CHALCOGENIDE BASED GAS SENSORS

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Evidence for direct application of the chalcogenide semiconductors for gas sensing is considered. Two kinds of sensitive thin film structures have been fabricated and studied, using both artificial dimorphite (As_4S_3) and As-Ge-Te alloys. The As_4S_3 thin films are porous with fibrillar morphology but the tellurium based films were polycrystalline. Resistive gas sensitive devices based on these chalcogenide films have been checked in media with nitrogen dioxide and propylamine ($C_3H_7NH_2$). The results are discussed in terms of the vapour - solid interaction that means the chemisorption of gas molecules and their trapping at charged centres. The gas-induced response is found to be high, fast and with a good reproducibility. The applications for environmental monitoring and process control are considered.

1. Introduction

The detection and emission control of the pollutants released by combustion, plants, and automobiles is of great importance. Therefore much efforts was devoted to develop sensors for monitoring the concentration of nitrogen dioxide, carbon oxide and others toxic gases in the environmental atmosphere. A variety of such sensors have been investigated using semiconductors, solid electrolytes, or organic materials.

Semiconductor gas sensors are most attractive because they are compact, sensitive, of low-cost, and have low-power consumption. Unfortunately it is not easy to develop a sensor, which combines all the mentioned advantages. The well known SnO_2 - based gas sensors are of general commercial interest and the most widely investigated [1]. These sensors operate at temperatures above 200 ^{o}C. Nevertheless, they are, not very selective and have a response time of about 30 min.

In this work we report on the development of thin film sensors based on chalcogenide semiconductors, for the detection of pollutants in the ppm range operating at room temperature. Both dimorphite (As_4S_3) and As-Ge-Te alloys were used for this purpose.

Dimorphite, one of the four known chemical compounds of the As-S system has been discovered as a mineral in the middle of the last century [2]. Artificial dimorphite can be obtained by melting of corresponding components in vacuum [3]. It exhibits typical semiconductor properties [4].

2. Experimental

Gas sensitive films were prepared by vacuum thermal evaporation of dimorphite or tellurium alloys onto Pyrex glass. Vacuum evaporation was performed under a working pressure of 10^{-5} *Torr* . The rate of dimorphite film growth as 5.0 μm/h. The thickness of the films was 7-8 μm. The growth

rate of the tellurium alloys based film was about $1\,nm \cdot s^{-1}$, and the thickness was about $100\,nm$. SEM TESLA BS340 was used for investigation the film surface morphology.

Propylamine and nitrogen dioxide were chosen as contaminant gases. Propylamine, $(C_3H_7NH_2)$ is a high volatile amine (at 20 $^{\circ}$C, L = 799 mg/l), which is evolved from various chemical plants and during processing of the fish muscle. Nitrogen dioxide is one of the most toxic gases released by combustion.

The vapours with different concentrations of these gases were obtained by using the experimental set-up described in [5]. After applying different gas concentrations the current-voltage and current transient characteristics were investigated. $I - U$ characteristics were measured in air, in gaseous media, and in air again. Gaseous media were obtained by using a calibrated permeation tube with a Dynacalibrator model 02 (Vici Metronics, USA). Ambient air was used as carrier and reference gas.

Transient characteristics have been carried out at constant applied voltage with computer controlled switching between toxic gaseous media and pure air. All the experiments were performed at room temperature.

3. Results and discussion

The surface morphology of the films is depicted in Fig. 1. It is seen from this photographs that As$_4$S$_3$ films exhibit a fibrilar morphology and high porosity. The fibrils are grown together and have the size of ~ 2.0 µm in length and 0.5 µm in diameter. Cavities are smaller but sometimes reach the fibril size. The As-Ge-Te based films are polycrystalline with a grain size of about 1.0 µm, and are textured in the substrate plane.
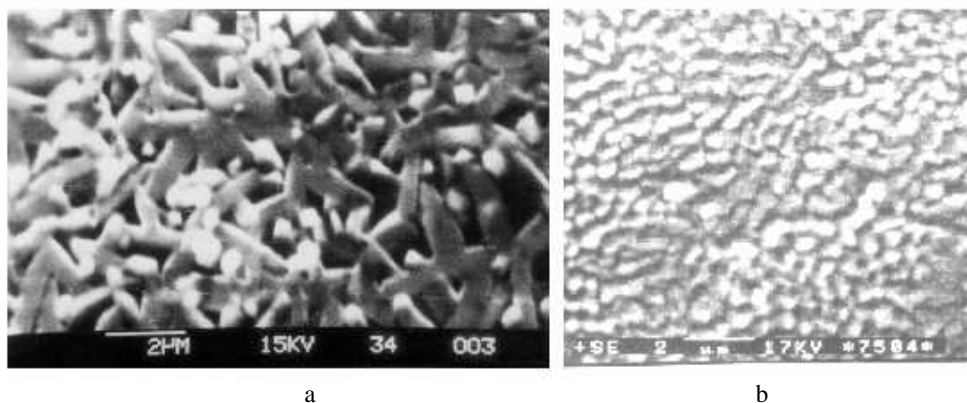

a   b

Fig. 1. SEM micrograph of As$_4$S$_3$ (a) and tellurium based (b) films.

Typical current-voltage characteristics of As$_4$S$_3$ and tellurium based structures measured in air and in propylamine vapor are shown in Fig. 2a and 2b respectively. It is seen that for As$_4$S$_3$ based sensor, for almost two orders of magnitude in current, the I-U characteristic is described by the power law: $I = A \cdot U^m$, where A is a proportionality factor and m is an exponent having the values *3.2* for air media and *3.5* for media with propylamine vapour. For tellurium-based alloys this dependence is linear and follows the Ohm's law. Moreover, the effect of propylamine is different for these two kinds of structures: resistance of the device based on As$_4$S$_3$ decreases and increases for tellurium based device.

The different effect of pollutants on As$_4$S$_3$ and As-Ge-Te based structures indicates that the mechanism of solid-vapor interaction differs. The power law of I-U characteristic in As$_4$S$_3$ based structures can be due to the limitation of the injection current from electrodes by the space charge in As$_4$S$_3$. Density of current vs. layer thickness in double logarithmic scale is shown in the inset of

Fig. 2a for air media. The dependence is quite strong (exponent about 5.0) and confirms the proposed mechanism of the current flow.
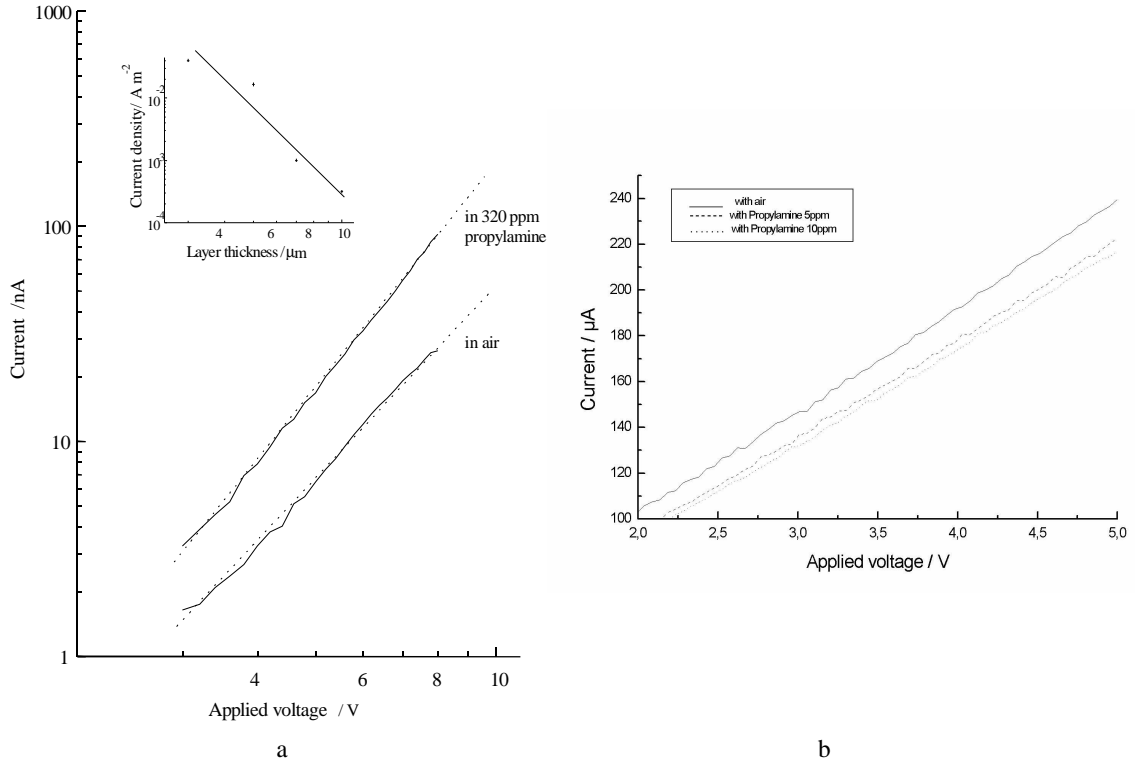

Fig. 2. *I-U* characteristics of As_4S_3 (a) and As-Ge-Te based (b) structures measured in air and in propylamine vapor. The inset of Fig. 2a shows the current density vs. the thickness of the As_4S_3 film.

Exponent m>3 imply an exponential trap distribution within a certain interval in the forbidden gap, which is given by the relation:

$$N(E)=N_0exp[E_v-E/\Delta] \qquad (1)$$

where N(E) is the trap density per unit energy level, E_V - the edge of the valence band, Δ - the parameter of the trap distribution, $N_0=N_t/\Delta$, N_t - the trap density within the interval between the equilibrium Fermi level and that in the case of the field. Adsorption of propylamine vapours lead to change in the slope of I-U characteristic, i.e to increase of Δ from $\Delta_a=0.055$ eV to $\Delta_p=0.062$ eV. Hence, absorbed propylamine vapours modifies the energetic distribution of traps in dimorphite film, giving rise to the increaseof the current. Furthermore, Fig. 2a shows that propylamine vapor does not lead only to a change in the slope of the I-U characteristic, but also to a shift to higher currents. The increase of the current can be due to a decrease of the trap concentration. We assume that the vapor-solid interaction between propylamine and dimorphite takes place in two steps: The absorption of propylamine, which occur preferentially via the fibrilar cavities, and the interaction of the vapor molecules with localized states in the bandgap of As_4S_3, which leads to their neutralization. Fig. 3 shows the transient characteristic of the gas induced current. The transient characteristic follows well the concentration profile shown at the bottom of the figures comprising concentration step from ambient air to 80 ppm propylamine and vice versa. But the response do not reach saturation for the given profile for both the absorption and desorption process. Saturation of gas induced current is reached approximately after 5 hours. Thus, the dimorphite based gas sensor effect can be attributed to bulk –conductance.

The operating mechanism of Ge-As-Te based sensors seems to be the variation of surface conductance in the presence of the gaseous atmosphere. In tellurium based alloys (as well as in others chalcogenides) the upper part of the valence band is formed by p - state lone - pair electrons. These electrons being weakly bonded can interact with dangling bonds, forming the specific charged defects [6]. Such interaction results in releasing of about 10^{13} - 10^{15} cm^{-3} holes. That's why under normal atmospheric condition and room temperature the films are p-type semiconductors. Because the maximum concentration of dangling bonds occurs on surface, a region rich in holes appears near the surface, and this gives rise to the bending of the energy band edges. Thus, a channel with an enhanced conductivity is formed at the surface of the film.
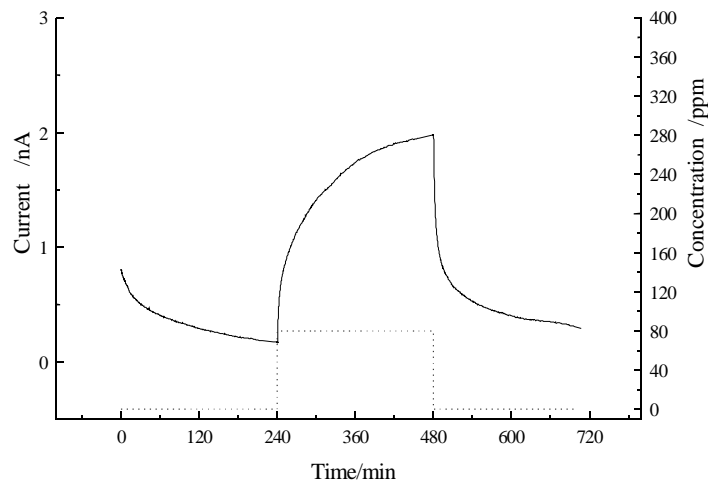
Fig. 3. Transient characteristic of gas induced current in As$_4$S$_3$ films after the application of 80 ppm of C$_3$H$_7$NH$_2$.

The mechanism of sensing is obviously related to the variation of surface conductance in the presence of gaseous atmosphere. The adsorption of gas molecules on the semiconductor surface produce either donor or acceptor - like levels. In particular, it is well known, that organic pollutants (including propylamine vapours), which are absorbed on the surface of solids, create donor centres. Therefore, due to adsorption of C$_3$H$_7$NH$_2$ vapours, the surface conductivity of the Ge-As-Te films diminishes and the resistance of the sample increases.
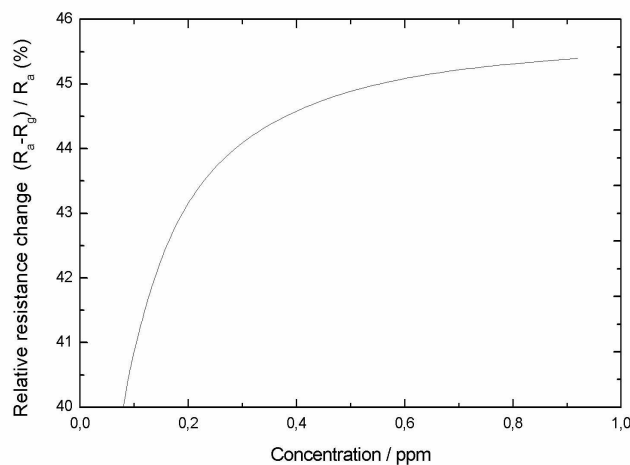
Fig. 4. Relative resistance change vs. NO_2 gas concentration: R_a and R_g are the electrical resistance of the sensor in air and in the presence of NO_2.

On the other hand, the adsorbed molecules of NO_2 on the surface of oxide semiconductor films, such as SnO_2, In_2O_3 etc. form acceptor centres.

As-Ge-Te alloys considered in this work show a remarkable sensitivity to nitrogen dioxide, but the increase of their electrical conductivity under NO_2, confirms the acceptor character of the NO_2 molecules. The relative resistance change towards NO_2 gas concentration is shown in Fig. 4. It can be seen, that chemisorptions of NO_2 diminishes the film resistance. That means, the vapour leads to the formation of surface acceptor centres, which tie up the electrons. The surface of the films becomes enriched in holes, and an additional conducting channel is opened.
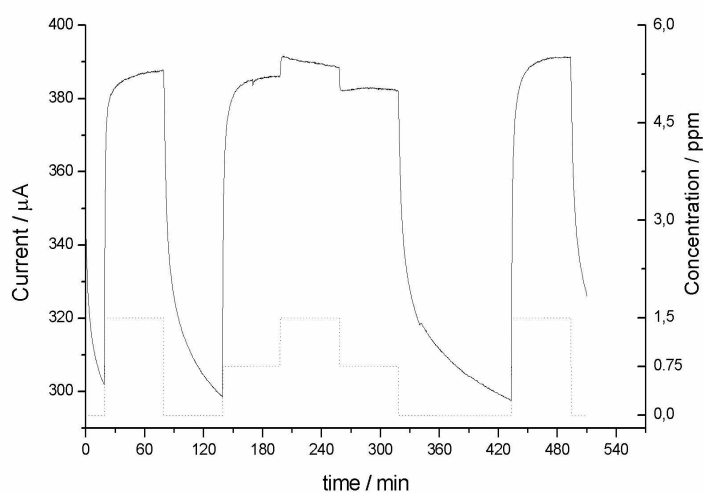

Fig. 5. Transient characteristic of tellurium – based films for pulses of NO_2 vapour at room temperature in air at U = 4 V. Dotted line shows the concentration of the gas.

Fig. 5 shows the current flow through a specimen under repeated switching on-off of the NO_2 gas mixture at constant bias voltage. The dotted line gives the switching schedule. The following concentrations steps of NO_2 vapour were applied: 0, 0.75, and $1.5\ ppm$. It is seen, that the current follows the schedule and there is no noticeable drift of the gas induced current. The response and the recovery times of the current (defined as the time to reach $90\ \%$ of steady-state values) are about $2-3$ min and 30 - 40 min respectively. For the transitions from 0.75 to $1.5\ ppm$ and back, the response and the recovery times are much shorter ($10-30\ s$ only).

4. Conclusion

High sensitive gas sensors can be developed using chalcogenide semiconductors. The sensors can operate at room temperature. They show considerably short response times and a good relative sensitivity in the ppm concentration range. These properties are suited for applications in environmental monitoring.

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