

## THE IMAGE FORMATION BY PHOTO – REACTION OF Ag OR Al WITH GLASSY CHALCOGENIDES: MECHANISMS AND APPLICATION

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The mechanisms and application of photo-dissolution (PD) of silver in chalcogenide glassy semiconductors (ChGS), as well as of electrically controlled photoreaction (ECPR) of aluminum with ChGS are extensively reviewed and discussed. It is shown that one of the main interesting applications of these phenomena is due to the possibility of their use for image formation, followed by the appearance of differential chemical etching rates between exposed and unexposed portions of either ChGS - Ag or Al - ChG – metal wafers. This property is utilized to form the surface relief, which results in a wide application of Ag (Al) – ChGS structures in the microelectronic lithography as high-resolution inorganic photoresists. The advantages of these photoresists are: the possibility to obtain layers with high homogeneity and low concentration of defects on a large area, the possibility of wet and dry processing, the high absorption coefficient of light, which enhances the accuracy of simultaneous or successive etching. It is significant that the spectral range of photosensitivity is very wide and includes UV, visible and IR regions. The sensitivity of ChGS to electron or ion beams has also been discovered and the possibility of their application in sub-micron lithography was demonstrated. Along with the traditional use of Ag - ChGS - Ag wafers in optics and optoelectronics their modern application in Programmable Metallization Cell (PMC) technologies is considered. Although the mechanisms of PD and ECPR effects are still not completely understood, it is clear that they are rather different. One of the aims of this presentation is to give a brief consideration of the mechanisms of the mentioned effects. Based on the experimental results concerning the kinetics of Ag photo-dissolution in glassy  $As_2S_3$  [1] and As-S-Ge alloys [2], the mechanism and regularities of the phenomenon in question is explained in terms of Elliott's model [3], which asserts a simultaneous ionic and electronic charge transport controlled by chalcogenide properties, illumination and temperature. This mechanism comprises at least three processes: 1) A solid state chemical reaction between Ag and the chalcogenide, which results in the formation of a superionic conductor with a high ( $10^{-5} - 10^{-3} \text{ Ohm}^{-1}\text{cm}^{-1}$ ) ionic conductivity; 2) Photo-creation of free holes at the doped / undoped chalcogenide interface, followed by their drift through the superionic chalcogenide to the Ag layer and production of ions by the reaction  $Ag^0 + h \rightarrow Ag^+$ ; 3) Motion of  $Ag^+$  ions in the opposite direction i.e. towards the boundary of the doped / undoped chalcogenide through the doped (superionic region). As far as the ECPR effect is concerned, it occurs in metal - ChGS structures based on metals (such as Al), which do not actively interact with ChGS in normal conditions. The interaction appears only when a transversal electrical field is applied. The rate of interaction is influenced by the direction and density of the electrical current flowing through the interface Al - ChGS, hence it is controlled by the electrical field strength and by all factors which lead to the ChGS conductivity variation, such as heating, illumination, radiation et al. Shown by X-ray photoelectron spectroscopy [4] the ECPR phenomenon is due to the transfer of matter with the subsequent chemical interaction both at the interface and inside the chalcogenide glass. By this transfer of matter, the Al atoms diffuse through the whole thickness of ChGS, showing almost a linear decreasing profile. Simultaneously the intensive oxidation of aluminum atoms occurs at the interface and as a result, an essential part of the aluminum electrode is transformed into  $Al_2O_3$ . As Al diffuses inside of ChGS and  $Al_2O_3$  is a wide-gap insulator the structure becomes more transparent and less reflective that consists of a key for optical image formation.

[1] D. Tsiulyanu, I. Stratan, *J. Non-Cryst. Solids* 136 (2010) 147.

[2] D. Tsiulyanu, I. Stratan, *Optoelectronics and advanced materials-RAPID COM.* 5 (2011) 851.

[3] S.R. Elliott, *J. Non-Cryst. Solids* 130 (1991) 85.

[4] A.M. Andriesh, V.I. Nefeodov, D.I. Tsiulyanu, A.N. Socolov, G.M. Triduch, *J. Techn. Phys.* 60, (1990) 148.