HIGHLY SENSITIVE TELLURIUM BASED SENSORS FOR THE DETECTION OF NITROGEN DIOXIDE

A. Tiuleanu
Technical University of Moldova

INTRODUCTION

During the past years, much effort is made to develop sensors for the detection of toxic gases in our environment. Sensing elements for solid-state sensor devices are the most appropriate for this purpose as they can be integrated in portable systems for applications on-line. Recently a novel class of gas sensors based on chalcogenide materials was proposed for monitoring pollutants in ambient air [1-3]. Most attractive in this respect are the thin films based on tellurium alloys, including As-Ge-Te system. These films show remarkable sensing properties to NO_2 at even room temperature.

The mechanism of gas detection of these materials is, however, still not completely understood, because for the lack of sufficient experimental data. In the present study the NO_2 sensing properties of tellurium-based films in dependence of the contact materials, the film thickness, the annealing and temperature have been investigated systematically. The possible mechanism of gas sensing is also discussed.

1. EXPERIMENTAL

Tellurium based thin films were deposited at different thickness by thermal vacuum evaporation from a crucible onto Pyrex glass substrates. The evaporation was performed at the working pressure of 10^{-5} Torr. Samples of different (30, 60, 110 and 200 nm) thickness were prepared by a variation of the distance between the evaporation crucible and the substrate, while the evaporation time has been kept the same. The surface morphology of the films was investigated with a SEM TESLA BS 340. In order to investigate the possible effect of film contacting, the electrode materials with work function greater (gold, ~ 5.3 eV) or smaller (indium, 4.12eV) than tellurium work function (4.95 eV [4]) have been used. Gold electrodes where deposited onto the film surface through thermal vacuum evaporation. Copper wires were then attached to the electrodes by silver paste. Indium contacts have been made with two "indium pillows", which were pressed on top of the sensitive film.

NO_2 vapor with a concentration of 0.75 to 18 ppm was obtained by using the experimental set up presented on Fig.1.Gaseous NO_2 media was obtained using a calibrated permeation tube (Vici Metronics, USA), which was incorporated into the experimental set-up. Ambient air was used as the carrier and reference gas.

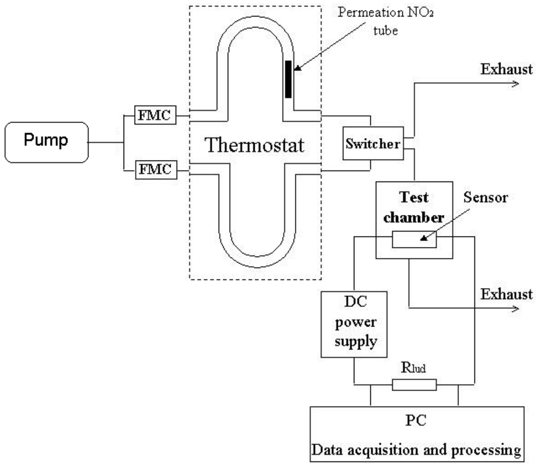


Figure 1. Schematic diagram of the gas diluting system combined with data acquisition set up.

The thin film sensing devices were put into a test cell (of 10 ml volume), which was placed inside the furnace. For the temperature measurement a platinum resistance temperature detector PT –100 was placed on the external wall of this cell.

Current / voltage and current transient characteristics have been carried out with different gas concentrations on samples, which were heated at different temperatures. In all cases the applied voltage varied between - 2.5 V and + 2.5 V in steps of 20 mV while the respective values of the current were measured. The delay time between two measurements was 2 s. The measurements were performed at temperatures between 20 ^{0}C and 200 ^{0}C.

The transient characteristics have been measured by computer controlled switching of the gas between NO_2 vapor and pure air at constant voltage of 4 V.

The sensor sensitivity was defined as the relative resistance variation expressed in percent:

$$S = 100(|R_a - R_g|)/C \cdot R_a \quad (1)$$

whereby R_a and R_g are the electrical resistances of the sensor in air and in the presence of NO_2 respectively. C is the gas concentration.

2. RESULTS AND DISCUSSION

Figure 2 shows the current / voltage characteristic of tellurium based films with Au electrodes in air and in the presence of NO_2 vapor.

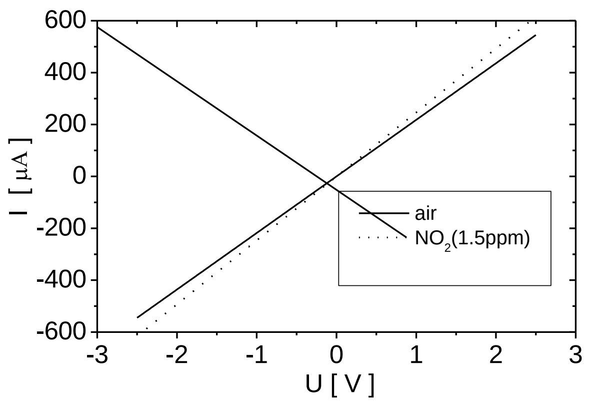


Figure 2. Current - voltage characteristics of tellurium based film with Au electrodes in air and in presence of 1.5 ppm of NO_2.

The devices with In electrodes exhibit the same characteristics. In all cases the I / V characteristics are linear and follow the Ohm' s law.

The influence of NO_2 vapor leads to an increase of the current independently of the direction of the bias voltage. It is significant to note the high value of the gas-induced current, which is in the range of dozens of microamperes, depending on the film' s geometry and bias voltage.

The sensor sensitivity as a function of film thickness is shown in Fig.2. As can be seen the sensitivity of the film strongly increases with thickness decrease. Such behavior can be expected in the case of a compact layer [5]. Inset of Fig. 3 shows the SEM view of a sensitive film. It can be seen that the morphology of the film shows a compact layer with crystals of about 0.5 - 1.0 µm in size textured in the substrate plane. In the case of a compact layer the current flows through two parallel channels, one of them is the geometric surface, which is affected by the gas reaction and the other is the gas-unaffected bulk. Because the surface part of the grains can be oxidized under interaction with atmospheric oxygen, the appearance of a grain boundary resistance, which is put in series with a surface channel of current flow, occurs. The decrease of layer thickness enhances the influence of surface grain boundary resistance and removes the bulk, gas-unaffected parallel resistance.

That is why the film conductivity decreases, while its sensitivity strongly increases with the thickness decrease.

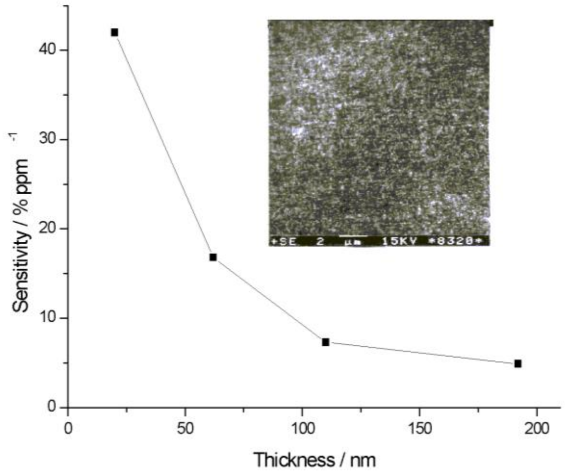


Figure 3. Effect of thickness on sensitivity to 1.5 ppm of NO_2, at room temperature. Inset shows the SEM micrograph of a film.

Figure 4 shows the response kinetics of tellurium-based sensors at different temperatures when the squared concentration pulse with 0.75 ppm of NO_2 in amplitude was applied. As temperature increases the film's conductance increases as well, the sensitivity decreases, while the response and recovery processes become faster.

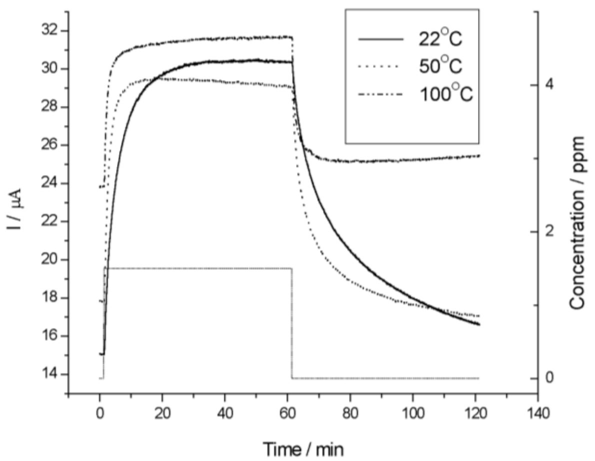


Figure 4. Response of tellurium based sensor to squared pulse of 0.75 ppm NO_2 at different temperatures

The sensor sensitivity to 0.75 ppm of NO_2 versus operating temperature is shown in Figure 5.. The temperature diminishes the sensitivity of the films; especially strong at temperatures higher than

80 °C. Inset of Figure 5 shows the response and the recovery times versus operating temperature. Both, response and recovery times decrease with operating temperature increase, while the recovery time diminishes more strongly. That is why at temperature of about 100 ^{0}C the response and recovery times are almost the same and result to be around 2 min to 4 min.

Thus, the best compromise between sensitivity and velocity of response-recovery times is achieved at around 50 ^{o} C. Figure 6 shows the current flow trough a sensor under repeated switching on-off of the NO_2 gas mixture at constant bias voltage and 50 ^{0}C operation temperature.

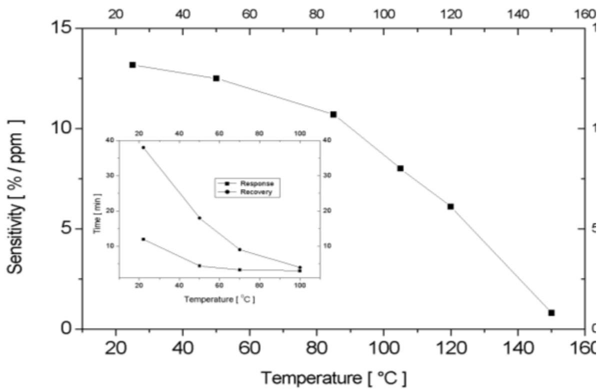


Figure 5. Sensitivity of tellurium based sensor to 0.75 ppm of NO_2 versus operating temperature. Inset shows the response and the recovery times versus operating temperature.

Were applied squared pulses of NO_2 vapor with concentration of 0 ppm, 0.75 ppm, and 1.5 ppm. It is seen that the current follows the schedule and there is no baseline drift or noticeable drift of the gas induced current.

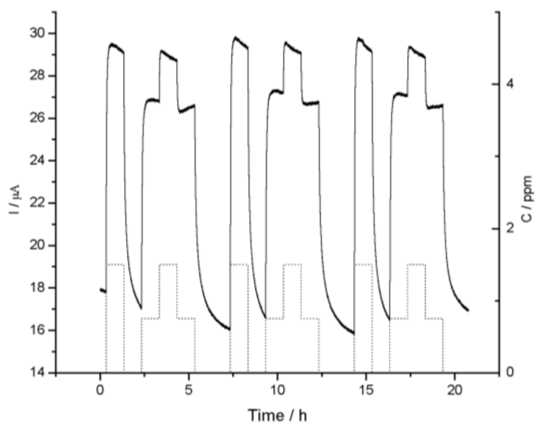


Figure 6. Transient characteristics of gas - induced current at 50 °C by exposure to various concentrations of NO_2 according to the profile shown in dotted lines of the bottom.

The results can be understood taking into consideration that tellurium based films belong to so called lone - pair semiconductors, which are materials that contain a large concentration of elements from V and VI groups of the periodic table. The main peculiarity of lone - pair semiconductors is that the lone - pair orbitals (in tellurium - $5p^4$ state) form the upper part of the valence band. If the crystalline network contains defects such as unsatisfied chemical bonds (dangling bonds) the interaction between these defects and lone - pair electrons occurs. The dangling bond interacts with neighboring lone - pair, bonding with it by distorting its environment [6]. Such interaction results in the release of about 10^{13} - 10^{15} holes / cm^3.

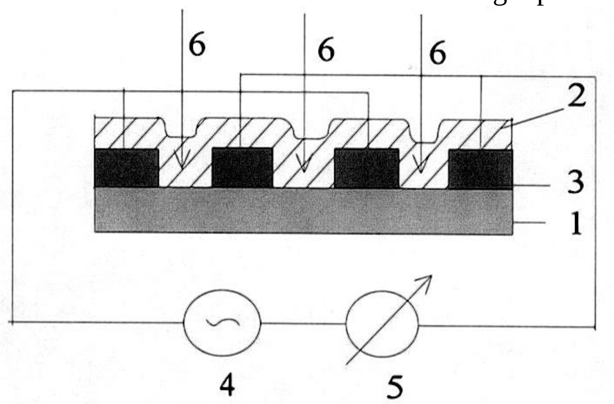
Thus, the dangling bonds act as dopant for lone-pair semiconductors and probably this is the key for understands the gas sensing with these materials. In fact, the surface of the semiconductor is the region where the periodicity of the crystal is interrupted and the maximum concentration of dangling bonds occurs. Because- of interaction with lone – pairs electrons, the hole enriched region is formed near the surface of the grains. Hence, the band edges of p-tellurium bend up at the surface and in the intragrain regions.

When the chalcogenide semiconductor is introduced into gaseous environment the adsorption of gas molecules occurs, which can produce either - donor or acceptor levels. The molecule of nitrogen dioxide has an odd electron [7] i.e. after covalently bonding of nitrogen to oxygen one of the atoms remains with a single unpaired electron. Being adsorbed on the surface of the chalcogenide semiconductor the molecule of NO_2 act as a dangling bond, that can accept a lone - pair electron to form an electron pair. Capture of a lone - pair electron means the transition of an electron from the upper part of the valence band to a NO_2 acceptor level, which result in realize of an additional hole.

Thus, the adsorption of nitrogen dioxide leads to increase in the majority carrier density and hence increasing of conductivity of the film.

3. SENSOR DESIGN

The proper choice of contact geometries is important in the design of reliable chalcogenide based gas sensor. Although there is no systematic investigation to utilize optimized contact geometries it was observed that each contacts geometry have specific advantages for detection certain gases. For chosen contact geometry, different operation modes may be used to obtain the electrical signal correlated with gas concentrations. The conductive chalcogenide based gas sensor can be fabricated for different operation modes. Figure 7 shows the scheme and the view of a multi-channeled NO_2 microsensor encapsulated in a standard TO - 8 socket with eight pins.



a)

b)

Figure 7. a) Cross section of the sensor: *1 - insulating substrates, 2 - sensitive chalcogenide film, 3 – contacted electrodes, 4 – power supply, 5 – monitoring device, 6 – applied gas.*
b). Sensor encapsulated in TO – 8.

Such a sensor exhibits the following parameters:

Measuring range	0 – 10 ppm
Sensitivity range	500 µA/ppm
Resolution	< 0,01 ppm
Response time at 20°C	< 30 s
Power consumption	~ 100 µW
Effect of temperature on sensitivity	~ 0,5% / °C
Effect of humidity	~ 0,1% per % r.H
Long-term sensitivity drift	< 3% per month

CONCLUSION

High effective NO_2 sensors can be manufactured using tellurium based thin films. The sensors can operate at room temperature. They show considerably short response times and a good relative sensitivity in the ppm and subppm concentration range. These properties are suited for their applications in environmental monitoring.

ACKNOWLEDGEMENTS

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