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– Lecture –

The surface phenomena in glassy and nanocrystalline chalcogenides at gas sensing

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The surface phenomena in chalcogenide glasses, including those caused by gas adsorption are extensively reviewed and discussed. A detailed quantitative analysis is made on experimental data taking on glassy and nanocrystalline thin films of As_2S_3 Ge_8 – Te system, physically grown in vacuum. Particularly are reported the measurements of the frequency dependence of the AC conductivity of these films in the frequency range 5 *Hz* to 13 *MHz*, in both dry synthetic air and its mixture with a controlled concentration of different gases. The AC conductivity in dry synthetic air, being frequency independent until ~ 10^4 *Hz,* increases as $\sigma(\omega) \sim \omega^n$ at frequences between $10^4 < \omega < 10^6$ *Hz*, with an exponent factor $n \approx 0{,}7$. The dependence $\sigma(\omega)$ exhibits a shouldar at frequency ~ 10^6 *Hz*, followed by a sharp increasing of conductivity with an exponent factor $n \approx 1{,}8$. Such behaviour of AC conductivity fits the generaly accepted model [1] of charge transport in desordered materials, which implies both extended states above mobility edges and localized states in the gap, including the states at the Fermi level with concentration estimated in this work as $N(E_F) = 1.3 \cdot 10^{21}\ eV^{-1}\ cm^{-3}$.

The variation of environmental conditions by applying of even very small (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 states adjacent to surface leading to modifications of transport mechanisms by the surface, as have been suggested in our previous works [2]. For instance, the adsorption of NO_2 molecules produces new acceptor levels at the surface, which results in a sharp increasing of hole concentration in the valence band of an ultrathin layer adjacent to surface and the transport by hopping via valence band edge states becomes negligible. Consequently, the mechanism of conductivity via extended states becomes the main in the whole frequency range until $\omega > 10^5$ *Hz,* i.e. until the charge hopping via localized states in the vicinity of Fermi level becomes predominant. The modification of surface transport mechanism by adsorption of gas species may be a way for improvement of sensitivity and selectivity of chalcogenide based gas sensitive devices. Finally, in this lecture the examples are given of the development of room temperature operating micro gas sensors based on glassy and nanocrystalline chalcogenides thin films designed to detect nitrogen dioxide and hydrogen sulfide in dry and aqueous media.

Keywords: Surface phenomena, Chalcogenides; Gas sensors

[1] N. F. Mott, E. A. Davis, Electron Processes in Non-Crystalline Materials, Clarendon Press, Oxford (1979).
[2] D. Tsiulyanu, M. Ciobanu and H.-D. Liess, Phys. Status Solidi, b, 253, 1046 -1053 (2016).