Measurements of the Hall Effect on Cu-As-Se-I Amorphous Thin Films*

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The manuscript reports on measurements of the Hall effect performed on Cu$_x$(As$_{38.5}$Se$_{54}$I$_{7.5}$)$_{100-x}$ amorphous thin films deposited onto glass substrates. Obtained results showed that conductivity of investigated samples is in the range from $10^{-12}$ $\Omega^{-1}$cm$^{-1}$ to $10^{-10}$ $\Omega^{-1}$cm$^{-1}$. Results also pointed to the switching of p-type conductivity for samples with 0 at% and 5 at% of copper to n-type conductivity detected for sample with 25 at% of copper. [DOI: 10.1380/ejssnt.2012.535]

Keywords: Hall effect; Amorphous thin films; Semiconducting films

I. INTRODUCTION

Amorphous chalcogenides, based on S, Se and Te, are in scientific and industrial high interest due to their high potential from the viewpoint of applications [1–4]. While halogen doping improves the electrophotographic properties of the amorphous selenium, chalcogenide glasses, containing elements from Ib group, exhibit high transparency in the infrared region and nonlinear refractive index [5, 6].

Previous investigations of glass from Cu-As-Se-I system have shown that increase of copper content changes their physical properties significantly [7]. Moreover, previous investigations indicated that copper content of 20-25 wt% is a critical, from the viewpoint of positive effect on strength of the glass matrix [8]. Bearing in mind well known fact that glass in thin film form usually exhibits different properties than its bulk counterparts and previously published results related to bulks from the same system [9], the scope of presented investigation is the influence of copper on electrical properties of As-Se-I amorphous thin films.

The Van der Pauw method [10] is a convenient measurement method, widely utilized for the evaluation of electrical properties in semiconductor materials, especially in form of thin films [11, 12]. The Van der Pauw method can be used to measure samples of arbitrary shape, although several basic sample conditions must be satisfied to obtain accurate measurements, such as that sample must be of uniform thickness, four point contacts placed at the edges of the samples must be used for the measurements, and the sample has to be homogeneous.

II. EXPERIMENTAL

Amorphous chalcogenide Cu$_x$(As$_{38.5}$Se$_{54}$I$_{7.5}$)$_{100-x}$ thin films where x = 0, 5 and 25 at%, are prepared under a vacuum of $10^{-5}$ Torr on glass substrates by a vacuum thermal evaporation technique. Bulk samples are synthesized in cascade regime from high purity elemental components (99.998%) and air quenched [13]. Powdered bulk samples are used as starting components for thin films preparation. Standard glass microscope slides are used as substrates. The film thickness is controlled during vapour-deposition process by interference optical method. Using standard optical and X-ray techniques the amorphous character of the samples is determined.

The surface morphology (quality of the thin film surface, thickness uniformity and its suitability for measuring the Hall Effect by Van der Pauw method) is observed using an atomic force microscope (AFM). Used Hall Effect Measurement System for measuring the Hall effect on Cu$_x$(As$_{38.5}$Se$_{54}$I$_{7.5}$)$_{100-x}$ thin films is Ecopia HMS-3000, made up of constant current source, terminal conversion system for materializing Van der Pauw law, and magnetic flux density input system. By using graph, it can check the specifications of current-voltage and resistance between terminals by four point probing. Obtained electrically basic specifications enable calculation of various data: $N_A$ — Bulk Concentration, $\mu$ — Mobility, $\rho$ — Resistivity, $R_{HA}$ — A-C Cross Hall

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The productivity of investigated samples is in the range from 10^{10} Ω^{-1}cm^{-1} to 10^{-12} Ω^{-1}cm^{-1} which corresponds to conductivity of bulk counterpart samples [9]. Results also pointed to the switching of p-type conductivity for samples with 0 at% and 5 at% of copper to n-type conductivity detected for sample with 25 at% of copper. This results are in accordance with previously determined p-type semiconductor properties on Cu_{x}(AsSe_{1.0}I_{7.5})_{100-x} bulk glasses for x=0 at%, 1 at%, 5 at%, 10 at% and 15 at% [14]. Switching from p to n-type of conductivity has also been reported in some other systems when reaching critical values of concentration of some investigated components [15, 16]. Results showing the switching from p to n-type of conductivity in Cu_{x}(AsSe_{5}I_{7.5})_{100-x} amorphous thin films, are in accordance with previously identified concentration of 21.44 at% as critical from the viewpoint of emerging of a new structural units in investigated system [8].

Based on the investigated system composition and previously published results related to similar systems [17, 18], the structural units that can be expected in investigated compositions with 0 to 5 at% Cu are corner shared As_{2}Se_{3} pyramids, As_{2}(Se_{1/2})_{4} ethylene-like units, As(Se_{1/2})_{2}I pyramids and CuI molecules. Addition of copper up to 25 at% leads to appearance of As_{2}Se_{4} and As_{4}Se_{3} cage like structure units [16] and some structural units with Cu, As and Se atoms (Cu_{2}AsSe_{4}, CuAsSe_{2} [19], Cu_{3}Se [20]). At the same time it can be expected that for 25 at% of Cu, all I atoms will be bonded to Cu atoms, Coefficient, N_{S} − Sheet Concentration, σ − Conductivity, R_{H} − Average Hall Coefficient, R_{HH} − B-D Cross Hall Coefficient and α − Ratio of Vertical/Horizontal.

All experiments are performed at room temperature (300 K).

### III. RESULTS AND DISCUSSION

Results of X-ray diffraction and AFM studies on Cu_{x}(AsSe_{5}I_{7.5})_{100-x} films are presented on Figs. 1 and 2, respectively. X-ray diffraction confirms that there are no Bragg peaks related to a crystalline phase, and the spectra are typical of an amorphous material.

AFM investigation revealed randomly distributed surface irregularities emerging from uniform film surface. Those irregularities were only 0.2 μm in diameter and not higher that 14 nm. Therefore investigated samples are of a good quality and uniformity, with irregularities that can be neglected, which justify application of the Hall effect measurement method.

Electrical parameters of Cu_{x}(AsSe_{5}I_{7.5})_{100-x} films for x= 0 at%, 5 at% and 25 at%, obtained from measurements based on the Hall effect are listed in Table 1.

Measurements of the Hall effect were performed on Cu_{x}(AsSe_{5}I_{7.5})_{100-x} amorphous thin films deposited onto glass substrates. Obtained results showed that conductivity of investigated samples is in the range from
leading to the lack of As(Se₁/₂)₂I pyramids, structural units that are expected to form in compositions with 0 at% and 5 at% of Cu.

IV. CONCLUSION

Obtained results based on measurements of the Hall effect, showed that conductivity of investigated Cuₓ(As₃₈₅Se₅₄I₇₅)₁₀₀₋ₓ thin film samples is in the range from 10⁻¹² Ω⁻¹cm⁻¹ to 10⁻¹⁰ Ω⁻¹cm⁻¹. Switching of p-type conductivity for samples with 0 at% and 5 at% of copper to n-type conductivity detected for sample with 25 at% of copper. This effect can be attributed to emerging of new structural units in investigated system.

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