Characterization of gas sensitive chalcogenide films by impedance spectroscopy

Dumitru Tsiulyanu

Technical University, bd. Dacia 41, MD - 2060, Chisinau, Republic of Moldova,
tsiudima@gmail.com

Gas sensing performance of chalcogenide thin films investigated by method of impedance spectroscopy is reported and discussed in order to assess their use in future gas sensors operating at room temperature. Along with already traditional use of Te films for such applications, the impedance spectra of quaternary $As_2S_3Ge_8$ – Te alloys were investigated in both dry synthetic and humed air, as well as their mixtures with different harmful gases. To elucidate the effect of tellurium, the quaternary compositions $As_2Te_{13}Ge_8S_3$ and $As_2Te_{130}Ge_8S_3$, with increasing concentration of Te have been considered along with pure tellurium films. The films of different compositions were prepared by thermal vacuum evaporation onto Pyrex or sintered alumina (Al_2O_3) substrates with a priory deposited platinum interdigital electrodes. Shown by AFM, SEM and X – ray analysis the phase – state of the films depends on composition, nature of substrate and rate of growing. The morphology of the films grown on sintered alumina substrates appears to consist of interconnected islands and dots, which facilitate the solid-gas interaction. It is shown that impedance spectra being strongly influenced by gaseous environment are also strongly influenced by material composition and phase -structural state of the film. Analyses of these spectra in Cole – Cole interpretation allowed evaluating the characteristic frequency, time constant, resistance and capacity of the films in both dry air and its mixture with target harmful gases. For nanocrystalline Te films the he effect of target gas is mainly due to variation of resistance of the film but capacitance does not vary essentially. The sensitivity for impedance or its imaginary part depends on frequency, being the highest to NO_2 (~50 % / ppm) but 8 % / ppm and only 10^{-2} % / ppm to H_2S and H_2 respectively. Impedance sensitivity to NO_2 is explained by "strong" chemisorption due to interaction of adsorbed species with lone - pair electrons, which form the upper part of the valence band of chalcogenide semiconductor. On the other hand, it is suggested that effect of H_2S and water vapors results from a "weak" chemisorption, while effect of H_2 is due to removal some amount of oxygen a priory adsorbed on the surface. Perhaps, these mechanisms of interaction occurs in studied here quaternary alloys as well, but addition of As, S and Ge atoms results in structural - phase transformations, appearance of new mechanisms of current flow and in modification of gas sensing peculiarities. Thus, as shown by X ray diffraction measurements, addition of 30,8 at% Ge, 11,6 at% S and 7,6 at% As (alloy $As_2Te_{13}Ge_8S_3$) transforms the film into an amorphous state with a dramatic increase of impedance by at least two orders of magnitude, followed by an increasing of gas sensitivity more than twice. This result shows how the composition and phase-structural state of the films control their gas sensing properties and abilities to be used in development of gas sensing devices operating at room temperature.