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Ohmic electrodes for dark electronic conductivity measurements in Ag_2S thin films

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Silver sulfide is an ionic compound with semiconductor properties. As a result, it exhibits a mixed conductivity – electronic and ionic, their separate measurement being a serious experimental problem. In the case of ionic conductivity, this problem is successfully solved by applying double electron blocking AgI/Ag contacts. In the present paper, ion blocking contacts are applied for DC measurement of the dark electronic conductivity of Ag_2S. It is demonstrated that the double AgBr/Au electrodes are ohmic and suitable for reliable evaluation of the electronic current parameters, in the volume as well as in the subsurface region of Ag_2S thin films.

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1. Introduction

The preparation of Ohmic contacts for DC measurements could be a serious problem when the electronic transport in semiconducting or insulating materials is studied. In the case of mixed conductivity - ionic and electronic, which exists in Ag_2S, the choice of contact material is much more complicated, since both components of the electric transport have to be measured separately. This problem was successfully solved at the beginning of the past century for dark ionic conductivity measurements, by applying double AgI/Ag electron blocking contacts [1]. Until now, the electronic component of the electric transport in Ag_2S has been measured with different metal electrodes like Pd, Au, Ag, Cu and Cd, which results in unreliable conductivity data [2].

The present paper aims to demonstrate that double AgBr/Au ion blocking electrodes are Ohmic and suitable for reproducible electronic conductivity measurements in Ag_2S.

2. Experimental

The samples studied are epitaxially grown stoichiometric Ag_2S films deposited onto mica substrates by thermal vacuum co-evaporation of high purity S (99.999%) and Ag (99.99999%) from separate sources. All details of this preparation technique are presented in a previous paper [3]. In the present study, samples with different thicknesses between 100 nm and 400 nm are investigated. As mentioned in [3], the film thicknesses are measured using a Tolanski Å-Scope Interferometer (Varian).

The electronic conductivity of Ag_2S films is measured with AgBr/Au electrodes. The choice of silver bromide as the ion-blocking material is based on the long-life stability of sulfur sensitized photographic materials, in which the sensitivity centres are Ag_2S nano-specks formed on the AgBr surface [4]. The electronic concentration in silver bromide is relatively low, but the electron drift mobility is high, comparable to the one in Ag_2S. Au or double Au/PbS electrodes are used also for control measurements, since lead sulfide is known as a purely electronic conduction material [5]. The configuration of all electrodes is arranged as 1 mm narrow planar strips, vacuum deposited onto the Ag_2S films surface. The double electrodes are prepared by consecutive thermal evaporation of AgBr or PbS and Au as the bottom and top electrodes on Ag_2S surface, respectively. The starting materials are of extremely high purity - 99.99999% for AgBr and 99.9% for PbS. In both cases, the halide or chalcogenide film thickness is 200 nm and the thickness of the Au film about 400 nm. Special precautions are taken in order to avoid any displacement of the metal electrodes out of the narrow AgBr or PbS strips, thus preventing undesirable direct contact of Au with the silver sulfide film. The electrodes extend beyond the Ag_2S film, and Au contacts are connected to the measurement circuit via highly conductive Ag paste.

All details of the conductivity measurements are described earlier [6]. It should be mentioned here that the electrical transport in the samples is measured parallel to the surface with a four arm Weathstone bridge, guaranteeing an overall accuracy of the evaluated resistance ±5 %. Short DC current pulses of about 1 second and 100 mA with alternate consecutive polarities are applied to the bridge, in order to avoid the undesirable effects of polarization or dissociation of Ag_2S at the film/electrode interface. A specially designed thermostat allows us to follow the temperature dependence of the resistance in dry pure nitrogen, within a temperature interval 20 °C – 170 °C with an accuracy of ± 0.5 °C. Before the conductivity measurements, the sample is annealed in the thermostat for one hour at 170 °C.

The surface morphology of the samples studied is investigated using a scanning electron microscope (SEM 515 Philips). Elemental analysis of the free or electrode covered area of the films is made by means of energy dispersive spectroscopy (EDS) and X-ray mapping (Philips SEM 505/EDAX 9100).

3. Results

Fig. 1 represents the Arrhenius plot of the DC conductivity σ_m of a 120 nm thick Ag_2S film, as measured with the different electrodes. It is clearly seen that the σ_m values are highest when AgBr/Au electrodes are used. However, when the intrinsic resistance of the PbS film is taken into account, the values of σ_m measured with PbS/Au correspond well with the Ag_2S conductivity data obtained with AgBr/Au electrodes. The comparison made for 400 nm thick silver sulfide films leads to the similar results.

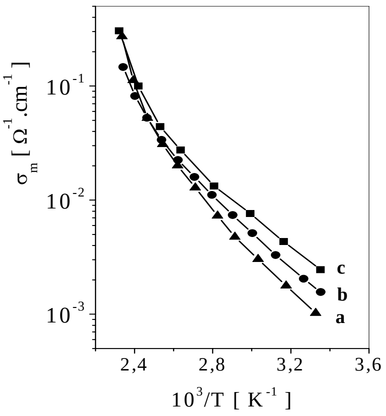

Fig. 1. Arrhenius plot of the DC-conductivity of a 120 nm thick Ag_2S film, as measured with (a) Au-; (b) PbS/Au- and (c) AgBr/Au-electrodes.

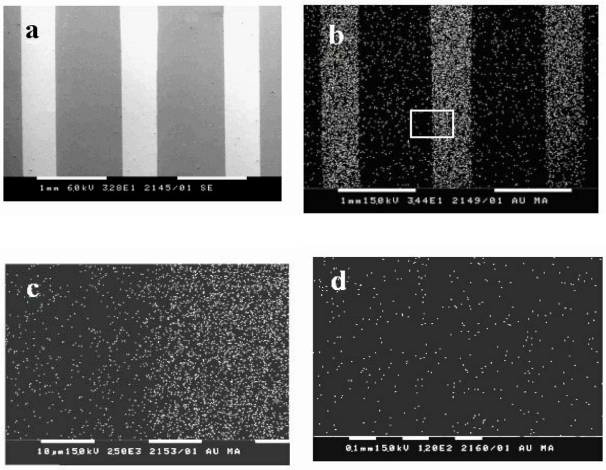

Fig. 2. Electron micrographs of a 400 nm thick Ag_2S sample with vacuum deposited Au electrodes on the film surface: (a) SEM secondary electron image, tilt angle 0 and EDS X-ray maps (Au M_α): (b) of the same sample, (c) selected area from (b), (d) virgin sample without electrodes.

The surfaces of 400 nm thick Ag_2S films with Au electrodes visualized in SEM is shown in Fig.2a. The corresponding EDS elemental analysis is shown in the same figure as Au distribution observed by X-ray mapping (Fig.2b). The electrode edge (Fig.2c) and the observable Au background by mapping films without any electrodes (Fig.2d) are also given at higher magnification for comparison. All parts of this figure demonstrate that some gold is diffused from the electrodes into the Ag_2S film. It should be noted here that the EDS electron probe microanalysis confirms the stoichiometric ratio Ag:S=2:1. Additionally, neither Au nor Br diffusion in Ag_2S samples from AgBr/Au electrodes is detected. For this type of electrode the current - voltage (I-V) characteristic is presented in Fig. 3 at room temperature. At the voltage values usually applied in this study (-3V - +3V), there is a linear dependence, which is valid for the entire temperature region studied. This is unambiguous evidence that AgBr/Au electrodes are Ohmic for Ag_2S, at least for the experimental conditions in the present paper.

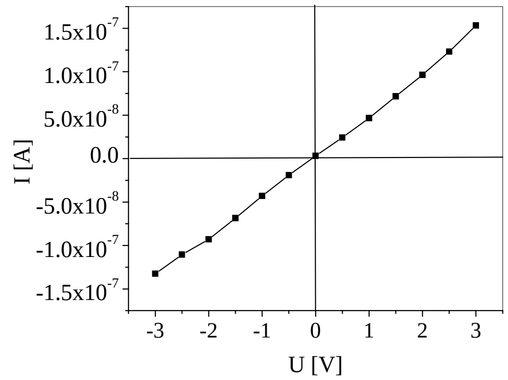

Fig. 3. Current – Voltage curve of a 120 nm thick Ag_2S film, as measured with AgBr/Au-electrodes.

4. Discussion

The results presented in this study clearly confirm that Au electrodes are not suitable for electric transport measurements in Ag_2S, since this metal diffuses very easily from the electrodes into the chalcogenide. According to the literature, Ag_2S could be strongly doped with Au above 400°C. Gold and silver are cognate metals and have a high affinity to intermix. This leads to Ag_2S decomposition, according to the following reaction [7]:

$$mAg_2S + nAu = Ag_{2m}Au_n + mS$$

Obviously, Au could penetrate into Ag_2S films even at room temperature, as follows from the X-ray mapping of the samples studied (Fig.2. b, c). It is well known that gold atoms and nanoclusters are deep electron traps in silver halides [8]. Therefore, it is reasonable to assume that this metal plays the same role in Ag_2S, thus reducing the concentration of free electrons. This could be an explanation of the lower conductivity measured with Au electrodes in the samples studied.

The best demonstration that the double electrodes proposed here are really Ohmic is the result that the bulk conductivity of Ag_2S thin films measured with AgBr/Au contacts is equal to that for single silver sulfide crystals [6]. Recently, we have shown that from the experimental conductivity data (Fig. 4) it is easy to separate the bulk σ_b from the surface component σ_s of the electronic transport in Ag_2S thin films with different thickness d. The measured conductivity per unit area σ_t follows a linear dependence on d, according to the equation (1):

$$\sigma_t = \sigma_m d = \sigma_s + \sigma_b d \qquad (1)$$

Thus, σ_s or σ_b are obtained from the intercept, respectively from the slope of the linear curves σ_t vs. d at different temperatures. It is shown in a previous paper [6] that following this procedure, the temperature dependences of σ_b and σ_s are obtained. These curves are also included in Fig.4.

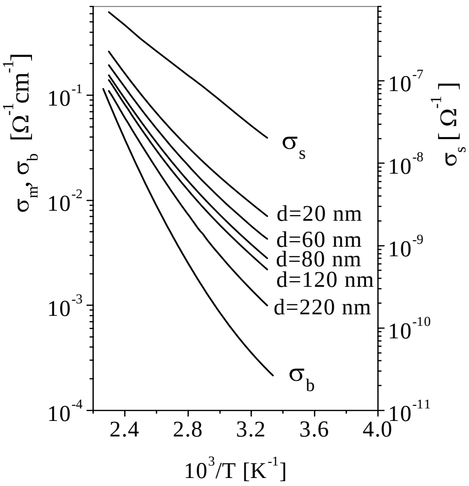

Fig. 4. Arrhenius plot of theDC conductivity of Ag_2S films of different thickness measured with AgBr/Au electrodes, as well as the bulk and surface conductivity of silver sulfide [6].

The measured high surface conductivity demonstrates for the first time that an electronic space charge layer exists near the Ag_2S surface. Proper analysis of σ_b and σ_s allows us to evaluate all parameters of the electronic transport in the bulk, as well in the subsurface region of Ag_2S: n_b and n_s – the intrinsic electronic concentration in the bulk and in the subsurface region respectively, μ_d - the electron drift mobility, λ - the thickness of the electronic space charge layer in the subsurface region, Φ_s – the surface potential and n_c – the concentration of the compensating surface charges. The results obtained for two different temperatures are summarised in Table 1 [6]. The data for λ, Φ_s and n_c at 303 K are missing, since in this extrinsic region the type and the concentration of the incorporated in Ag_2S impurities are unknown.

Table 1. Parameters of electronic transport as well as of the space charge layer of Ag_2S thin films [6].

T[K]	385	303
n_b [cm^{-3}]	5.87×10^{14}	8.39×10^{12}
μ_d [cm^2/Vs]	99	181
n_s [cm^{-2}]	1.45×10^{10}	7.01×10^{8}
λ [nm]	165	-
Φ_s [mV]	24	-
n_c [cm^{-2}]	1.02×10^{10}	-

Additionally, the band gap calculated from the bulk activation energy of σ_b for the intrinsic region is E_{gap} = 1.3 eV. It should be stressed that the values of n_b, μ_d and E_{gap} correspond very well with the most reliable data of these parameters for Ag_2S single crystals [9] and thin films [10,11].

Finally, the coincidence of electronic conductivity measured with AgBr/Au and PbS/Au electrodes does not mean that a double electrode based on lead sulfide is also suitable for electron transport measurements in Ag_2S. PbS is soluble in silver sulfide and about 2% of lead could be incorporated into the Ag_2S crystal lattice at 200°C [12]. This quantity has to be lower in the temperature interval 20° - 170°C studied in the present paper. However, it could not be neglected when the intrinsic electronic properties of silver sulfide are investigated. Therefore, PbS/Au electrodes are used for starting experiments only, in order to confirm that the measured conductivity is purely electronic.

5. Conclusions

The present paper offers new AgBr/Au double electrodes, suitable for the investigation of electronic transport in Ag_2S. These electrodes are simultaneously ohmic and ion blocking, which allows us to measure the intrinsic electronic conductivity of epitaxially grown thin films. Furthermore, it is shown that by applying AgBr/Au electrodes, an enhanced surface conductivity as compared to the bulk of the Ag_2S is established, thus demonstrating for the first time the existence of an electronic space charge below the silver sulfide surface. These results prove the applicability of AgBr/Au electrodes in other electronic transport measurements, not only in thin films but also in single crystals of silver sulfide.

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