Chapter 25
Surface Phenomena in Glassy Chalcogenides by Gas Sensing

Dumitru Tsiulyanu, Marina Ciobanu, and Olga Mocreac

Abstract The surface phenomena in glassy chalcogenides (GCh), including those caused by gas adsorption, are reviewed and discussed. A detailed quantitative analysis is made on experimental data taken on glassy and nanocrystalline chalcogenide based thin films of $As_2S_3Ge_8$ – Te system, physically grown in vacuum. Particularly the measurements of the frequency dependence of the AC conductivity of these films in the frequency range 5 Hz–13 MHz are reported, in both dry air and its mixture with a controlled concentration of different gases. The behavior of AC conductivity fits the generally accepted model of charge transport in disordered materials that implies both the extended states above mobility edges and the localized states in the gap, but the variation of the environmental conditions by applying of even very small amount (ppm) of toxic gases, dramatically influences the AC conductivity spectra. This is evidence that for some chalcogenide materials the surface phenomena disturb the energetic distribution of the states adjacent to the surface leading to modifications of the transport mechanisms by the surface. The modification of the surface transport mechanism by adsorption of gas species alters the physical parameters of the surface, i.e. the work function, the diffusion and the dipolar potential, the screening length, etc., which lead to variation of both surface and total electrical conductivity, impedance and its spectral distribution, as well as of electric capacity of functional structures based on these materials. The examples are given of the development of room temperature operating functional structures designed to detect nitrogen dioxide and hydrogen sulfide in dry and humid media via variation of their impedance or capacitance.

Keywords Surface phenomena · Chalcogenide films · Gas sensors

---

D. Tsiulyanu (✉) · M. Ciobanu · O. Mocreac
Department of Physics, Technical University, Chisinau, Moldova

P. Petkov et al. (eds.), *Nanoscience and Nanotechnology in Security and Protection against CBRN Threats*, NATO Science for Peace and Security Series B: Physics and Biophysics, https://doi.org/10.1007/978-94-024-2018-0_25

25.1 Introduction

The influence of the surface of the glassy calcogenides on their physical properties has been observed at the early stage of investigation of these materials. Firstly, the effect of surface was exanimated for the glassy As_2Se_3 via studying the kinetics and spectral distribution of surface photoconductivity under the conditions of mechanical and chemical treatment of the bulk samples [1, 2]. The impact of the surface conditions was shown to be impressive: The surface photoconductivity increases as the quality of the surface improves, moving from samples with abrasive surfaces to those treated chemically, and further to those with polished surface. Later attempts were made to clarify the influence of gas adsorption on the electrophysical properties of this calcogenide glass by applying water vapor, ammonia, carbon oxide or carbon dioxide, as well as molecular oxygen [3]. It has been found that both surface conductivity and photoconductivity exhibit some sensitivity to gases, especially to H_2O and NH_3 vapors. On the other hand, it was pointed out that the variation of the electrophysical parameters of the As_2Se_3 samples with the polished surfaces is insignificant under application of any of the mentioned gases. The real interest in the surface phenomena in structures based on glassy or nanostructured calcogenides has appeared after publications dedicated to the process of detection of propylamine ($C_3H_7NH_2$) and nitrogen dioxide with films of artificial dimorphite (As_4S_3) and Te [4–6]. Later, gas sensitive films based on different compositions in binary, ternary and quaternary chalcogenide systems have been reported [7–10], along with a number of extensive reviews on fundamental and applicative aspects of the interaction of gases with chalcogenide materials, including the elemental tellurium [11, 12]. From the mentioned publications it turns out that the sensitization of the surface phenomena, that is their influence on the electrophysical parameters of the materials in question, increases dramatically with the increase of the spatial (and possibly the compositional) disorder of the surface. Although the study of the surface phenomena in either glassy or nanocrystalline chalcogenides is still at the early stage, such behavior can be explained in terms of interaction between the lone pair electrons of the chalcogen atoms and their "dangling" bonds at the surface, as namely at the surface the maximum concentration of dangling bonds (unshared electrons) occurs. This interaction means the capture of electrons from the valence band, which results in formation of region adjacent to the surface enriched (accumulation) in holes, so that the bands bend up [13]. Consequently one reason for the surface phenomena in chalcogenide materials, caused by gas adsorption, can be the formation of new surface states, i.e. the donor or acceptor like levels, which control the band – bending at the surface, owing to variation of the hole density in the accumulation region. Another reason can be the variation of the hole mobility in the accumulation (surface) region in the presence of gaseous media as a result of a possible modification of the charge transport mechanism. As the last effect must be essential in the case of AC conductivity, the present work is conducted to analyze the surface processes in chalcogenide thin films by gas adsorption, considering their AC