Electrical properties of silver selenide thin films prepared by reactive evaporation

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Abstract. The electrical properties of silver selenide thin films prepared by reactive evaporation have been studied. Samples show a polymorphic phase transition at a temperature of 403 ± 2 K. Hall effect study shows that it has a mobility of 2000 cm^{2}V^{-1}s^{-1} and carrier concentration of 10^{18} cm^{-3} at room temperature. The carriers are of n-type. X-ray diffraction study indicates that the as-prepared films are polycrystalline in nature. The lattice parameters were found to be $a = 4.353$ Å, $b = 6.929$ Å and $c = 7.805$ Å.

Keywords. Thin film; silver selenide; reactive evaporation; electrical conductivity.

1. Introduction

Silver selenide attracts the interest of researchers because of its application in the switching devices. The binary and ternary semiconductors are the basic materials for schottky barriers, solar cells and electronic engineering. Moreover, silver selenide belongs to the family of superionic conductors, which are of present and future technological interest. It is a well known fact that silver selenide undergoes a polymorphic phase transition. Many researchers have reported different values for this transition temperature. Damodara Das and Karunakaran (1989, 1990) reported the thickness dependence of transition temperature and activation energy. The low temperature phase below 400 K was identified as b-Ag$_2$Se with a structure of orthorhombic and the high temperature a-Ag$_2$Se has bcc structure. According to Abdullayev $et\ al$ (1983), silver selenide exists as a high temperature cubic phase (a) and low temperature orthorhombic (b) and tetragonal phase with transition temperature of about 408 K or 395 K. Moreover, the b to a transition does not occur directly but through an intermediate phase; the duration of this new phase increases from cycle to cycle. The structural data available in literature are contrary for the low temperature phase. The compound has been described as tetragonal, orthorhombic and monoclinic by different authors. Ridder and Amelinckx (1973) reviewed different structural parameters reported by different researchers. This may be due to the differences in the preparation technique.

Many methods have been used for the preparation of silver selenide thin films. Damodara Das and Karunakaran (1989) prepared the films by vacuum evaporation of silver selenide alloy followed by annealing. Abdullayev $et\ al$ (1983) used the explosive evaporation of the powdered compound in vacuum on different substrates. Okabe and Ura (1994) prepared films by flash evaporation. Sharma $et\ al$ (1990) reported chemical bath deposition technique. Somogyi and Safran (1995a,b) and Safran $et\ al$ (1992) adopted a method to deposit silver from a molybdenum boat on to substrates at 120°C and sublimated selenium over it at a substrate temperature of 200°C at a rate of 0.05 to 0.1 nm s^{-1}. Kulkarni $et\ al$ (1995) had reported the conversion of silver films to silver selenide films by chemical method. Bernede $et\ al$ (1982) used a method of evaporating powdered silver selenide from a tantalum boat. But it undergoes partial decomposition. The films show metallic behaviour between 77 K and 300 K and with a chemical composition, Ag$_{2-x}$Se$_{1+x}$ with $0.01 \leq x \leq 0.05$.

Kaito $et\ al$ (1982) used a method of vacuum deposition of selenium on glass substrates cooled to liquid nitrogen temperature. Holey silver films were prepared by vacuum evaporation on cellulose acetobutyrate. The selenium films were wet stripped from the substrate and mounted on the holey silver films. Ag$_2$Se crystals were produced by reaction of selenium films with silver films at room temperature. Constantinescu (1976) investigated the properties of thin films prepared by separate evaporation of components (Ag first and then Se) in a vacuum of about 10^{-6} m·bar on NaCl and KCl substrates. Saito $et\ al$ (1981) also reported the same technique. This variety in the preparation technique leads to composition inconsistency. In this context we tried a method in which not much work has been reported. We report here preparation of the Ag$_2$Se thin film by reactive evaporation and its electrical conductivity, Hall coefficient and mobility.

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2. Experimental

In the present work we report the reactive evaporation of silver selenide thin films. This technique is also known as Gunther's technique or three-temperature method (Anderson 1966). It is based on the fact that continuous condensation of a given vapour at a given rate takes place only if the temperature of the substrate drops below a certain critical value. For many binary systems, it has been found that a stoichiometric interval exists with limited degree of freedom in selecting the individual components and substrate temperature for obtaining a particular compound of the system (George and Pradeep 1985; John *et al* 1994). In this work we employed a conventional vacuum system with two separate sources. The silver atoms reaching the substrate react with selenium atoms present on the substrate surface, and the compound film is formed. The need of synthesis of compound from elements prior to deposition, which is a tedious process, can be eliminated by this technique. Moreover, the requirement of high temperature for evaporation of compound and subsequent decomposition are eliminated. Because of the high volatile elemental pressure, some unreacted volatile element is likely to be trapped in the growing film, changing the film properties, especially at low substrate temperature is the disadvantage of this technique.

Cleaned optically flat glass substrates were used for the preparation. High purity silver (99·999%) and selenium (99·99%) were utilized for evaporation. Silver was evaporated from a molybdenum boat and selenium from a glass crucible kept in a molybdenum basket. The glass substrate was mounted on a substrate holder with a heating arrangement and temperature was measured with the help of a fine wire chromel and alumel thermocouple. The temperature of the substrate was maintained at 398 ± 5 K throughout the deposition. The rate of deposition and impingement rate were calculated for different components. The impingement rate is given by the equation

$$dN_m/A_r\, dt = N_a r_m d'/M_m,$$

where N_a is the Avogadro number, r_m the density of the bulk material in g cm^{-3}, M_m the molar mass of the material in g mol^{-1}, A_r the reactive surface area in cm^2 and d' the deposition rate in cm s^{-1}. The following deposition parameters were used for obtaining silver selenide thin films.

Impingement rate of silver
$$\approx 1\cdot93 \times 10^{15} - 2\cdot07 \times 10^{15} \text{ atoms cm}^{-2}\text{s}^{-1}.$$

Impingement rate of selenium
$$\approx 1\cdot08 \times 10^{15} - 1\cdot187 \times 10^{15} \text{ atoms cm}^{-2}\text{ s}^{-1}.$$

Substrate temperature = 398 ± 5 K.

The deposition rate was controlled by adjusting the current through the filaments. A vacuum of the order of 10^{-5} m·bar was maintained in the chamber throughout the deposition. The substrate temperature had been maintained at the coating temperature for 45 min to 1 h after deposition to stabilize the reactions.

Electrical conductivity and Hall effect measurements were carried out on the as prepared samples. Film thickness were measured using the well known Tolansky's multiple beam interferometric technique (Tolansky 1948).

3. Results and discussion

The most accepted crystal structure of low temperature Ag$_2$Se is orthorhombic with the $P2_12_12_1$ space group. Figure 1 shows the X-ray diffraction pattern of a typical silver selenide thin film prepared at a substrate temperature of 398 ± 5 K. This indicates the existence of (002), (013), (004) and (014) planes of reflections of orthorhombic phase of silver selenide. When annealed no additional peak was found. Table 1 shows the *d* spacing observed along with the standard data (ASTM card 24-1041). The lattice parameters were calculated and its values are $a = 4\cdot353$ Å, $b = 6\cdot929$ Å and $c = 7\cdot805$ Å, which are very close to the reported values. Damodara Das and Karunakaran (1989) reported the XRD pattern showing only (002) and (004) planes. Kulkarni *et al* (1995) obtained a film of orientations (002), (111), (210) and (204) planes. The grain size of the as prepared films has been calculated using the Scherrer formula. It is found that the grain size is of the order of 36 nm.

The electrical characterization was carried out in a conductivity set-up coupled with a rotary pump to pump down to 10^{-3} m·bar. Samples with dimension $2\cdot5 \times 30$ mm were used for the study. A constant voltage was applied across the sample and the variation of current with temperature was studied using silver paste as the ohmic contact. Figure 2 shows the variation of conductivity (*s*) with temperature of the sample for four continuous heating and cooling cycles. It shows the existence of hysteresis in the conductivity with temperature. Films showed a
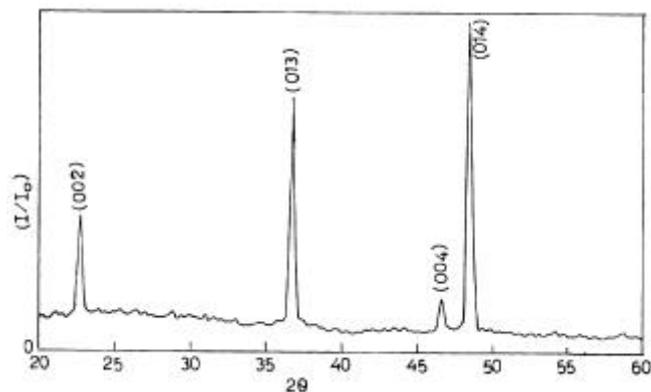

Figure 1. X-ray diffractogram of the silver selenide thin film prepared at 398 K.

semiconducting nature up to 403 K and then it showed a metallic nature with rise in temperature. The polymorphic phase transition temperature was observed at 403 ± 2 K for every sample. The reverse transition occurred at about 373 ± 5 K while cooling. This shows the reversible nature of the transition. The transition temperature was observed to decrease to 390 ± 2 K for the second cycle of heating. From the figure it is clear that after the second cycle of heating and cooling the electrical properties remain the same i.e. the conductivity variation with temperature retraces nearly the same path of second cycle. Abdullayev *et al* (1983) studied the phase transition phenomenon using the kinematic electron diffraction technique. Analysis of this pattern revealed that heating results in the conversion of the initial *b*-Ag_2Se to *a*-Ag_2Se while cooling induces the reverse process. According to them the temperature of the reverse transition from the *a* to *b* phase was found to increase with repeated thermal cycling; while it was only 343 K for the first cycle, it had increased to 383 K by the sixth cycle. In the present case the reverse transition temperature decreased from 378 K in the first cycle to 367 K in the second cycle and it was 373 K in the third and fourth cycles.

The grain size was found to increase from 36 nm to 43 nm after the first thermal cycle. These observations

show that the phase transition process is the result of an increase in the number of crystallization centres, the critical dimension of which can be achieved in a very short time. The increase in electrical conductivity after the first thermal cycle can be expected because of the increase in the grain size and removal of imperfections by heating cooling cycle as evident from the XRD measurement. Phase transition temperature is inversely proportional to the thickness of the film and the bulk material shows much less transition temperature (Damodara Das and Karunakaran 1990). Therefore, the decrease in transition temperature after the first cycle is invariably due to the increase in the grain size. The shift in phase transition temperature, ΔT, can be expressed using the following expression assuming that the grains are spherical

$$\Delta T = T_B - T_T = \Delta sT_B/Lt,$$

where L is the heat of transformation, T_B the transition temperature in the bulk material and T_T the transition temperature in the thin film state with thickness t; $\Delta s = s_2 - s_1$ is the change in the function of specific external surface and grain boundary surface energies during phase transition. s_1 refers to the high temperature and s_2 refers to the low temperature phases (Damodara Das and Karunakaran 1990). This expression is valid in our case also as the grain size is a function of thickness and we replace thickness to grain size. T_T can increase or decrease, depending on whether Δs is positive or negative. In the phase transition of Ag_2Se thin films, since the transition temperature increases with a decrease of thickness, it can also be inferred that Δs is negative.

Silver selenide is a non-stoichiometric compound in both *a* and *b*-phase and dissolved Ag atoms are present. The phase transition and hysteresis are related to the kinetics of the nucleation of the phase transition of the *b*-phase and clustering of Ag atoms at trapping centres (Kumashiro *et al* 1996). The high temperature phase
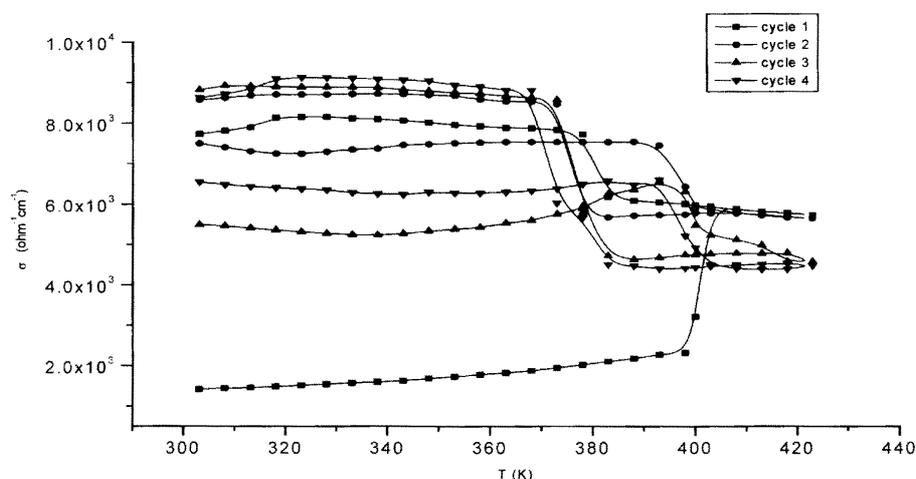
Table 1. X-ray diffraction data for Ag_2Se thin film prepared at 398 K.

(*hkl*)	Standard pattern (ASTM card: 24-1041)		Prepared film	
	d (Å)	I/I_0	d (Å)	I/I_0
(002)	3·877	6	3·9141	36
(013)	2·429	31	2·4436	66
(004)	1·940	7	1·9455	13
(014)	1·872	23	1·8773	100

Figure 2. Variation of conductivity (*s*) with temperature showing four continuous cycles.

behaves as a metal and its structure is body centred cubic, with lattice parameter $a = 0.498$ nm and two Ag_2Se molecules in a unit cell. The Se and Ag atoms, which are statistically distributed among 42 interstitial sites of the unit cell, preferentially filling up the largest interstices, form the *bcc* lattice. Such a structure predicts that all the Ag ions are mobile. Hence ionic conductivity due to Ag ions is large in the high-temperature phase and increases slightly with increasing temperature.

From the $\ln I$ vs $1/T$ curve the activation energy was calculated. It was found that activation energy was 0.058 eV for films of thickness of the order of 200 nm. Figure 3 shows the $\ln I$ vs $1/T$ graph from 300 K to 400 K. Ferhat and Nagao (2000) studied the electrical properties of Ag_2Se from 70 K to 300 K. At room temperature they observed a conductivity of 770, 1988 and 826 $ohm^{-1} cm^{-1}$ for their three different samples.
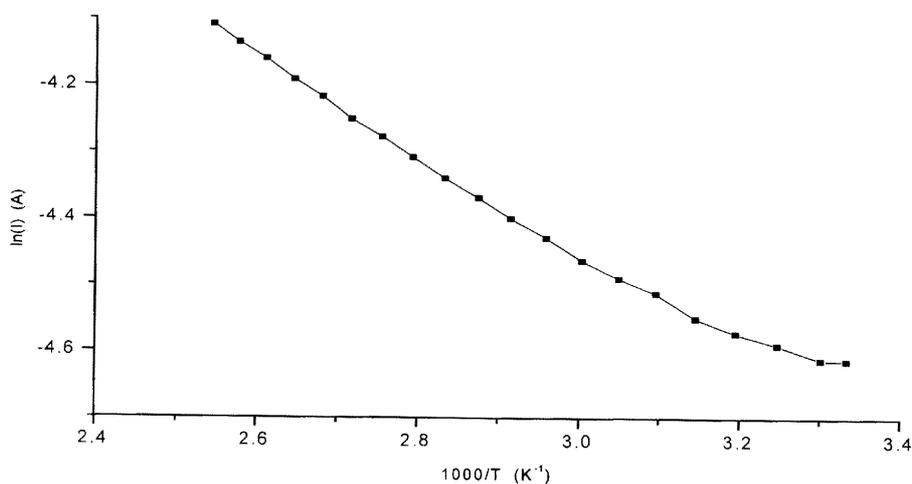
Figure 4 shows the variation of Hall coefficient, R_H, with temperature. R_H decreases with increase in temperature. At and around the transition temperature it shows a sudden fall and then remains almost constant. The variation of mobility, μ_H, with temperature is shown in figure 5. Mobility varies from 2000 $cm^2 V^{-1} s^{-1}$ to 250 $cm^2 V^{-1} s^{-1}$ with temperature. The type of carrier was found to be of electrons. Damodara Das and Karunakaran (1989) reported a value of 2000 $cm^2 V^{-1} s^{-1}$ for mobility at room temperature. Somogyi and Safran (1995a,b) also reported the drastic fall in μ_H near the transition temperature.

Carrier concentration varies from 10^{18} cm^{-3} to 10^{19} cm^{-3} with increase in temperature. At the phase transition temperature it was observed that the carrier concentration suddenly increased by a factor of ten. Somogyi *et al* (1994) observed irregularities in mobility and Hall coefficient of monocrystalline and polycrystalline

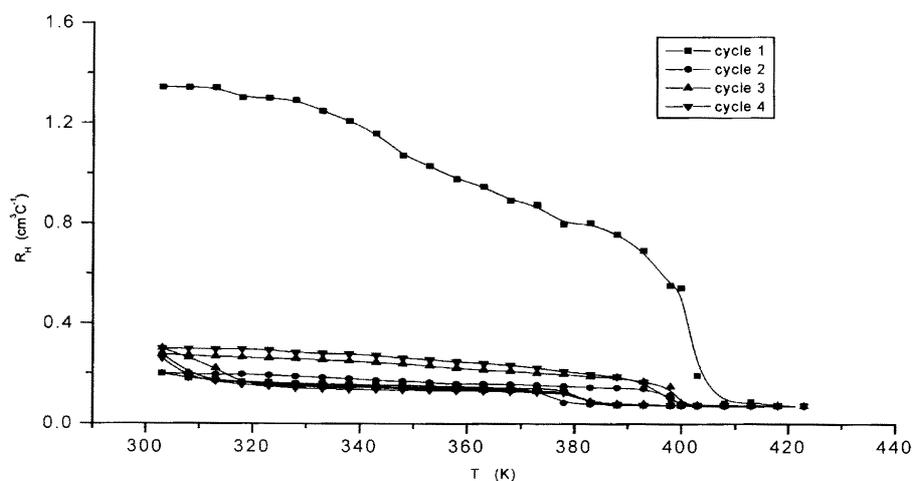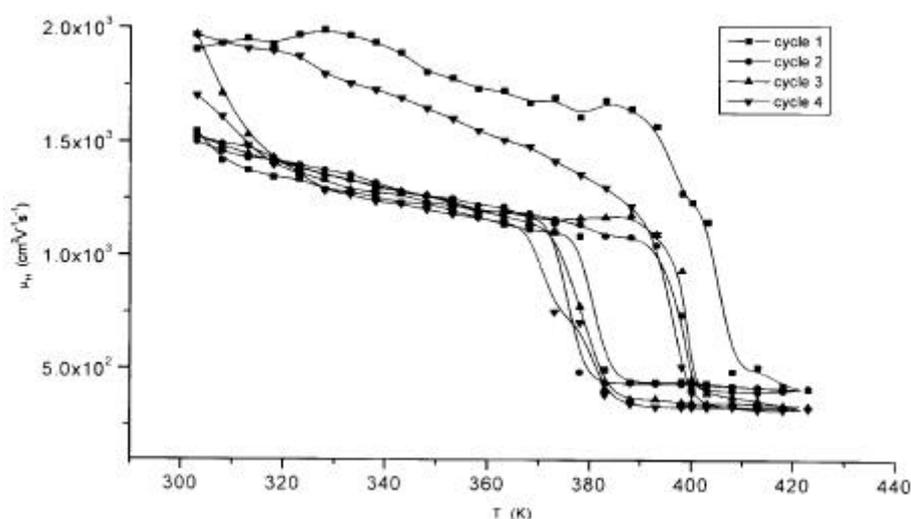**Figure 3.** Variation of ln (I) versus inverse temperature of a typical silver selenide thin film below 400 K.

Figure 4. Variation of Hall coefficient (R_H) with temperature showing four continuous cycles.

Figure 5. Variation of Hall mobility (μ) with temperature showing four continuous cycles.

samples of silver selenide. But in the present work we did not observe such irregularities.

4. Conclusions

Silver selenide thin films were prepared by reactive evaporation. X-ray studies revealed the formation of silver selenide. Films formed were of polycrystalline nature. Samples showed a semiconducting nature up to 403 K above which, they showed a metallic behaviour. This may be due to its structural change from orthorhombic to cubic phase. The polymorphic phase transition was observed at 403 ± 2 K. The decrease in transition temperature is due to the increase of grain size after the thermal cycle. The Hall coefficient, carrier mobility and carrier concentration were measured.

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