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Chalcogenide-based chemical sensors for atmospheric pollution control*

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Abstract: The authors report about characterization of chalcogenide-based thin films, as a materials for gas-sensing applications. The sensing behavior of the As–S–Te films was tested with environmental pollutant gases such as NO_2, CO, and SO_2. A significant sensitivity has been observed for nitrogen dioxide. The detection range for NO_2 was between 0.95–1.9 ppm in ambient air. The response and the recovery time is rapid, with good reproducibility and high sensibility. All the measurements were performed at room temperature. Gas-sensing applications are considered.

INTRODUCTION

Semiconductor gas sensors are most attractive because they are compact, sensitive, low-cost, and have low power consumption. Furthermore, the films should be achieved through relatively simple and reproducible preparation. Unfortunately, it is not so easy to get sensors where all mentioned advantages are combined. In order to achieve these properties, new sensing materials are required to exhibit different performances than the state of the art [1].

In recent years, a considerable attention has been given to the possibility of using chalcogenide glassy semiconductors as the sensitive layer in chemical sensors for the analysis of industrial solutions [2] and pollutant gases [3]. Significant progress can be obtained by investigating the changes of the conductivity of these layers as sensitive parameter.

The conductivity measurements are one of the oldest and one of the most sensitive methods used in surface physics. Adsorption processes, as well as alternatures of the surface structure, cause pronounced resistance changes. Various techniques for its studies such as photoelectric, thermoionic, or contact potential difference (Kelvin probe) methods, can be used [4].

In the present paper, the authors report about the response of thin films based on chalcogenide semiconductors of the ternary system As–S–Te to low NO_2 concentrations. In addition to this, it has been shown that these sensors exhibit a small sensitivity to other pollutant gases in air, such as SO_2 and CO.

EXPERIMENTAL

Ingots of As–S–Te were obtained by the melt-quenching method from pure Te, As, and Ge in evacuated quartz ampoules. Chalcogenide-based sensitive layers were prepared by thermal vacuum deposition onto glass substrates. It was performed under a working pressure of 10^{-5} Torr. The velocity of the film

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growth was about 1 nm s^{-1}, and the thickness of the layers was 2–3 µm. Sensitive structures were made with a sandwich configuration of successive vacuum deposition of aluminium contact, chalcogenide thin film as sensitive layer, and another aluminium contact on a glassy substrate.

NO_2 vapor with concentration of 0.95–1.9 ppm was obtained by means of calibrated diffusion tubes incorporated in an experimental set-up described in [3]. Carbon oxide media has been obtained by mixing the carrier gas and the test gas (CO) in the gas mixture controller. As both carrier and test gases flowed through flow-mass controllers, the concentration of CO in the test chamber could be changed in the range of 0 to 500 ppm.

Current-voltage and current transient characteristics have been carried out by applying different gas concentrations. These characteristics were measured in air, in gaseous media, and in air again. In all cases, applied voltage was changed with a step of 20 mV between –5 V and +5 V. The delay time between the measurements was 2 s. All the experiments were performed at room temperature. Ambient air with r.h. of 32–42% was used as the carrier and the reference gas.

RESULTS AND DISCUSSION

Sensor response upon NO_2 exposure

The chemical sensing properties and the transient response characteristics of the As–S–Te- based chalcogenide layers were further examinated by using the conductivity method described in [5]. Figure 1 shows the typical current-voltage characteristic of thin films studied in air and in the presence of nitrogen dioxide vapor with concentrations of 0.95 and 1.9 ppm. There are linear dependences that follow Ohm's law. The effect of NO_2 vapor consists in increasing of the current with the change of the bias voltage. Resistance of the investigated films do not vary so essentially as in the case of nitrogen dioxide–arsenic tetrasulphide interaction [3]. The effect of the influence of vapor of carbon oxide is the same as the effect of NO_2.

Transient characteristics have been carried out at a constant bias voltage with computer-controlled switching between NO_2 or another vapor and pure air. Figure 2 shows the transient characteristic for nitrogen dioxide. The dotted lines give the schedule of switching and applied gas concentration. The steps correspond to concentrations, of nitrogen dioxide vapor of 0 and 0.95 ppm. It was observed that already small NO_2 gas concentrations such as 0.95 ppm, lead to current change by around 7.5 mA. The response and recovery time [defined as the time to reach 90% of steady-state values of the gas-induced

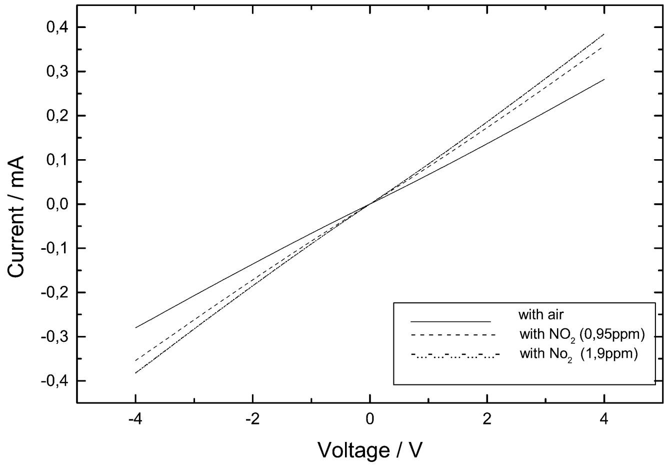

Fig. 1 Current–voltage characteristics of As–S–Te-based films in air and in presence of NO_2 vapor.

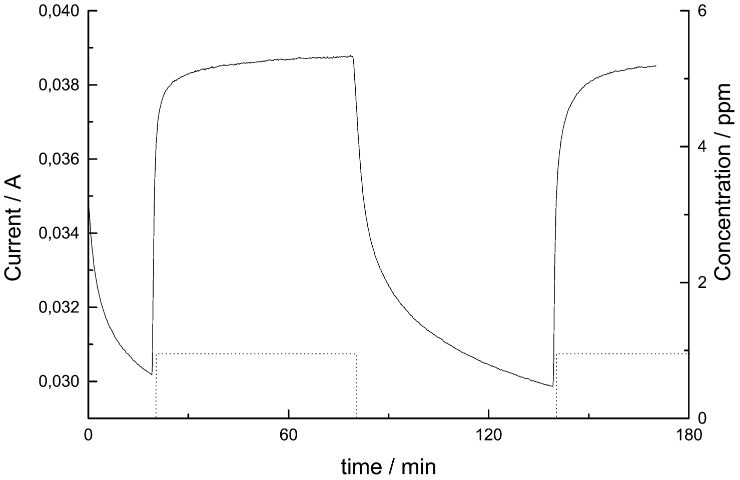

Fig. 2 Transient response of chalcogenide-based sensitive layers to various NO_2 concentrations according to the profiles shown at the bottom.

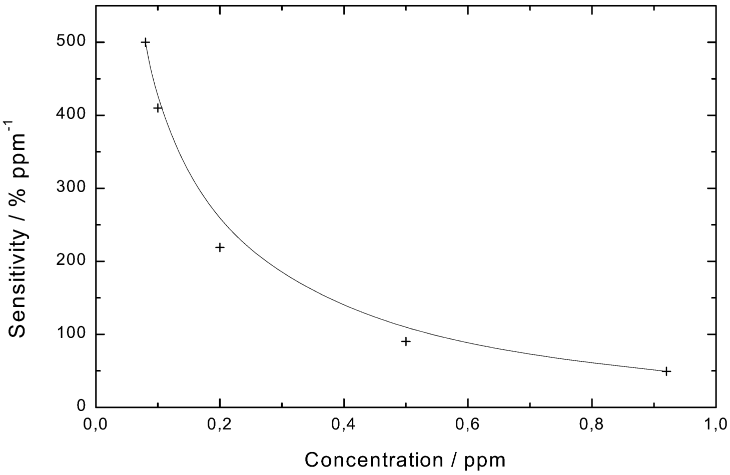

Fig. 3 Sensitivity vs. NO_2 gas concentrations.

current (τ_{90})] is found to be high and quit reversible, while the response time is fast and the reproducibility satisfactory.

As follows from Fig. 2, recovery time for NO_2 is longer than the response one. That means, that the adsorption of the nitrogen dioxide on the surface of chalcogenide-based layer can be a strong chemisorption process. It can lead to the formation of the covalent chemical bonds, namely strong *p*-bonds in which the holes captured by adsorped NO_2 particles participates.

Figure 3 shows the sensor's sensitivity toward NO_2 vapor at different applied gas concentrations. The sensitivity is defined as the relative variation of the resistance of the sensitive thin film in per cent per ppm of applied gas concentration:

$$S = \frac{R_g - R_a}{n R_a} \cdot 100$$

where R_a and R_g are the electric resistance of the sensor in air and in presence of NO_2 respectively and n is the gas concentration.

Sensor sensitivity to another pollutant gases

The response of the chalcogenide-based thin films to various gases like NO_2, CO, and SO_2 is shown in Fig. 4. It can be seen that As–S–Te-sensitive layers exhibit a high response toward low concentrations of NO_2 and a low cross-sensitivity to other studied gases.

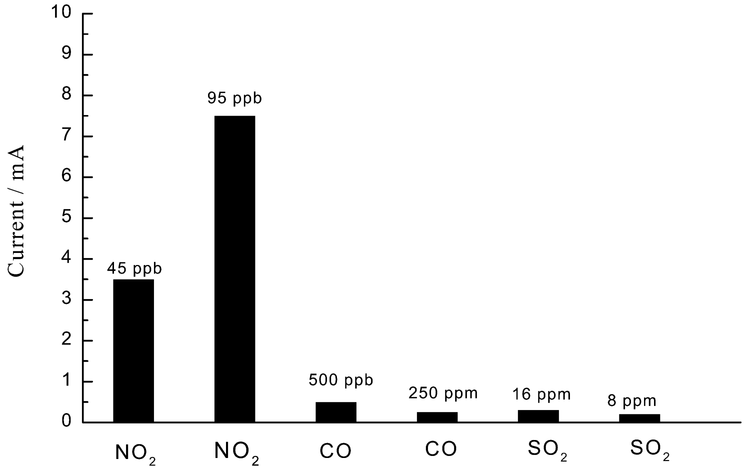

Fig. 4 Relative resistance change of As–S–Te-based thin films by exposure to NO_2, CO, and SO_2 gases.

CONCLUSIONS

As–S–Te ternary alloys-based gas sensors exhibit a high sensitivity at low concentration of NO_2. This sensitivity depends not only on the gas concentration, but also on the applied bias voltage. Moreover, these sensors already operate at room temperature with a high sensitivity in the ppm and sub-ppm ranges and have a good selectivity. These facts point out, that chalcogenide-based gas sensors are a new kind of solid-state, low-cost, and low-power-consumption chemical sensor that are very well suited for environmental monitoring.

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