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Thin Chal-AgI films as gas sensor

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Thin films of glassy $(GeS_2)_{1-x}$ $(AgI)_x$ system have been studied. The films have been coated on cantilever-based gas sensors and studied upon exposure to water, acetone, and ammonia vapours. The results reveal that the sensor acted like a resonance microbalance, showing highest sensitivity towards the analyte with the highest molecular weight, i.e. towards acetone. Modification of the surface of the sensitive layer after the exposure to ammonia is associated with chemisorption of the analyte molecules on it and results in increase sensitivity towards water due to the chemisorbed NH_3 molecules.

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1. Introduction

The silver-containing amorphous materials are subject of intensive research since many years due to their promising optical [1] and electrical features [2]. The glasses have been widely investigated because of the high ionic conductivity they posses [3], in view of their application as electrolyte material in the solid state batteries [4]. Other prospective applications of chalcogenide coatings are as optical storage media [5], memory devices [6], and sensitive elements in various sensor systems [7], etc. In the literature only a few papers have reported chemical sensors based on chalcogenide glassy materials in the form of membranes [7] or thin films [8].

Relatively new method of gas sensing and monitoring is the method of micromechanical cantilever-based chemical sensors. The mechanism of the gas sensing is related to the sorption of the gas molecules onto the sensitive layer and reflects on the effective mass of the cantilever/coating structure. The changes in the effective mass are registered by shift in the resonance frequency.

The performance of the cantilever-based chemical sensors depends not only on their mechanical characteristics – geometrical dimensions, spring constant, and resonance frequency – but also on the physical and chemical properties of the sensitive layer. In this respect development of new materials as sensitive layered materials is an important task in ever increased requirements in the environment monitoring and fight with the environmental pollution.

In this work we report results from study of the sorption properties of thin films from the system Ge-S-AgI and their applicability as sensitive layers in micromechanical cantilever-based chemical sensors upon exposure to various analytes.

2. Experimental details

Film preparation and characterization

Bulk samples from the Ge-S-AgI system were prepared by melt-quenching technique using 5N purity elements of Ge and S, and AgI compound (Alfa Aesar, 99,99%). The compositions of the $(GeS_y)_{100-x}$ $(AgI)_x$, specimens ware varied by x, the molar concentration of AgI, from 0 to 20 mol.% and by the Ge/S ratio y = 1,2; 1,5; 2. Evacuated ampoules with the initial substances were heated in a rotated furnace with a constant heating rate of 3 K/min up to a final temperature of 1200 K. X-ray diffraction results obtained by use of diffractometer APD-15 Philips 2139 with CuK_α radiation and Ni filter in the 2θ range from 10^o to 60^o revealed the glassy state of the obtained samples.

Films studied as active layer in the sensor system were deposited on Si/SiO_2 cantilevers and on monocrystalline silicon substrates (for control of the thin film properties) in vacuum system Leybold LB 370, with a residual gas pressure of $1.33.10^{-4}$ Pa. The preparation conditions described elsewhere [9] is chosen proper for layers production uniform in the thickness and homogeneous in depth with composition close to the respective bulk material. Typical film thickness was about 0.2 μm as measured by interference microscope. The composition of the bulk samples and thin films were investigated by Energy Dispersive X-ray Analysis (EDAX) using scanning electron microscope (JEOL, model JSM 35 CF with x-ray microanalyser – Tracor Northeren TN - 2000).

Cantilevers preparation and measurements

The cantilevers fabrication process used in the study is a modification of the double-sided silicon micromachining process developed for manufacturing of piezoresistive AFM sensors, applying conventional CMOS processing.

The procedure of the cantilever preparation is described elsewhere [10]. Fig. 1 presents the rectangular cantilever beam coated by thin Ge-S-AgI film.

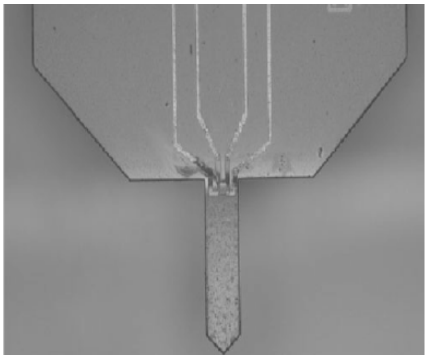

Fig. 1. Cantilever sensor functionalized with thin $Ge_{30}S_{60}(AgI)_{10}$ film.

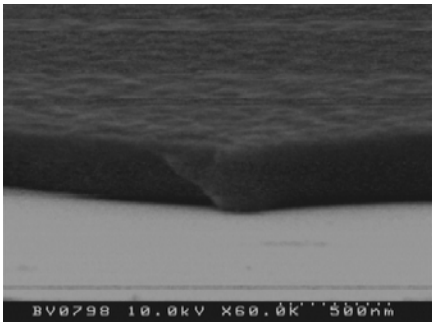

Fig. 2. Cross-section SEM micrograph of $Ge_{30}S_{60}(AgI)_{10}$ layer.

The set-up for sensor measurements consists of a measurement cell with a gas-handling system (based on mass-flow controllers (MFCs, Tylan FM-260) and an electrical measurement circuit, described in detail elsewhere [11]. The experimental process is fully automated for control of the gas-flow rates and for the data acquisition. The sorption properties of the Ge-S-AgI thin films were investigated upon exposure to water, acetone, and ammonia vapours, which were delivered to the measurement cell with a carrier gas (dry nitrogen) with a total flow rate of 150 ml/min. The analyte was injected in the chamber with decreasing volume concentrations (the portion of the analyte in the total gas flow) interlaced with purging the measurement cell with the dry inert carrier gas (N_2).

3. Results and discussion

Thin films under study are amorphous proved by XRD and with smooth surface as seen from the cross-section micrograph (Fig. 2). The dynamic response (the resonant frequency) of the functionalized microcantilever sensor with a Ge-S-AgI thin film we studied upon exposure to ethanol, acetone, and ammonia vapours with various concentrations between 8 and 54 vol.% in a gas-flow mode and the results are presented in Figure 3. The signal evolution consists of two parts: the first part represents the sorption process of analyte molecules onto or into the sensitive Ge-S-AgI film (decrease of the resonance frequency) and the second part reflects the desorption of analyte molecules from the layer during the purging of the measurement cell with dry nitrogen. The signal magnitude increases with the analyte concentration; thus, the largest responses were detected for 54 vol.% analytes. As seen from Fig. 3, the response is reversible, which means that the analytes are primarily physisorbed on the chalcohalide surface. The initial resonance frequency was reached again after the analyte vapours have been removed from the cell and the cantilever acted as a resonant microbalance.

The sensor is more sensitive towards the acetone, the analyte with higher molecular weight than toward the water. This could be due to partial penetration of small water molecules with relatively high electric dipole moment ($D(H_2O) = 1.85D$ [12]) into the amorphous film and/or formation of weak bonds with, for example, silver atoms from the sensitive coating. The resonance frequency shift of the sensor over a wide range of analyte concentrations demonstrates a linear increase shown in Fig. 4. The responses towards the analytes are relatively weak, suggesting also physisorption of the gas molecules on the surface of the sensitive layer. Their in-depth absorption is hindered by the dense structure of the amorphous $Ge_{30}S_{60}(AgI)_{10}$ films (density of the corresponding bulk sample 3.2±0.1 g/cm^3). The leading slope of the analyte injection transition process should be explained by the saturation time of the chamber volume rather than by the response time of the sensor itself. Further, we exposed the cantilever sensor to ammonia and the corresponding change in the resonance frequency is shown in Fig. 5. Initially, the baseline was established by purging the measurement cell with dry nitrogen for 7 min, as in the previous experiments. The exposure to ammonia vapour with concentration of 54 vol.% resulted in a very large response (360 Hz), which was one order of magnitude higher than that for the other analytes. New purging with nitrogen was not able to recover the initial baseline, which was now shifted about 90 Hz. We tried to recover the sensor with water vapour and dry nitrogen, but the new baseline appeared to be very stable, even after several days of purging with water vapour and nitrogen in different proportions. It can be supposed that ammonia molecules were chemisorbed on the surface of the sensitive coating, leading to an increase of the microcantilever beam mass and consequently to a decrease of its resonance frequency. The chemisorbed ammonia modified the chalcohalide surface and made it more susceptible for physisorbed analytes, especially for water molecules as shown from the experimental results presented in Fig. 6.

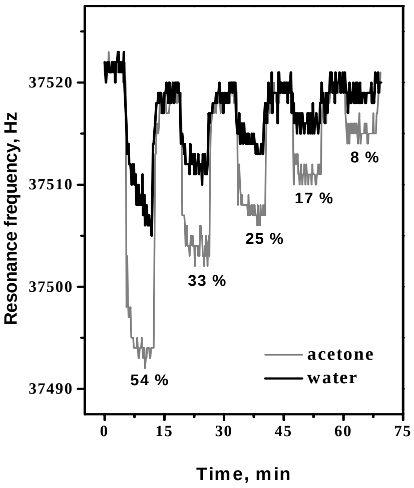

Fig. 3. Dynamic time responses upon exposure to cantilever as a function of the analyte concentration.

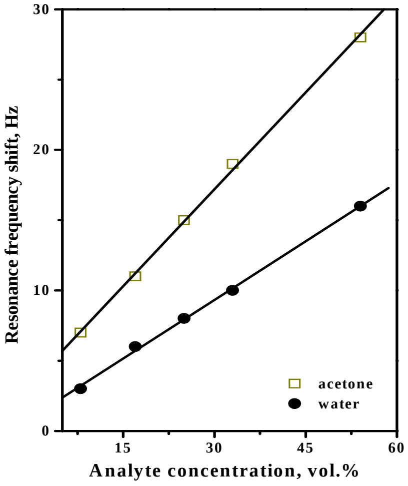

Fig. 4. Resonance frequency shift of the various vapours of the cantilever sensor.

The initial experiment, showed the weakest sensitivity (graph (a)). Ammonia vapour causes chemical modification of the chalcohalide surface resulting in the formation of additional binding sites for water molecules and shift of the baseline down due to the added mass of ammonia molecules on the cantilever beam (graph (b)). The sensitivity towards water vapour increases strongly (100 Hz shift for 54 vol.% as compared with 16 Hz for the same concentration) as seen from the figure. After a few days of continuous measurement cycles, the surface became slightly 'exhausted', i.e. some ammonia molecules were purged out of the cantilever. The baseline was shifted to the higher frequencies because of the mass-loading effect and the sensitivity slightly decreased due to the lower number of binding sites (graph (c)). The higher sensitivity was re-established after second processing of the cantilever in ammonia vapour.

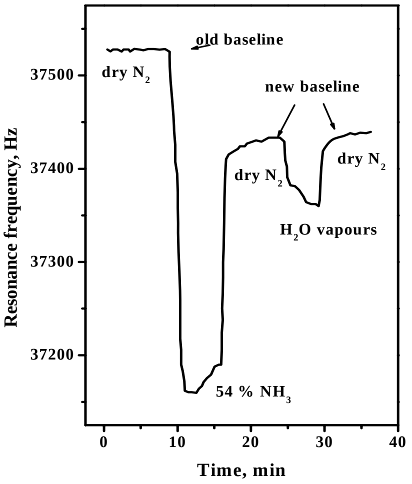

Fig. 5. Dynamic time response upon exposure to ammonia.

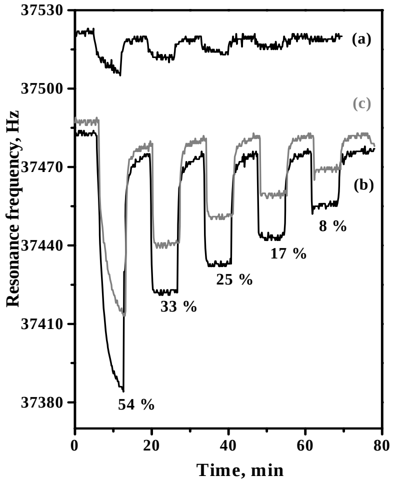

Fig. 6. Dynamic time responses upon exposure to various water concentrations of the cantilever sensor (a) as-deposited; (b) after chemical modification with ammonia, (c) after 'exhausting' of the modified surface.

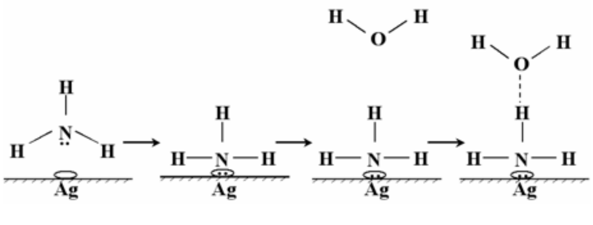

Fig. 7. Likely mechanisms of chemical modification of the sensitive layer upon exposure to ammonia and of the resulting enhanced sensitivity towards water vapor.

5. Conclusions

Thin Ge-S-AgI films coated on cantilever-based gas sensors and studied upon exposure to water, acetone, and ammonia vapours showed that the sensor acted like a resonance microbalance, showing the highest sensitivity towards the analyte with the highest molecular weight, i.e. towards acetone. Modification of the surface of the sensitive layer after the exposure to ammonia is associated with chemisorption of the analyte molecules on it. The result is an increased sensitivity towards water due to the chemisorbed NH_3 molecules.

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