Impedance characterization of Te based gas sensitive films

Dumitru Tsiulyanu, Olga Mocreac
Departamentul Fizica, UTM
Chisinau, R.Moldova
tsiudima@gmail.com, doleaster@gmail.com

Abstract. Gas sensing performance of Te films investigated by method of impedance spectroscopy is reported and discussed. The films have been prepared by thermal vacuum evaporation onto sintered alumina (Al_2O_3) substrates with a priory deposited platinum interdigital electrodes. The morphology of the films appears to consist of interconnected islands and dots, which facilitate the solid-gas interaction. It is shown that impedance spectra are strongly influenced by gaseous environment. Analyses of complex impedance spectra allowed evaluating of some physical parameters of the films, in both dry air and its mixture with hydrogen, nitrogen dioxide and hydrogen sulfide taken as target gases. The interfering sensitivities to these gases at room temperature have been assessed.

Keywords: Impedance, Te films, Gas sensitivity, H_2, NO_2, $H_2 S$

I. INTRODUCTION

Glassy chalcogenide based films may be used for the detection of harmful gases at room temperature. Firstly this possibility has been pointed out in the early 2000s [1, 2] for microcrystalline Te films, but later the gas sensitive amorphous films based on pure Te have been reported [3-5] . In order to estimate the possible application of these materials in gas sensors, the authors have measured at gas sorption, the variation of different physical quantities (resistivity, current, resonance, work function etc.). Also, different pollutant and toxic gases (NO, NO_2, CO, NH_3 , NH_4 etc.), as well as the volatile organic compounds or water vapor have been used as a target gas.

Although the cross sensitivity to mentioned gases is essential different, the distinguishing between them becomes important. One of possibilities to obtain a selective detection of gases has been mentioned at the early stage of investigation of semiconducting gas sensors [6] and consists in a fast sweeping of sensitivity of a single sensor at different frequencies. In the present work, we report the results of gas sensing measurements performed by investigation of impedance spectra in a large frequency range 5Hz – 13MHz, at room temperature.

II. MATERIAL AND METHODS

Tellurium based thin films have been prepared by thermal evaporation of polycrystalline Te from tantalum boats onto ceramic Al_2O_3 substrates at a working pressure of 10^{-5} Torr.

The ceramic Al_2O_3 substrates had the previously deposited platinum interdigital electrodes with an electrode width of 15 μm and interelectrode distances of 45 μm The growth velocity of the film was in the order of 30 nm/s, and the area of deposition around 5 mm^2. The thickness of the films was about 60 nm, being determined using micro interferometer MII - 4. Structural investigations of grown films were carried out by the X –ray analyses and scanning electron microscopy (SEM). The films were encapsulated in standard TO – 16 sockets and their contacts were thermally bonded to socket pins by means of copper wires.

Impedance measurements were carried out in frequency range of 5 Hz to 13 MHz using a HP4192A impedance analyzer. For these experiments the thin film sensing devices were put into a test cell (of 10 ml volume) in which the gases were injected parallel to the film surface. Constant flow (100 ml/min) was maintained by mass flow controllers (MFC, Wigha, Germany). In this work, the a.c. gas sensitivity was defined as relative variation of impedance for a selected frequency in mixture of carrier gas with a target one and pure carrier gas, divided by target gas concentration (C), in percent / ppm:

$$\eta = \frac{\left| Z_a - Z_g \right|}{Z_a C} 100\% \qquad (1)$$

III. SURFACE MORPHOLOGY AND PHASE - STRUCTURE

The surface morphology of the films was made visible with a VEGA TESCAN TS 5130 MM scanning electron microscope at an acceleration voltage of 30 kV. X-ray analyses using a DRON –YM1 diffractometer with FeK α radiation was applied for structural investigations of the grown films. The rotation velocity of the scintillation counter was 2 (or 4) degrees/min. Figures 1 shows the SEM images of the elemental Te, grown on sintered alumina (Al_2O_3) substrates by deposition rate of ~ 30 nm/s. As can be seen the films grown on sintered alumina consists of agglomerated islands, resulting in the films with great surface roughness.
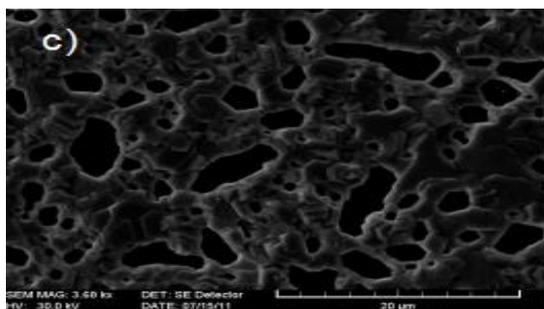
Fig. 1. SEM images of pure tellurium thin films grown on sintered alumina (Al_2O_3) substrates.

The XRD patterns of pure Te, films deposited on alumina substrates are shown in Figure 2. It is evident that the pure Te films show very small peaks corresponding to crystalline phases of Te, indicating their nearly amorphous nature. These results are in agreement with SEM observation.
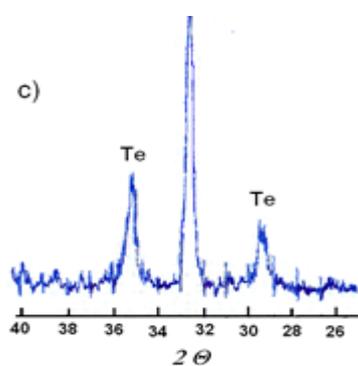

Fig. 2. XRD diffraction pattern of pure tellurium thin films grown on sintered alumina (Al_2O_3) substrates.

IV. IMPEDANCE CHARACTERIZATION

It is well known that impedance measurements allow to calculate the equivalent circuit and to distinguish between contributions from the surface, bulk or contacts to film conductivity [7].

Figure 3a shows the Nyquist diagrams obtained from data measured in pure dry air for thin film devices based of pure Te thin films at room temperature (22ºC). The diagram shows the slightly depressed semi-circular arc with the center placed below the real axis; owing to the presence of different circuit elements in the thin film device [7].
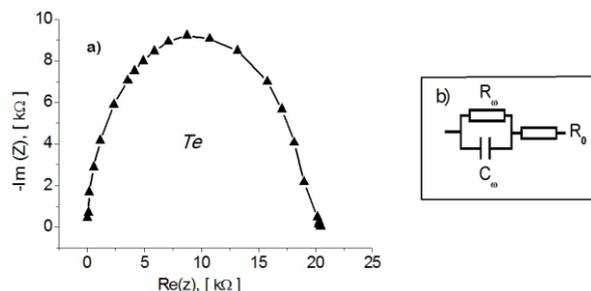

Fig. 3. Nyquist diagram of thin film devices based on pure Te in dry air, at 22ºC (a) and suggested equivalent circuit (b).

Figure 4 illustrates the frequency dependent impedance of Te thin films. It is seen that the impedance of pure *Te* films strongly falls with frequency increase.
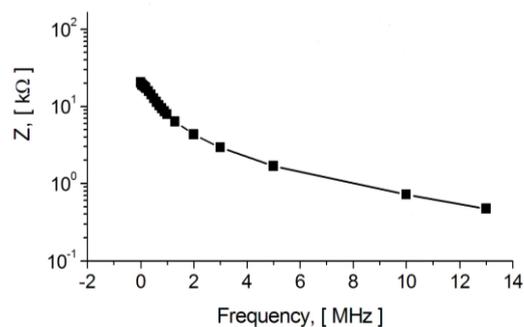

Fig. 4. Impedance of Te films versus frequency of applied voltage, at room temperature (22^0C).

Figures 5 shows the complex impedance diagrams in the Cole-Cole presentation (Nyquist diagram) of thin film devices based of *Te* films, measured both in dry air and upon exposure to NO_2, at room temperature (22ºC). Addition of nitrogen dioxide to dry air does not change the general shape of the impedance spectra of pure tellurium films; that is, it influences all elements of suggested equivalent circuit shown in Figure 3b suggested in figure.
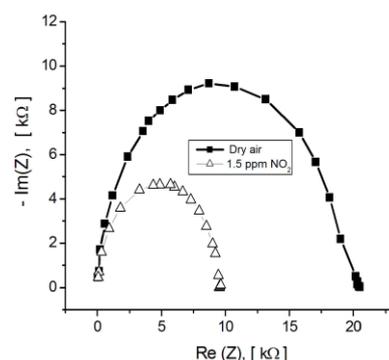

Fig.5. Nyquist diagrams of Te films in both dry air and its mixture with NO_2, at room temperature (22^0C).

It is seen that as the environment is changed from dry air to its mixture with gas in question, both real and imaginary parts of impedance are essentially influenced.

Figure 6 shows the frequency dependent sensitivity of the films in question towards NO_2, at room temperature.
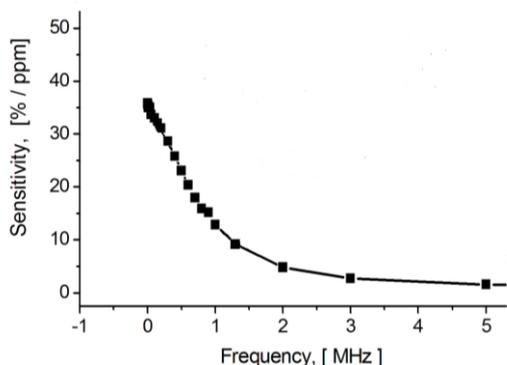

Fig.6. Sensitivity spectra of Te thin films to 1,5 ppm NO_2 in dry air at room temperature.

It is observed that Te films show remarkable sensing properties to NO_2, but this sensitivity appears to be strongly influenced by the frequency of electric field modulation. The sensitivity diminishes quite slowly and tends to saturation at approximately 3 *MHz*.

Thus, the Te films are suitable for the development of NO_2 sensors operating at room temperature. In this context becomes important the interfering effect of the other accompanying gases in the environment. Figure 7 reports the complex impedance spectra of tellurium-based films upon exposure to different test gases: NO_2, H_2 and H_2S. It is seen that addition of these gases to dry air does not change the general shape of curve, i.e. they influences all elements of the equivalent circuit.
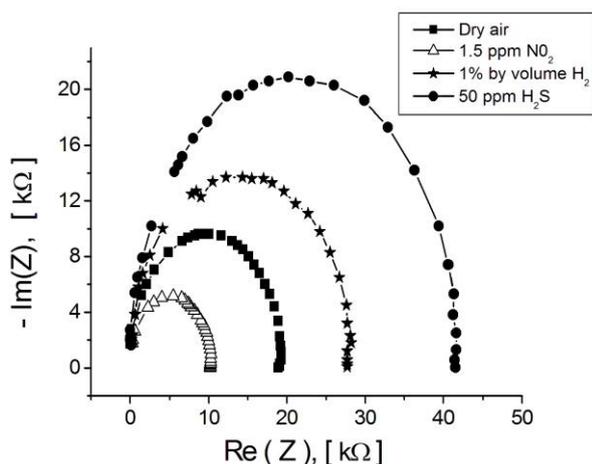

Fig.7. Nyquist diagrams of tellurium thin films in different environmental conditions, at room temperature.

From these diagrams, both the characteristic frequency (the frequency at which the imaginary part reaches its maximal value) and impedance of the film at this frequency have been estimated. The estimated values (Table 1) shows that the addition of NO_2 to dry air leads to decrease the impedance, while the addition of H_2 or H_2S results in its increasing.

TABLE 1. IMPEDANCE OF TELLURIUM BASED FILMS AT CHARACTERISTIC FREQUENCY, BY DIFFERENT ENVIRONMENTS

Environment	f_m, [kHz]	Z, [kΩ]
Dry air	900	13,3
1,5 ppm NO_2	1500	7,5
H_2 1% by volume	600	19,8
50ppm H_2S	400	29

In this context it becomes interesting to analyze the frequency dependences of sensitivity to different target gases through the impedance change. Figure 8 (a, b) shows the sensitivity spectra of pure tellurium films toward nitrogen dioxide , hydrogen sulfide and molecular hydrogen at room temperature. Although the sensitivity towards these gases differs very much, always there is a frequency dependent edge of sensitivity, which is also dependent of nature of adsorbed species.
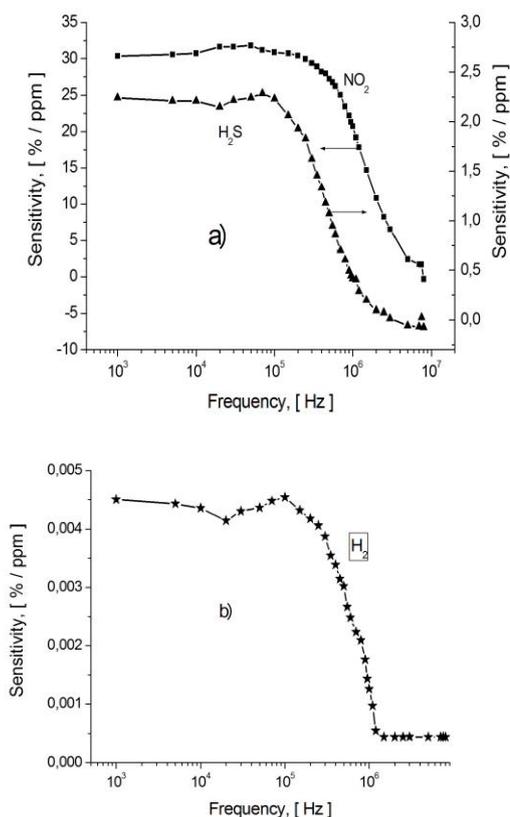

Fig.8. Sensitivity of tellurium thin films toward different gases vs. frequency of applied voltage.

At this edge, the sensitivity increases with frequency decrease, reaching saturation at low (dependent of gas species) frequencies. Comparison of the saturation sensitivity towards the gases in question shows that the sensitivity to NO_2 is more than 10 times higher than towards H_2S and by 4 orders of magnitude higher than towards molecular hydrogen.

V. Discussion

Chalcogenide materials considered in this work belong to disordered, so called lone – pair semiconductors. The states of lone - pair (unshared) p - electrons of chalcogen atoms in these materials display in a band, which overlaps with valence band, forming its upper part. The interaction between lone – pair electrons of chalcogen's atoms , as well as their interaction with "dangling" bonds create the specific charge defects C_3^+ and C_1^- (Fig. 9 a), that operates as localization states in the forbidden gap, pinning the Fermi level closely to valence band, i.e. determining the p – type of conductivity [8]. The interaction of lone-pair electrons with "dangling" bonds has to be maximal at the film's surface, as namely at the surface the maximum concentration of dangling bonds occurs. This interaction means the capturing of electrons from the valence band, which results in formation of a holes enriched (accumulation) region adjacent to the surface, so that the bands bend up, as shown in Figure 9 (b). In this context, the surface phenomena caused by gas adsorption can be considered as an external control of the band - bending at the surface, owing to variation of hole density in the accumulation region, in the presence of gaseous media.
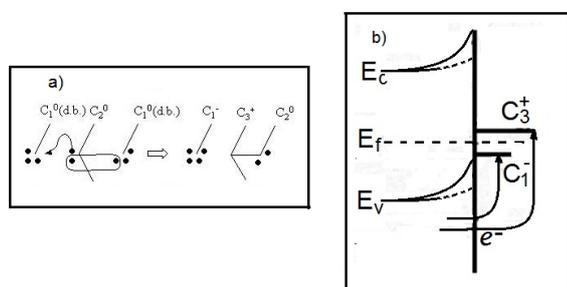

Fig.9. Model of the dangling bonds - lone pair electrons interactions (a) and band - bending at the surface (b).

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, accompanied with releasing of an additional hole [9]. Thus, the adsorption of nitrogen dioxide leads to increase the concentration of majority carriers in the adjacent to the surface layer, which results in both further bands - bending and increasing the electrical conductivity of the film. The high sensitivity, as well as the large frequency range of response to NO_2 support this mechanism of "strong" chemisorption, owing to interaction between the odd electrons of NO_2 molecules and lone – pair electrons of chalcogen's atoms of the films.

Elemental hydrogen occurs only as bi – atomic gas molecules at normal conditions. These molecules do not comprise unpaired (dangling) electrons, i.e. cannot be expected the strong chemisorption of hydrogen on the surface or within the chalcogenide film. Besides, the high concentration of oxygen in carrier gas promotes formation of a catalytic gate [10], which can be removed by other gases. Thus, assuming that the molecular hydrogen removes priory adsorbed oxygen, the decreasing of surface conductivity of the film can be expected [11].

VI. Conclusions

The phase – structural state of the Te, grown onto sintered alumina substrates, via a high speed thermal deposition in vacuum, is predominantly amorphous. The impedance spectra of these films are very sensitive to gaseous environment even at room temperature. Due to different mechanisms of interaction, the addition of NO_2 decreases impedance, whereas addition of H_2 or H_2S increases it in a large range of frequencies. The NO_2 sensing mechanism involves the "strong" chemisorption, which results in an increase of band bending and surface electrical conductivity.

References

[1] S. Marian, D. Tsiulyanu, H-D. Liess, Sens. Actuators B 78, 191, 2001.

[2] S. Marian, D.Tsiulyanu, T. Marian, H - D. Liess, Journ. Pure Appl. Chem.73, 2001.

[3] D. Tsiulyanu, O. Mocreac, Sens. Actuators , B 177, 1128, 2013.

[4] D. Tsiulyanu, O. Mocreac, M. Ciobanu, M. Enachi, G.Volodina, Journal of nanoelectronics and optoelectronics, 9, 282, 2014.

[5] P. Petcov, D. Tsiulyanu, W. Kulish, C. Popov, Nanoscience Advances in CBRN Agents Detection, Information and Energy Security, Springer, Dordrecht, p.535, 2015.

[6] G. Sberveglieri, Sens. Actuators, B, 23, 103, 1995.

[7] R. Macdonald, Impedance spectroscopy, Wiley, New York, p.341, 1987.

[8] M. Kastner, H. Fritzsche, Philos.Magaz. B 37, 199, 1978.

[9] D. Tsiulyanu, M.Ciobanu, H.-D. Liess, Phys. Status Solidi B 253,1046, 2016.

[10] I. Lundstrom, Sens. Actuators, B, 35-36,11, 1996.

[11] D. Tsiulyanu, A. Moraru, "Nanocrystalline tellurium films: Fabrication and gas sensing properties", in: Nanoscience Advances in CBRN Agents Detection, Information and Energy Security, Springer, pp. 389 – 408, 2015.