Effect of Harmful Gases on the A.C. Conductivity of Tellurium Thin Films

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Abstract **– Impedance spectra of tellurium films with interdigital platinum electrodes have been investigated in NO_2 and H_2S gaseous media at room temperature. Analyses of Nyquist complex diagrams allowed evaluating the characteristic frequency, time constant, resistance and capacity of the film in different target gases. It is shown that the spectra of both real and imaginary parts of impedance are strongly influenced by gaseous environment. The**

gas sensitivity for impedance or its imaginary part depends on frequency, being ~50 % / ppm for nitrogen dioxide and ~ 8 % / ppm for hydrogen sulfide respectively.

It is suggested that effect of NO_2 and H_2S results respectively from "strong" and "weak" chemisorptions of these molecules on the surface and intra grain regions.

Keywords–- Impedance,* A.C.; *Tellurium, NO_2, H_2S

I. INTRODUCTION

Tellurium evaporated thin films show p- type conductivity, which depends [1-3] on thickness, rate of deposition and annealing process. Interesting semiconducting properties of Te films have stimulated their wide investigation and propositions for applications as thin films infrared detectors [4], strain - sensitive [5] and writing memory [6] devices.

Recently, tellurium thin films have been found to be sensitive to toxic and harmful gases [7-9], which allowed proposing them for the development of gas sensors [10]. Different gases may be easily detected at room temperature using these films. 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 by Sbeveglieri [11] and consists in a fast sweeping of sensitivity of a single sensor at different frequencies. The sensitivity of sensor to different gases at different frequencies can be rather different. That is, by monitoring a.c. conductance at specific frequencies, the sensitivity to different gas components can be enhanced [12]. Moreover, a.c. measurements allow obtaining impedance or admittance spectra of a sensor, to calculate equivalent circuit and to distinguish between contributions from the surface, bulk or contacts to film conductivity [13].

In the present paper the a.c. conductivity of microcrystalline tellurium thin films with platinum interdigital electrodes have been investigated in dry synthetic air, nitrogen dioxide and hydrogen sulfide gaseous media at room temperature. An analysis of impedance spectra in a complex interpretation has allowed to represent the equivalent circuit, as well as to point out the effect of harmful gases on frequency dependences of real and imaginary parts of impedance of the films.

II. EXPERIMENTAL

Tellurium thin films of $\approx 100nm$ thickness, were prepared by thermal vacuum evaporation of pure tellurium from tantalum boat onto ceramic substrates with a priory deposited platinum interdigital electrodes (Fig. 1a). The electrode structure was structured at SIEMENS AG with electrode width of $15\mu m$ and interelectrode distances of $45\mu m$. The evaporation of tellurium was performed at the working pressure of $10^{-4} Pa$. The growing velocity of the film was in the order of 10 nm/s and the area of deposition around 10 mm^2.

The surface morphology of the films was controlled with a SEM TELSA BS 340 and was pointed out to be the same as in previous paper [3]. The film was encapsulated in a standard TO – 8 sockets and then the contacts were thermally bounded to socket pins, using the copper wires.

The sockets with thin film sensing devices were put into a test cell (of $10ml$ volume) in which the gases were injected with a flow rate of $100ml/\min$, parallel to the film surface.

Different gaseous media were obtained by using the experimental set up described in [14]. NO_2 and H_2S vapors with concentrations of $15ppm$ and $50ppm$ respectively were obtained by using calibrated permeation tubes (Vici Metronics, USA), which were incorporated subsequent into the experimental set – up. Dry synthetic air was used as the carrier and reference gas.

A.c. measurements were carried out in frequency range of $5Hz$ to $13MHz$ using a HP4192A impedance analyzer.

III. RESULTS AND DISCUSSION

3.1 Impedance behavior under dry air

Before checking the effect of different harmful gases on a.c. conductivity the tellurium films were aged by 12 months in normal conditions and the measurements have been performed under synthetic dry air. Figure 1b shows the typical complex impedance diagram in Nyquist plot obtained in pure synthetic dry air from a thin film device at room ($22^\circ C$) temperature.

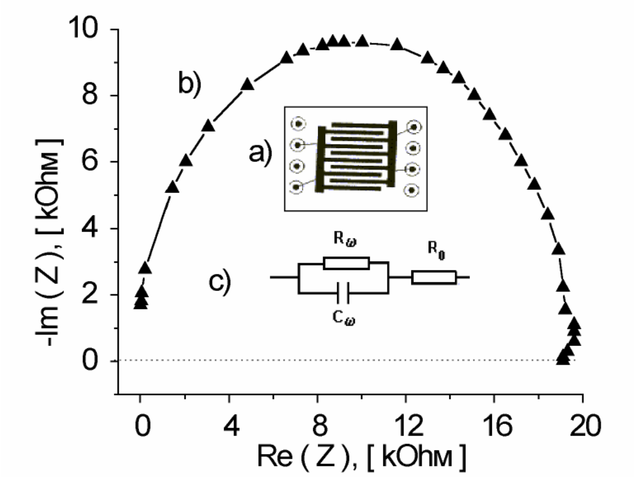

Fig.1. a) Interdigital electrode structure used to measure the a.c. conductivity;

b) Nyquist diagram of an aged at $22^\circ C$ tellurium thin film in pure synthetic dry air;

c) Suggested equivalent circuit.

The diagram shows a slightly depressed semi – circular arc with a center displaced below the real axis, owing to presence of distributed elements in tellurium-based device [13]. These elements can be related to grain boundary heterogeneity of polycrystalline material [15], more exactly to grain boundary and intra – grained regions [3, 9]. A simplified equivalent circuit inserted in Fig. 1 (c) can interpret the Nyquist plot. The frequency independent serial resistance R_0 is assigned to a sum of Ohmic resistance due to electric connection, but resistance R_ω and capacity C_ω are distributed to others contributors, the grain boundary resistance and capacity being the main.

The circle of Nyquist – diagram shown in fig. 1b is depressed owing to the dependence of both C_ω and R_ω on frequency. From the left and right intercepts of semi – circle with the $\mathrm{Re}(Z)$ axis the values of R_0 and $R_r = R_\omega + R_0$ can be estimated. Thus, R_0 was found to be very small, only about 5 Ohm. That is the arc practically passes through the origin and the right intercept gives the value of $R_r \approx 20kOhm$.

For a parallel R_ω C_ω circuit the impedance is given as:

$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{1}{\frac{1}{R_\omega} + i\cdot\omega\cdot C_\omega} = \frac{R_\omega}{1 + i\cdot\omega\cdot C_\omega\cdot R_\omega} = \frac{R_\omega(1 - i\cdot\omega\cdot C_\omega\cdot R_\omega)}{1 + (\omega\cdot C_\omega\cdot R_\omega)^2} \qquad (1)$$

where $Y(\omega)$ is the admittance, $i = \sqrt{-1}$ is the imaginary number , $\omega = 2\pi f$, f -the frequency.

Thus, the real and imaginary parts of the impedance are:

$$\mathrm{Re}(Z) = \frac{R_\omega}{1 + \omega^2 R_\omega^2 C_\omega^2} \qquad (2)$$

and

$$\mathrm{Im}(Z) = \frac{\omega\cdot C_\omega R_\omega}{1 + \omega^2 R_\omega^2 C_\omega^2} \qquad (3)$$

From these system of equations the values of R_ω and C_ω of the film can be evaluated as:

$$R_\omega = \frac{\mathrm{Im}^2(Z) + \mathrm{Re}^2(Z)}{\mathrm{Re}(Z)} \qquad (4)$$

and

$$C_\omega = \frac{\mathrm{Im}(Z)}{\omega\left[\mathrm{Im}^2(Z) + \mathrm{Re}^2(Z)\right]} \qquad (5)$$

From equations (4) and (5) the resistance R_m , capacitance C_m and time constant $\tau_m = (2\pi f_m)^{-1}$ of the film can be estimated at characteristic frequency f_m ,wich is the frequency at which the imaginary part - $I_m(Z)$ reaches its maximum value:

$$\tau_m = \omega_m^{-1} = \frac{1}{2\pi f_m} = R_m C_m \qquad (6)$$

Because of heterogeneity of the material-electrode system the relaxation time (time constant) τ_m , estimated from the complex impedance represents a mean value for the complete thin film device.

The characteristic frequency (f_m), impedance (Z) and estimated from equation (6) the time constant (τ_m) of the sample in dry synthetic air, are listed in table 1.

3.2 Impedance behavior in gaseous media of NO_2 and H_2S .

Fig. 2 reports the spectra of the real part of impedance of tellurium films upon exposure to different test gases.

TABLE1. CHARACTERISTIC FREQUENCY, IMPEDANCE AND R-C VALUES AT DIFFERENT ENVIRONMENTS

Environment	f_m kHz	Z kOhm	τ_m 10^{-7} s	R_m kOhm	C_m pF
Dry air	900	13,3	1,8	19,2	9,6
1,5 ppm NO_2	1500	7,5	1,1	11,8	9,3
50ppm H_2S	400	29	4	44,5	9

It is seen that addition of 1,5 ppm of NO_2 to dry synthetic air diminishes the real part of impedance by ~ 10 kOhm in the frequency range 1,0 - 10^3 kHz. On the contrary, the addition of 50 ppm of H_2S to dry synthetic air enhances the real part of impedance by ~30 kOhm in the much shorter frequency range: 1,0 – 100 kHz. This behavior is compatible with spectra of imaginary part of impedance (Fig. 3). They exhibit the maximums strongly influenced by harmful gases species. The NO_2 vapors diminish the peak of imaginary part of impedance shifting it to higher frequencies but the addition of H_2S vapors results in a vice-versa behavior. Analysis of these spectra allowed determining the influence of tested harmful gases on all elements of the equivalent circuit of the sample.

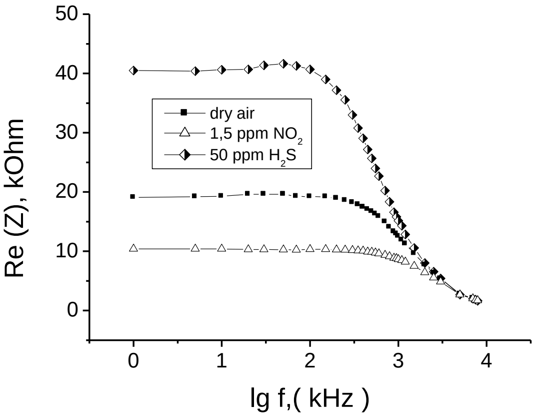

Fig. 2. Effect of target gas on the real part of impedance.

The values of characteristic frequency, impedance and time constant τ_m of the film at this frequency, by indicated concentrations of NO_2 and H_2S at room temperature, are summarized in table 1.

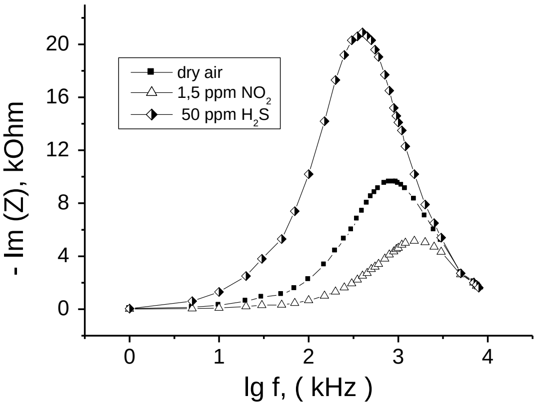

Fig. 3. Spectra of imaginary part of impedance upon exposure to different test gases.

Listed in this table values of R_m and C_m (thé résistance and capacitance at characteristic frequency) have been obtained from Eq. (4) and (5) applied to the data of Fig.2 and Fig.3.

From this table, it is seen that as the environment is changed from dry air to its mixture with gases in question, the resistance R_m is mainly influenced and capacitance C_m does not very essentially. And what is more, the addition of NO_2 decreases both impedance and R_m (at characteristic frequency, which also is gas influenced) but addition of H_2S increases these parameters. In this context it becomes interesting to analyze the frequency dependences of sensitivity to different target gases.

3.2.1 Nitrogen dioxide

D. c. resistance of tellurium films is known to decrease reversibly in presence of NO_2 due to interaction of adsorbed species with lone – pair electrons, which from the upper part of the valence band [14]. Apparently by changing from d.c. to a.c. technique the mechanism of interaction can not be modified but the sensitivity (or selectivity) can be increased.

Fig. 4 shows the sensor sensitivity as a function of the measurement frequency during the exposure to 1,5 ppm NO_2. The sensitivity (here and further) is defined as absolute variation of measured value (impedance or imaginary part of impedance) for a selected frequency in mixture of carrier gas with NO_2 divided by the measured value in the carrier gas at the same frequency, in percents per ppm.

The response curves for either impedance or imaginary part are nearly independent on frequency until approximately 300 kHz, then go down, but sensitivity to NO_2 is maintained until 10 MHz.

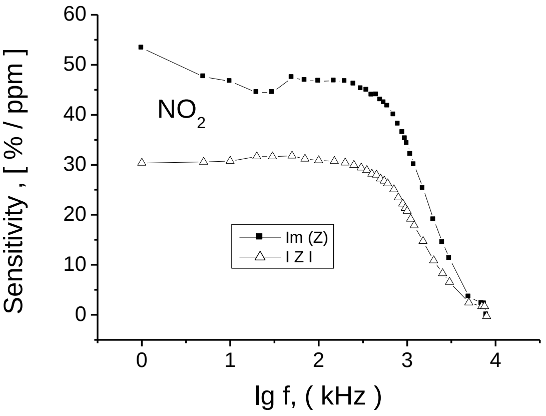

Fig.4. Sensitivity to NO_2 for impedance and its imaginary part as a function of frequency.

The sensitivity in d.c. and impedance measurements amounts to approximately 30 % /ppm, but evaluating the imaginary part as the sensor response results in an increasing of sensitivity until ~50 % /ppm. The high sensitivity, as well as the large frequency range of response to NO_2 supports the early-proposed mechanism of nitrogen dioxide interaction with chalcogenides [14], which involves ″strong″ chemisorption due to interaction between odd electrons of NO_2 molecules and lone – pair electrons of tellurium based chalcogenides.

3.2.2. Hydrogen sulfide

As sensing of hydrogen sulfide by tellurium films has been investigated early [9], here we show only some peculiarities related to sensitivity of such films to H_2S at a.c. measurements, as well as make some comments related to mechanism of interaction between this gas and chalcogenide tellurium thin film.

As have been pointed out (Fig. 2 and 3) hydrogen sulfide leads to increasing of both real and imaginary parts of impedance of the film. Fig. 5 shows the results from a.c. impedance measurements, in which the sensor sensitivity for impedance and its imaginary part are, plotted as a function of the measured frequency during exposure to 50 ppm H_2S. First it is observed that sensitivity of tellurium films to H_2S is by ten times smaller then sensitivity to NO_2. Further, the sensor sensitivity evaluated from imaginary part exhibits a maximum at frequency of around 100 kHz. Evaluation of sensor response by this maximum results in an evident increase of sensitivity. Being of about 8 % / ppm it is four times higher than the sensitivity evaluated either from impedance or d.c. measurements.

Taking into consideration that the electron configurations of water and hydrogen sulfide are similar the interaction of tellurium film with H_2S is likely, to take place similar as proposed early [14] mechanism of interaction of water vapor with these films.

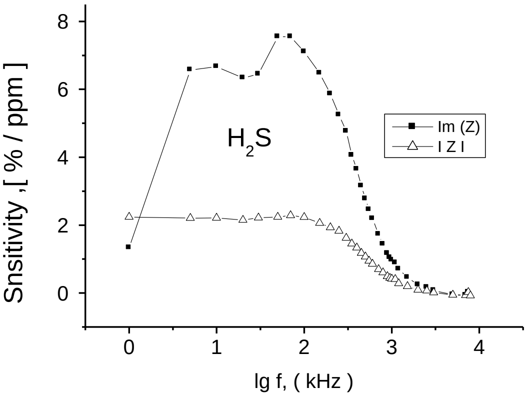

Fig.5. Sensitivity to H_2S for impedance and its imaginary part versus frequency.

That is, as the molecule of H_2S approaches the surface of positive charged tellurium film, it rotates and orientates its dipole moment perpendicular to this surface with negative pole inward. Simultaneously the free hole becomes more and more localized at the point of the surface that H_2S molecule approaches and a very week bond due to forces of electrostatic polarization is formed. And what is more, the orientation polarization of same H_2S molecules on the surface is accompanied by their stretching along the dipole, which can result in a "weak" form of chemisorbtion.

IV. CONCLUSIONS

A.c. conductivity of tellurium thin films is strongly influenced by composition of gaseous environment. The effect of harmful gases is mainly due to variation of both real and imaginary parts of film’s impedance. Addition of NO_2 decreases, whereas addition of H_2S increases them in a large range of frequencies.

The sensitivity for either impedance or its imaginary part strongly depend on harmful gas species (NO_2 or H_2S) and applied frequency, because of different mechanisms of interaction between these gases with tellurium based films, which involves ″strong″ or "weak" forms of chemisorbtion respectively.

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