

A Solution Growth Technique for the Preparation of Copper (II) Selenide Thin Films

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A solution growth technique has been developed for the deposition of thin films of copper(II) selenide on glass substrate using a copper(II) salt solution, triethanolamine, ammonia, and sodium selenosulfate as the reacting agents. The material has been characterized through X-ray powder photography, optical absorption, and Hall measurements at room temperature. The films are found to be degenerate and p type with a Moss-Burstein shifted direct band gap of 2.14 eV.

Introduction

In recent years, chalcogenide thin films of different metal ions having semiconducting properties have found worldwide application in various fields of science and technology. When copper(II) selenide was brought in contact with a proper metal an asymmetrical resistance or rectification appeared (1, 2). However, early measurements by Schroeter (3) and Meissner (4) showed that it has metallic conduction. Nevertheless many text books on solid state treat CuSe automatically as a semiconductor, probably owing to the rectifying effect. Since single crystals of CuSe are not obtainable because of the phase transition at 53°C (5), early work on the preparation of CuSe was carried out by a direct synthesis of pure and precisely weighed components in an evacuated and sealed quartz tube at 600°C (6, 7). However, no method has yet been developed for depositing thin films of CuSe by a solution growth technique.

In this paper we report the method of preparation of thin films of CuSe by a solution growth technique and its characterization through X-ray powder photography, optical absorption spectrum, and Hall measurements.

Experimental Techniques

A total of 5 ml of 0.5 M cupric sulfate solution was taken in a 50-ml beaker to which about 8 ml of 9.8% triethanolamine (TEA) was added. With TEA less than 8 ml, a curdy white precipitate was formed which dissolved with the application of the above mentioned volume of TEA. About 6 ml of 0.25% ammonia and 5 ml of 0.45 M sodium selenosulfate solutions were then added in succession to the reaction mixture. The volume of the resulting solution was made up to 50 ml with distilled water. The bath solution was continuously stirred during the addition process with a magnetic stirrer. The solution was then poured into another beaker containing a scrupulously cleaned glass substrate, clamped vertically.

The color of the solution gradually became dark and after some time it turned deep brown to black. About 4 hr later the substrate was taken out, washed with distilled water, and dried in air. A deep brown film was found to be deposited on both sides of the substrate and on the wall of the beaker. The film thickness was determined by an optical interference method (Fizeau).

The composition of the film deposited was determined by X-ray powder diffraction technique using a Debye-Scherrer Camera and $\text{CuK}\alpha$ radiation. The material was scraped off the substrates for this purpose. The optical band gap of the deposited films was determined from their absorption spectra measured with a Cary 17D spectrophotometer. The Hall measurements for several samples of different thicknesses were performed at room temperature (30°C) to determine the carrier concentration, Hall mobility, and type of the majority carriers present. Hall voltage was measured by the

four-electrode method (8) with a compensating circuit across the Hall probes. Silver paint was used as ohmic contacts to these films. Specific conductances of the films were also determined.

Results and Discussion

Room temperature deposition for about 4 hr yields film thicknesses of the order of $0.3\text{--}0.4\ \mu\text{m}$. The diffraction lines obtained from the X-ray powder photograph of these films are shown in Table I. The tabulation also shows the standard diffraction lines of pure copper(II) selenide (hexagonal) powder taken from the ASTM Diffraction Data File. The comparison between the two shows that the process described above yields CuSe films. Hall effect measurements were carried out for samples of various thicknesses in the range of $0.3\text{--}0.4\ \mu\text{m}$ in a magnetic field of 8036 G. The Hall coefficients (R_H) of these samples were between

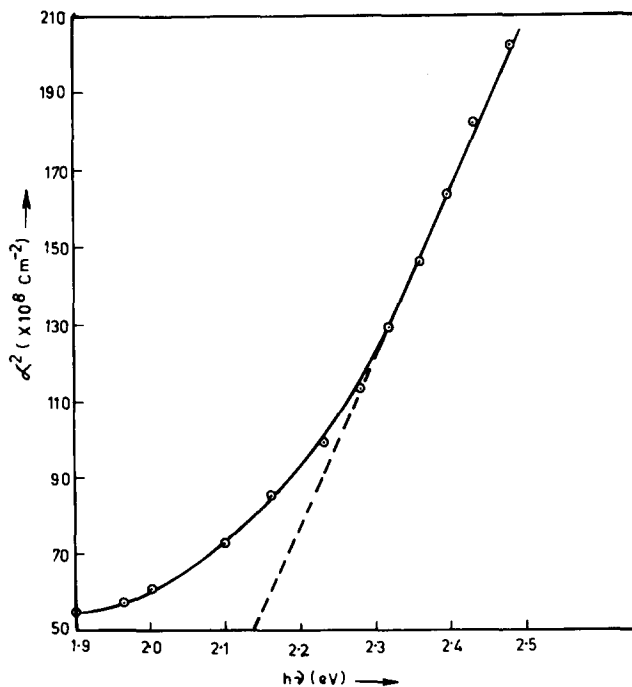


FIG. 1. Optical absorption spectrum of CuSe thin film deposited on glass substrate.

TABLE I
X-RAY DIFFRACTION LINES OF CuSe PREPARED BY
THE PRESENT METHOD

Serial number	Observed d values (Å)	d values (Å) from ASTM file for CuSe and relative intensity	Possible identification (hkl)
1	3.417	3.35(60)	101
2	3.191	3.18(90)	102
3	2.824	2.88(100)	006
4	2.189	2.19(30)	106
5	1.973	1.967(80)	110
6	1.912	1.913(4)	112
7	1.849	1.819(60)	108
8	1.781	1.785(4)	114
9	1.726	1.698(10)	200, 201
10	1.682	1.676(10)	202, 109
11	1.401	1.401(10)	207
12	1.289	1.287(6)	208
13	1.150	1.158(40)	10, 14

$(6-8) \times 10^{-4} \text{ cm}^3\text{C}^{-1}$. The experiments showed that they have a positive sign. The small Hall constants indicate a very high concentration of charge carriers. The carrier concentrations were calculated by using the equation $R_H = 1/ne$, where n denotes the carrier concentration and e the electronic charge. Carrier concentrations in the range $(7-10) \times 10^{21}/\text{cm}^3$ for these samples were obtained, which are very close to that for a bulk material reported by Ogorelec and Selinger (7). Such a high concentration of charge carriers makes the CuSe film a degenerate material. The Hall mobilities and conductances of these samples have been calculated to be $(0.5-2.5) \text{ cm}^2/\text{V-sec}$ and $(0.7-4) \times 10^3 \text{ S cm}^{-1}$, respectively. The sign of the Hall constant indicates that the majority of carriers are holes. Since no dopant has been added to the solution, the degeneracy exhibited by the CuSe films is likely to be due to the presence of copper vacancies. The change of the optical den-

sity with wavelength which has been obtained for the CuSe thin film from the Cary 17D spectrophotometer has been used to determine the absorption coefficient α , for the sample at various photon energies. A plot of α^2 vs $h\nu$ is found to be linear as shown in Fig. 1, suggesting that the band gap of CuSe is direct. Extrapolation of this curve to zero absorption coefficient gives the optical energy gap of the semiconductor, which is about 2.14 eV. The semiconductor being degenerate, its optical energy gap is equal to its actual band gap plus the Moss-Burstein shift (9). Hence the actual band gap is less than the optical energy gap determined in the present investigation.

Conclusion

A solution growth technique has been developed for depositing CuSe thin films on glass substrate. The films were found to be degenerate and p type in nature.

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