Evidence for the Concentration Induced Extinction of Gas Sensitivity in Amorphous and Nanostructured Te Thin Films

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***Abstract* - The extinction of sensitivity to nitrogen dioxide induced by high gas concentration have been observed in ultrathin tellurium films. The phenomenon becomes apparent in both continuous and nanostructured films shown by AFM, SEM and XRD analyses to be in amorphous state. Sensitivity of 30 nm thickness Te film decreases near linearly with concentration increase between 150 and 500 ppb of nitrogen dioxide. The results are explained in terms of formation of a nitrogen dioxide catalytic gate in which a molecule adsorbs (and desorbs) without reacting.**

***Keywords* - Gas sensitivity, Extinction, Nanostructured tellurium, NO_2.**

1. INTRODUCTION

Tellurium thin films exhibit sensitivity to toxic and harmful gases [1-2], which allowed proposing them for the development of gas sensors [3]. The sensitivity to these gases, as well as to oxygen, nitrogen and water vapors [4] depends on substrate microstructure and its temperature during film deposition [5,6]. Besides, the film thickness strongly influences both the sensor sensitivity and conductivity. Decrease of a Te film thickness from 120 nm to approximately 40 nm results in increasing of sensitivity toward NO_2 by more than 10 times [7]. The current flow through two parallel channels explains such a behavior [8]. In a compact layer, the current flows through two parallel channels, one of them being the surface channel, which is affected by the gas reaction and the other is the gas-unaffected bulk.

Decreasing the layer thickness leads to enhancing the influence of the surface resistance and removing the bulk, gas-unaffected parallel resistance. In this context it appeared to be interesting making experiments with ultrathin (less than 40 nm) compact layers. On the other hand, layer's compactness can be controlled by deposition rate. It is known for a long time [9] that the deposition rate strongly influences the growth of Te film. The increase of deposition rate is associated with a shortening of the lifetime of atoms migrating on the substrate surface, decreasing of degree of crystallite order and increasing the compactness of the film.

In this study, the nitrogen dioxide sensing properties of compact tellurium films grown by high evaporation rate were examined with respect to SEM, XRD and AFM characterization. In order to elucidate the influence of substrate microstructure, the films were deposited on both continuous (Pyrex glass) and priory nanostructured (Al_2O_3) substrates.

Apart from an essential reduction of the response time, a new unexpected phenomenon consisting in concentration-induced extinction of gas sensitivity was observed.

2. MATERIAL AND METHODS

Tellurium (purity 99.999 %) based thin films of different thicknesses were deposited both onto Pyrex glass and nanostructured Al_2O_3 substrates with thermal vacuum evaporation. The evaporation was performed from a tantalum boat at the working pressure of $\approx 10^{-4}$ Pa, without heating or cooling the substrate. The growing rate of the film was around 30 nm / s, the area of deposition being around 70 mm^2. Rectangular samples of different thicknesses were prepared by variation of evaporation time, while the distance between the evaporation boat and the substrate has been kept the same - 20 cm. The thicknesses and the shape of the films have been measured after their preparation using an Atomic Force Microscope (SIS SCAN Control/C). The surface morphology of the films was investigated, using a VEGA TESCAN TS 5130 MM scanning electron microscope (SEM). X –ray analyses using the DRON –YM1 diffractometer by Fe$K\alpha$ radiation was applied for the structural investigations of the grown films. Rotation velocity of the scintillation counter was 2 (or / and 4) angle degrees /min.

Two Indium pillows were pressed on top of the Te film surface in order to serve as electrical contacts for the gas-sensing element. The distance between electrodes was ~ 5mm so that the sensing aria consists of about 30 mm^2. NO_2 vapor with a concentration of 0.15 to 1.0 ppm was obtained by using the experimental set up described in

[10]. The membrane pump provides the flow of the carrier gas (ambient air) which is split into two independent streams. Both lines lead to a thermostat, where they are connected to U-shaped glass tubes in which the carrier gas is saturated by gas of interest at constant temperature. The saturation takes place in one U-shaped glass tube, where a NO_2 calibrated permeation tube (Vici Metronics, USA) is placed. The second line is used either for dilution or as the reference. Both lines are fed through a diluting – switching system to the waste or the test sell, respectively. A PC with a data acquisition board manufactured by National Instruments Inc. was used for processing.

The thin film sensing devices were put into a test cell (of 10 ml volume) and the gases were injected with a flow rate of 100 ml /min, maintained by mass flow controllers (MFC, Wigha, Germany), parallel to the film surface.
The current transient characteristics have been carried out with different gas concentrations at room temperature with an applied voltage of 5 V. In order to transform the resistance signal into voltage signal, the sample was connected in series to a load resistance using a d.c. voltage supplier. In all measurements, the load resistance was chosen to be approximately by an order of magnitude less than the sample resistance.

The sensor sensitivity was defined as a relative variation of the resistance expressed in percent / ppm :

$$S = \frac{R_a - R_g}{cR_a} \times 100 \qquad (1)$$

were R_a and R_g are the electrical resistance of the sensor in air and in the presence of gas (NO_2) respectively, and c: concentration [ppm] of the gas measured.

3. RESULTS

3.1. The thickness, morphology and phase structure of Te thin films

The thickness, topography, morphology and phase structure of Te films were examined before investigating their sensitivity to NO_2 vapour. Figure 1 shows the atomic force microscope (AFM) images of an as - prepared Te thin film with thickness of about 110 nm, grown on a Pyrex substrate. The film was scratched in order to assess its thickness.

It is seen that except of separate jumps (which can be caused by measurement process) the surface of the film is smooth. The average roughness of 5μm ×5μm areas is about 2-3nm.

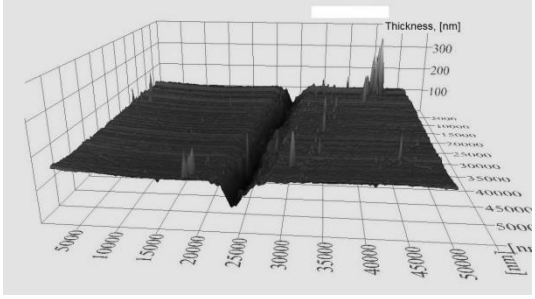
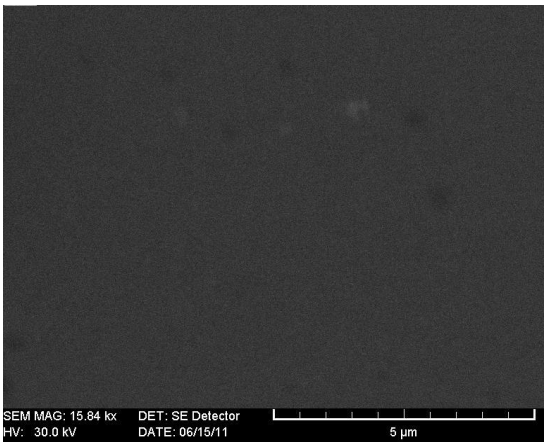
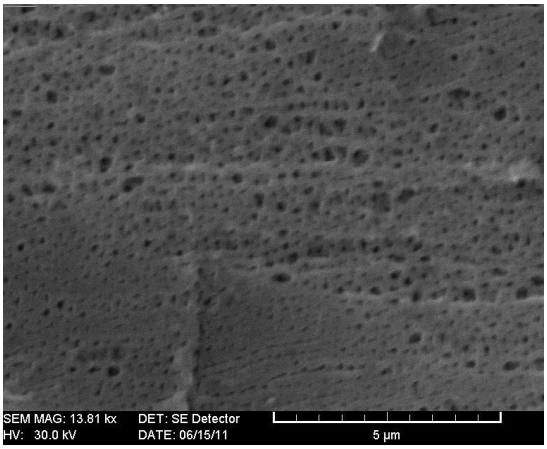


Fig.1. AFM images of a tellurium film (110 nm) grown on a Pyrex –glass substrate.

Figure 2 (a, b) shows the SEM images of tellurium films grown on both continuous (Pyrex glass) and priory nanostructured by electrochemical methods (Al_2O_3) substrates. SEM analyses confirms that the films are smooth and without any traces of crystallites.



a)



b)

Fig.2. SEM micrographs of Te films grown: a) on Pyrex –glass and b) on nanostractured Al_2O_3 substrates

X-ray diffraction (XRD) data are in agreement with the above observations. Fig 3 shows the XRD diffraction pattern of a Te film grown on Pyrex – glass substrate. The peaks corresponding to Te (shown by dotted lines) were not found, indicating the predominantly amorphous nature of the film.

3.2 Gas sensing characterization

Figures 4(a) and 4(b) show the current flow through tellurium thin (~ 110 nm) films grown on Pyrex-glass and nanostructured Al_2O_3 substrates respectively, under repeated switching on-off of the NO_2 gas mixture at constant bias voltage, room temperature (25 ^{0}C) and relative humidity of 32%. Humidification of the carrier gas was accomplished using saturated solution of the salt $CaCl_2$ in water, but the platinum resistance temperature

detector PT – 100 close to the sensor served as a temperature controller.

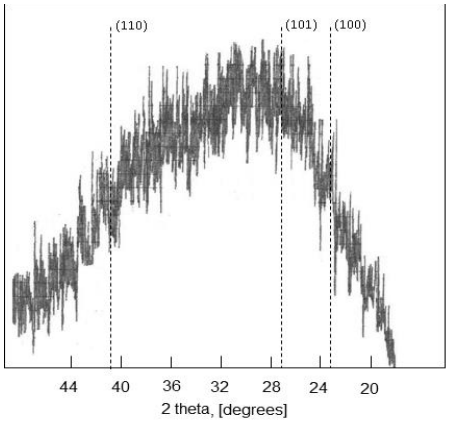


Fig.3. XRD diffraction pattern of amorphous tellurium film grown on a Pyrex glass substrate. Dotted lines show the places corresponding to peaks of crystalline Te with orientation indicated by round brackets.

There were applied squared pulses of NO_2 vapor. The dotted line gives the switching schedule. It is seen that the current follows the schedule showing a usual behavior: the transition of concentration from 0.5 to 1.0 ppm of NO_2 results in increasing of current.

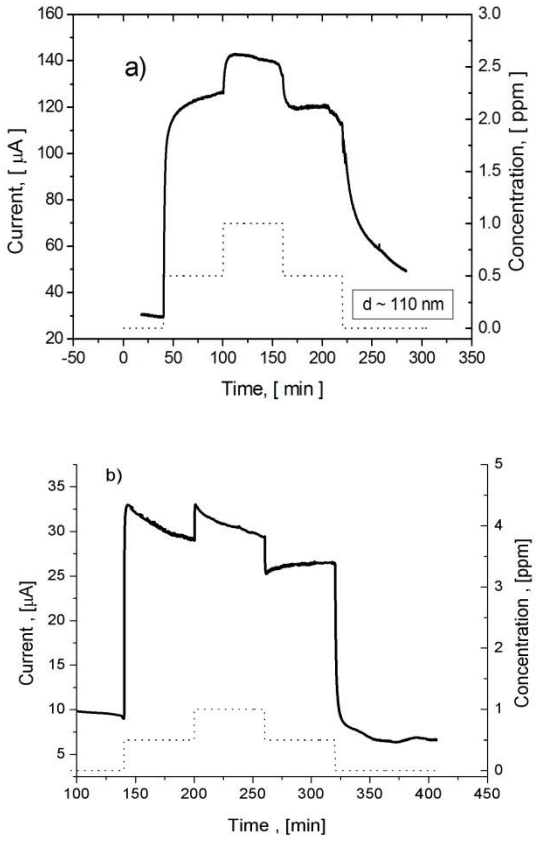


Fig.4. Transient characteristics of gas - induced current by exposure of Te films (thickness ~110 nm) to various concentrations of NO_2 according to the profile shown in dotted lines of the bottom. Substrate: a) Pyrex –glass; b) Nanostructured Al_2O_3.

The recovery time is longer than response time, which consists only a few seconds. There is no also a noticeable baseline drift.

It is clearly seen the influence of substrate microstructure: growing of the film on nanostructured substrate (Al_2O_3) results in an evident shortening of both response and recovery times.

Figures 5(a) and 5 (b) illustrates the transient characteristics of gas - induced current in Te ultrathin (~30 nm) films grown on Pyrex-glass and nanostructured Al_2O_3 substrates respectively, by exposure to various concentrations of NO_2 according to the profile shown by dotted lines at the bottom. Surprisingly, but in these films the transition from 0.5 to 1.0 ppm of NO_2 results in decreasing of current i.e. extinction of sensitivity induced by high NO_2 concentration .

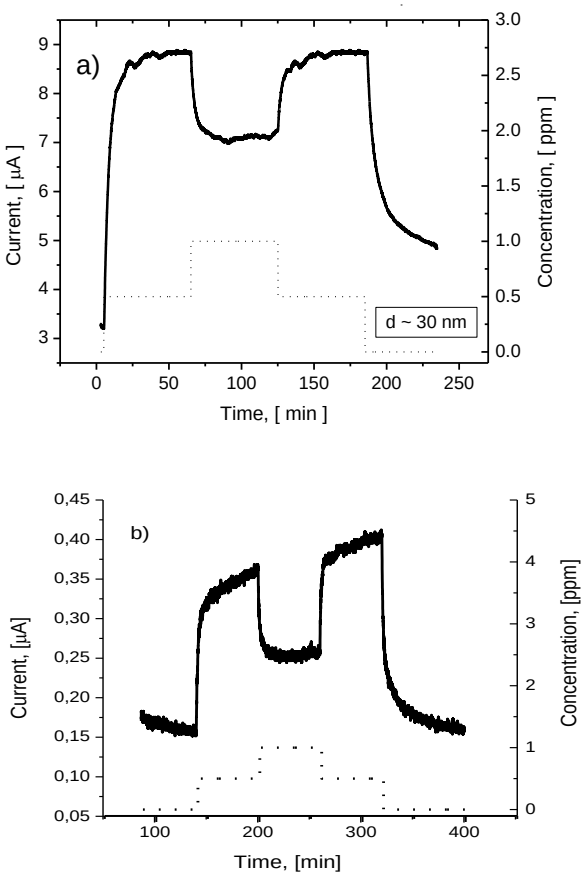


Fig.5. Transient characteristics of gas - induced current by exposure of Te films (thickness ~30 nm) to various concentrations of NO_2 according to the profile shown in dotted lines of the bottom. Substrate: a) Pyrex –glass; b) Nanostructured Al_2O_3.

The diluting system of our experimental set-up allowed investigating the effect of gas concentration on device sensitivity in limits 0.15 - 0.5 ppm. Figure 6 presents the sensitivity of a Te sensor (thickness ~30 nm) grown on a Pyrex –glass substrate versus concentration of nitrogen dioxide diluted in ambient air at room temperature. The Te based sensor grown on a nanostructured Al_2O_3 substrate exhibits a similar dependence. As one can conclude, the sensitivity of the

sensor is near linearly damped by gas concentration increase.

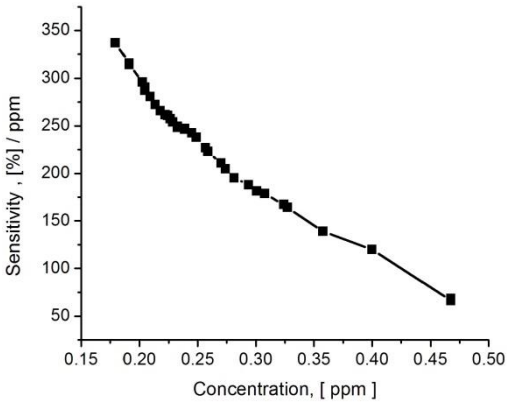


Fig. 6. Sensitivity of an amorphous Te sensor grown on a glass substrate (thickness ~ 30 nm) vs. NO_2 concentration.

4. DISCUSSION

Tellurium and its alloys belong to so-called lone - pair (LP) semiconductor materials. The main peculiarity of LP semiconductors is that the upper part of the valence band is formed from p - state lone-pair electrons [11]. Being weekly bond, these electrons interact with dangling bonds, which serve as acceptors. Such interaction results in the releasing of about 10^{13} - 10^{15} cm^{-3} holes, leading to p-type conductivity.

Because namely on the surface the maximum concentration of dangling bonds occurs, a hole enriched (accumulation) region is formed at the surface. Gas sensing is due to variation of hole density in the enriched (surface) region in the presence of gaseous media. It is known that adsorption of gas molecules on the semiconductor surface can produce either donors or acceptors. Nitrogen dioxide molecule comprises an odd electron that is after covalently bonding of nitrogen to oxygen one of the atoms remains with a single unpaired electron [12]. Being adsorbed on the surface of the Te film the molecule of NO_2 act as a dangling bond that can accept a LP electron to form an electron pair via reaction:

$$NO_2 + Te \rightarrow NO_2^- + Te^+ \qquad (2)$$

Capture of lone-pair electrons, i.e. their transition from the upper part of the valence band to NO_2 acceptor levels is accompanied with the release of additional holes (majority carriers) and results in increasing of conductivity of the film. The concentration induced extinction of sensitivity, i.e. decrease of conductivity can be due to a nitrogen dioxide catalytic gate created because the film surface may be NO_2 covered in an it excess [13]. The initial reactions for different concentrations of nitrogen dioxide take place therefore on different types of surfaces. Moreover, it seems, during the transient the switching phenomena predicted by Lundstrom [13] occurs (Fig. 5 a,b), where one type of coverage is rapidly transformed to another. As follows from our experiments, the other factors that determine identification of damping effect are the thickness of the film and its phase structural state (or compactness). SEM and XRD spectra show the sensitive tellurium films, physically grown in the present work by high rate of thermal deposition in vacuum on glass substrate, to be amorphous. The last is obviously due to the increase of pressure of tellurium vapours in the substrate aria, which lowers the lifetime of atoms migrating on the substrate surface to be trapped in the suitable position with the minimum of surface energy. The density of tellurium films strongly increases with deposition rate increase and at deposition rate larger than 8,6 nm/s the density does not depend on the film thickness [9]. As in the present work the Te films were prepared using much higher rates of deposition (~ 30 nm / s) they definitely should be attributed to the compact layers. In such a layer the current flows through two parallel channels [8]: a) the surface channel, which is strongly affected by the gas reaction, and b) the bulk channel, in which the gas reaction is controlled by diffusion processes. Electrically that means two parallel resistors R_s (surface) and R_b (bulk) differently affected by pollutant gas in question, although the microscopic mechanism of gas interaction may be the same. Obviously, the bulk channel can be removed reducing the film thickness to nanoscale (< 30 nm). In such a case, the reaction sites of the film are fully involved in sensing response even at very low concentration of nitrogen dioxide. The excess of NO_2 concentration results in formation of a catalytic gate that dampens the sensitivity.

While the proposed mechanism of concentration damping of sensitivity is not perfect, this phenomenon has to be taken into consideration by development of semiconductor thin film gas sensors.

5. CONCLUSIONS

Non-crystalline Te thin films were grown on glass and nanostructured Al_2O_3 substrates without their cooling by high (~30 nm/s) deposition rate. The films exhibit high sensitivity to low concentration of NO_2 at room temperature. The films grown on nanostructured Al_2O_3 show a considerably short response time. The gas concentration increase results in extinction of sensitivity of the film. The formation of a catalytic gate on the surface at excess of nitrogen dioxide can explain this phenomenon, so that the initial reactions for different concentrations take place on different types of surfaces.

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