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PROPERTIES OF VACUUM DEPOSITED Ag_2Se THIN LAYERS

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A recent vacuum deposition method using the topotaxial reaction of Ag and Se allowed us preparation of both epitaxial and polycrystalline Ag_2Se layers on NaCl and silica substrates. Low temperature and reproducibility of Ag_2Se layers facilitate investigation of this ionic semiconductor. The formation and the reversible phase transition (orthorhombic – cubic) of Ag_2Se films are revealed by transmission electron microscopy. Galvanomagnetic properties of 87 nm thick layers with different carrier concentrations were investigated in the temperature range of 77 – 430 K. Properties of poly- and monocrystalline samples are compared. Influence of the phase transformation on the electrical properties are shown.

1. Introduction

Silver chalcogenides became objects of very exciting investigations as a jumpwise increase of their conductivity was observed at a critical temperature during heating [1]. The only selenide of silver, Ag_2Se, has been widely investigated since the late fifties [2-4]. Early works discussed questions of the preparation of Ag_2Se, its crystallographic and electronic properties, and its first order polymorphic phase transition [2-10]. Experimental work was probably limited by the difficulties of the

reproducible preparation of Ag_2Se, especially in its thin-film form by electrochemical methods [11-13].

In this work, Ag_2Se layers, obtained by the reaction of vacuum deposited Ag and Se, are investigated by electrical measurements and electron microscopy. Properties of the layers prepared by the selenization of mono- and polycrystalline Ag layers are discussed and compared.

2. *Layer preparation*

Ag_2Se have been obtained first by electrochemical methods [11-13]. A more convenient method was the melting of the substances together at 1000 – 1100 °C in vacuum, keeping this high temperature for several (up to 10) hours, followed by slow cooling [13,14]. Dhere and Ghoswami [14] applied vacuum deposition after the above process in order to get thin films. The formation of the compound directly on the surface was carried out by Sharma [15], depositing the components of stoichiometric ratio simultaneously from tungsten boats. He applied an annealing of the deposited films for several hours. The disadvantages of the latter methods are the long heat treatment procedures at high temperatures. In this work, a low temperature vacuum technolgy was used to obtain Ag_2Se layers.

It was shown by decoration techniques that the density of nucleation centres on the surface of as-cleaved NaCl monocrystals was about 1.5×10^{11} cm^{-2}. The nucleation density was increased up to and above 1×10^{12} cm^{-2} by chlorine adsorption on the NaCl surfaces treated with water. Presence of active impurities on the surface (chlorine) and an increased nucleation density facilitate the epitaxial growth of the silver in the [100] direction. Futhermore, the temperature for epitaxial growth is decreased, down to 80 °C for Ag [16-18].

Ag_2Se layers have been obtained on NaCl and Si substrates, however, by successive deposition of (monocrystalline or polycrystalline) Ag films and selenium. The reaction occured during the Se deposition. To obtain epitaxial monocrystalline Ag layers, the cleaved (100) NaCl substrates were rinsed with double-distilled water that was dried in air and exposed to pure chlorine gas for 5 min [18]. Polycrystalline Ag layers were deposited onto either air cleaved (100) NaCl or Si wafers covered with SiO_x. (Samples obtained by the selenization of mono- and polycrystalline silver films will be referred to as A-type and B-type samples, respectively).

The substrates were fixed on a plate oven. The substrate temperature was kept at about 120 °C during silver deposition. Silver was deposited of different thicknesses, by thermal evaporation from a tungsten boat, at a rate of 1 nm/s. Selenium was deposited at 200 °C onto the silver films at a rate of 0.1 nm/s or less. Due to these conditions, the formation of the binary alloy occured already during the Se deposition. Slightly more selenium was evaporated than necessary for stoichiometry, what assured that the entire amount of Ag turned to selenide. The Se excess was then sublimated from the surface by keeping the samples at the deposition temperature for 20 to 60 minutes.

3. *Microscopic observations*

Figure 1 shows the cross-sectional transmission electron micrographs (XTEM) of a monocrystalline (a) and a polycrystalline (b) Ag layer deposited on pretreated NaCl and on SiO_x/Si substrates, respectively. The XTEM preparation was carried out by a special mechanical preparation followed by ion beam thinning described in Ref. 19.

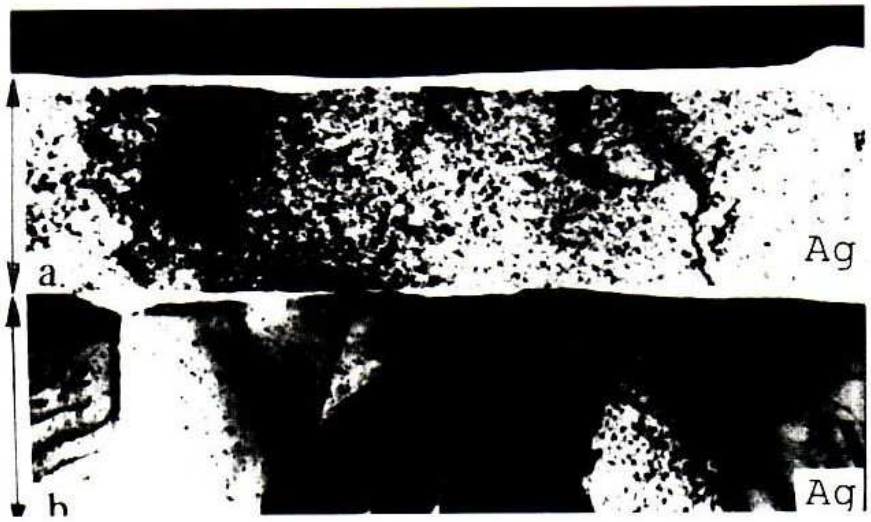

Fig. 1. Cross-sectional transmission electron micrographs of (a) single crystalline and (b) polycrystalline silver films deposited on pretreated NaCl *and oxidised* Si *substrates, respectively. The thickness of the Ag layer was 500* nm.

Figsures 2a and 2b show XTEM micrographs of the fully selenized monocrystalline and polycrystalline Ag layers. It is clearly seen that the Ag_2Se layer developed from a (100) oriented Ag film (A-type) is a (100) monocrystal, having relatively smooth and parallel interfaces. However, the Ag_2Se films developed from a randomly oriented polycrystalline Ag exhibit large single crystals and film surface is extremely rough (B-type).

Figure 3 shows the transmission electron micrographs of an Ag_2Se film prepared by the reaction of a single crystalline Ag film of 30 nm thickness and selenium (A-type). The low temperature orthorhombic modification (a) with parameters $a = 0.43$ nm, $b = 0.71$ nm and $c = 0.7$ nm and the high temperature bulk centered cubic modification (b) ($a = 0.498$ nm) could be imaged in situ by changing the intensity of the investigating electron beam. These results are in agreement with literature data obtained for thinned Ag_2Se bulk samples [8]. The phase transformation has been reached at 100 kV accelerating voltage with current densities above 0.5 A/cm^2.

Similarly to the results of electrical measurements discussed later, the reversibility and the hysteresis of the phase transition have been detected also by these in situ microscopic observations.

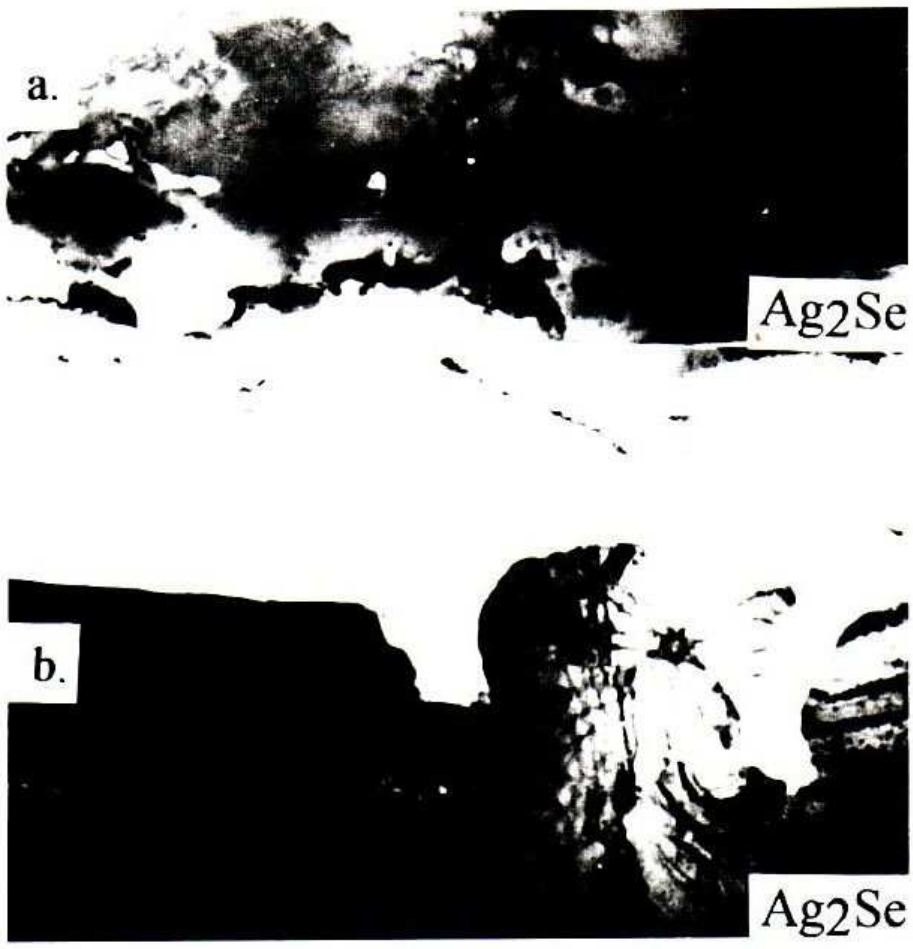

Fig 2. Cross-sectional transmission electron micrographs of (a) monocrystalline and (b) polycrystalline silver films after selenization and Ag_2Se *formation on pretreated* NaCl *and oxidised* Si *substrate, respectively.*

4. Galvanometric measurements

Non-conducting character of the substrate materials allowed us to investigate electrical properties of the Ag_2Se layers. Van der Pauw measurements have been

performed by DC technique. Preliminary experiments have proven the presence of an ionic transport of the electric charges. For these measurements, a compromise between contradicting requirements (sensitivity of measurements and ionic transport) had to be found. Therefore, low sample currents (<10 mA) were used and each measurement was immediately repeated with the opposite polarity. The applied magnetic field was 0.35 T. The temperature range included the critical temperature of the phase transformation: 77 K – 430 K. Electric contacts to the layers have been made either by vacuum deposited gold layers or by droplets of conducting silver paste.

Electric conductivity and Hall effect have been measured and carrier concentration (n) and carrier mobility (μ) have been calculated: $n = -1/(eR_H)$ and $\mu = R_H/\rho$, where R_H is the Hall constant, e is the electron charge and ρ is the resistivity. Heating and cooling cycles were applied during the temperature-dependence measurements. All the samples have shown n-type conductivity in the whole temperature range of investigations.

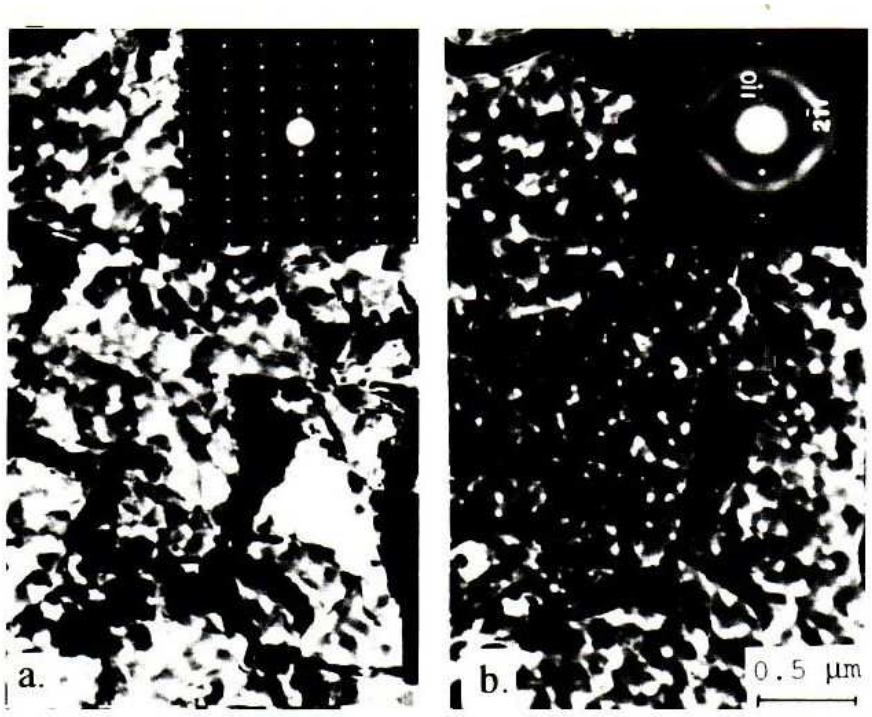

Fig. 3. Transmission-electron-microscopic view of the low temperature or orthrombic phase (a) and the high–temperature cubic phase (b) of a 87 nm *thick* Ag_2Se *film deposited on pretreated* NaCl *substrate. The same areas are shown. Insets show selected area electron diffraction patterns.*

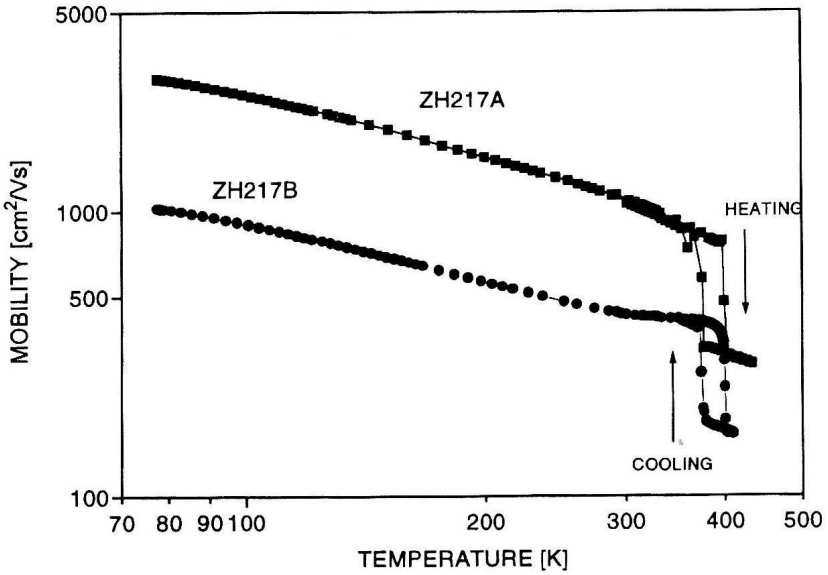

Fig. 4. Temperature dependence of the electron mobility of Ag_2Se *layers in heating and cooling regimes.*

Figure 4 shows typical mobility versus temperature plot of one A- and one B-type sample. Practically no differences in their behaviour have been found. Figure 4 shows also the influence of the phase transformation on the mobility of electrons. Such sudden changes were observed also with $\rho(T)$ and $n(T)$ curves. A hysteresis of the mobility is clearly seen, demonstrating the hysteresis of the phase transition. It was observed first by galvanomagnetic measurements [20, 21].

The determination of the exact value of the critical temperature requires that the last temperature point before the transformation and the first one after the jump-wise change in parameters are very near to each other. For this a special temperature program was applied for electric measurements. The heating rate in the region of phase transformation was very low (less than 1 K/min).

5. *Conclusions*

Ag_2Se layers have been prepared by a new temperature vacuum technology based on the possibility of the low temperature deposition of mono- and polycrystalline Ag layer on chlorine-pretreated and on as-cleaved NaCl or SiO_x/Si surfaces, respectively. Formation of the binary alloy takes place also at low temperatures in vacuum conditions during the Se deposition.

Electron – microscopic, electron – diffraction and galvanomagnetic studies have demonstrated properties of thin Ag_2Se layers. Results are in agreement with the

results obtained on bulk material and other layers. Hysteresis of the phase transformation has been shown both by electron microscopy and galvanomagnetic measurements. The results show that this convenient low temperature technology effectively facilitates further investigation of physical properties of Ag_2Se layers and further research in the field of better understanding of the ionic conductors. Also, feasibility of devices can be simplified.

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SVOJSTVA TANKIH SLOJEVA Ag_2Se NAPARENIH U VAKUUMU

Nedavna metoda naparavanja u vakuumu primjenom topotaksijske reakcije Ag i Se omogućuje izradu epitaksijskih i polikristaliničnih Ag_2Se slojeva na NaCl i kremenim podlogama. Niska temperatura i ponovljivost Ag_2Se slojeva olakšava proučavanje tog ionskog poluvodiča. Stvaranje i reverzibilan fazni prijelaz (ortorombski-kubni) Ag_2Se sloja ustanovljen je transmisijskom elektronskom mikroskopijom. Galvanska svojstva sloja debljine 87 nm s različitim koncentracijama pokretnih nositelja naboja ispitivana su u području temperature 77–430 K. Ispitan je utjecaj faznog prijelaza na električna svojstva.