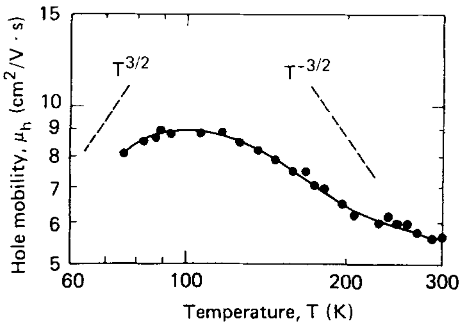

FIG. 2. Log-log plot of hole mobility versus temperature.

first approximation, it would appear that ionized impurity scattering, which has a characteristic $T^{3/2}$ dependence, dominates for $T < 90$ °K. There is some doubt as to the importance of acoustic phonon scattering at higher temperatures, contrary to the results of previous investigators.[2,3,5] The slope for temperatures greater than 100 °K is too shallow for the $T^{-3/2}$ dependence of acoustic phonon scattering. The shallow slope may be due to the influence of impurity scattering, but the fact that the data deviate from the $T^{3/2}$ dependence even more as the temperature increases suggests that another scattering mechanism is prevalent at the higher temperatures.

Least-squares fits of the data to other functional forms of μ_h were attempted. In all cases it was assumed that the various mechanisms were independent so that the general form could be expressed as

$$\frac{1}{\mu_h} = \sum_i^N \frac{1}{\mu_i}. \tag{3}$$

The maximum number of mechanisms attempted in the analysis was $N = 5$, which included ionized and neutral impurity, acoustic and optical phonon, and piezoelectric scattering. The best fit, presented in Fig. 3, is

$$\frac{1}{\mu_h} = \frac{A}{T^{3/2}} + \frac{B}{T^{1/2}[\exp(\theta/T) - 1]}, \tag{4}$$

where $A = 66.4$ V s °K$^{3/2}$ cm^{-2}, $B = 2.97$ V s °K$^{3/2}$ cm^{-2}, and $\theta = 200$ °K.

The first term of Eq. (4) corresponds to ionized impurity scattering. Conwell and Weisskopf[9] obtain this form by using a classical Rutherford scattering model. The same temperature dependence was obtained by Dingle[10] and Brooks[11] using a screened potential model. The second term corresponds to optical phonon scattering. The original formulation is due to Howarth and Sondheimer,[12] who solved the Boltzmann transport equation with a relaxation time as defined by Frohlich and Mott.[13] It was later corrected to its present form by Petritz and Scanlon.[14]

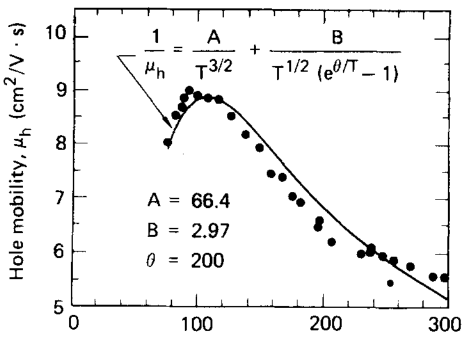

FIG. 3. Linear plot of hole mobility versus temperature, showing data and best fit.

This letter presents preliminary findings of an in-depth study of the properties of reactively sputtered Cu_2S. Hall measurements at temperatures down to that of liquid helium are in progress; a more definitive statement on the low-temperature scattering mechanism and the energy levels of defects is forthcoming.

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[1] Hirahara, J. Phys. Soc. Jpn. **6**, 428 (1951).
[2] G.B. Abdullaev, Z.A. Aliyarova, E.H. Zamonova, and G.A. Asadov, Phys. Status Solidi **26**, 65 (1968).
[3] G.P. Sorokin and A.P. Paradenko, Izv. Vyssh. Uchebn. Zaved. Fiz. **5**, 91 (1966) [Sov. Phys. J. **9**, 59 (1966)].
[4] G.P. Sorokin, I. Ya. Andronik, and E.V. Kovtun, Izv. Akad. Nauk SSSR Neorg. Mater. **11**, 2129 (1975) [Inorg. Mater. USSR **11**, 1828 (1975)].
[5] J. Bougnot, F. Gustavino, G.M. Moussalli, and M. Savelli, in *International Workshop on Cadmium Sulfide Solar Cells and Other Abrupt Heterojunctions, April* 30–*May* 2, 1975, *Newark, Delaware*, edited by K.W. Boer and J.D. Meakin (Institute of Energy Conversion, University of Delaware, Newark, 1975), p. 337.
[6] G. Armantrout, J. Yee, E. Fischer-Colbrie, D. Miller, E. Hsieh, J. Leong, K. Vindelov, and T. Bron, in *Thirteenth IEEE Photovoltaic Specialists Conference, Washington, D.C.*, 1978, (IEEE, New York, 1978), p. 383.
[7] L.J. van der Pauw, Philips Res. Rep. **13**, 1 (1958).
[8] S.S. Devlin, Ph.D. thesis, Case Institute of Technology, 1964.
[9] E.M. Conwell and V.F. Weisskopf, Phys. Rev. **77**, 388 (1950).
[10] R.B. Dingle, Philos. Mag. **46**, 831 (1955).
[11] H. Brooks, Adv. Electron. Electron Phys. **8**, 85 (1955).
[12] D. Howarth and E. Sondheimer, Proc. R. Soc. London Ser. A **219**, 53 (1953).
[13] H. Frohlich and N.F. Mott, Proc. R. Soc. London Ser. A **171**, 496 (1939).
[14] R.L. Petritz and W.W. Scanlon, Phys. Rev. **97**, 1620 (1955).