IMPEDANCE SPECTROSCOPY OF SENSITIVE TO HARMFUL GASES TELLURIUM THIN FILMS

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Impedance spectra of tellurium thin films with interdigital platinum electrodes have been investigated in different gaseous media. For the first time it is pointed out that tellurium films exhibit sensitivity to H_2 at room temperature along with sensitivity to NO_2 and H_2S. Analyses in Cole – Cole interpretation allowed evaluating the characteristic frequency, time constant, resistance and capacity of the film in different target gases. It is shown that impedance spectra being strongly influenced by gaseous environment do not change their general shape. The effect of target gas is mainly due to variation of resistance of the film but capacitance does not vary essentially. The sensitivity for impedance or its imaginary part depends on frequency, being the highest to NO_2 (~50 % / ppm) but 8 % / ppm and 10^{-2} % / ppm to H_2S and H_2 respectively. It is suggested that effect of H_2 is due to removal the amount of adsorbed oxygen on the Te surface, whereas effect of NO_2 and H_2S results respectively from "strong" and "weak" chemisorptions of these molecules on the surface and intra grain regions.

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1. Introduction

Tellurium based films may be used for the detection of harmful gases at room temperature. First this possibility has been pointed out for NO_2 [1], then have been reported sensors operable at room temperature based on tellurium thin films to detect CO and propylamine [2] as well as NH_3 [3].

Different modern methods, such as electron and atomic force microscopy, X – ray diffraction, Raman and X – ray photoelectron spectroscopy have been used to study the interaction of gases with these films, but the investigations are still in progress.

Recently was found that tellurium films exhibit sensitivity to H_2S [4] and weakly to water vapor, oxygen and nitrogen [5]. In the present study we rapport evidence for tellurium films to be sensitive also to H_2. Thus, a number of 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 [6] 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 [7]. Moreover, a.c. measurements allow obtaining impedance or admittance spectra of a sensor, calculating equivalent circuit and distinguishing between contributions from the surface, bulk or contacts to film conductivity [8].

In the present paper the impedance spectra of tellurium based thin films with interdigital electrodes have been investigated in different gaseous media, including H_2.

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2. Experimental

Tellurium based 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 $10nm/s$ and the area of deposition around $10mm^2$. 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 [1]. The micro sensor 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 [5]. NO_2 vapor with a concentration of $15ppm$ was obtained by using a calibrated permeation tube (Vici Metronics, USA), which was incorporated into the experimental set – up. Dry synthetic air was used as the carrier and reference gas.

Hydrogen and hydrogen sulfide gaseous media, with concentration 1% by volume and $50ppm$ respectively, were obtained from cylinders (Linde, Germania). Impedance measurements were carried out in frequency range of $5Hz$ to $13MHz$ using a HP4192A impedance analyzer.

3. Results

3.1 Impedance behavior under dry air

Before checking the effect of different harmful gases on the impedance behavior of tellurium-based films with interdigital electrodes, the a.c. measurements have been performed under synthetic dry air.

Fig. 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. The film was aged by 12 months in normal conditions.

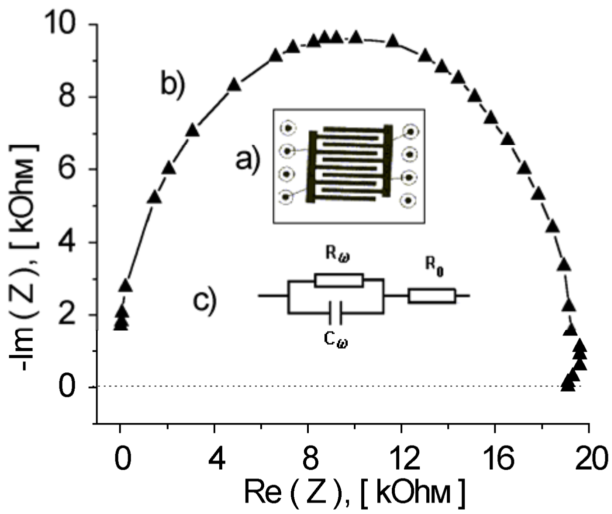

Fig.1 a) Interdigital electrode structure used to measure the a.c. conductivity;
b) Nyquist diagram of an aged at $22^\circ C$ tellurium thin film in pure synthetic dry air;
c) Suggested equivalent circuit.

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 [8]. These elements can be related to grain boundary heterogeneity of polycrystalline material [9], more exactly to grain boundary and intra – grain regions [3, 4]. 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 $5Ohm$. That is the arc practically passes through the origin and the right intercept gives the value of $R_r \approx 20kOhm$. 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.

For the simple parallel $R_m C_m$ circuit, it is determined by:

$$\tau_m = \omega_m^{-1} = \frac{1}{2\pi f_m} = R_m C_m \tag{1}$$

where f_m - is the characteristic frequency at which the imaginary part - $I_m(Z)$ reaches the maximum value, R_m and C_m are the resistance and capacity of the film at characteristic frequency f_m. The characteristic frequency was estimated to be about 900 kHz. The impedance and estimated from equation (1) time constant τ_m at characteristic frequency of the sample in dry synthetic air, are listed in table 1 together with these parameters in others environmental conditions.

For a parallel R_ω C_ω circuit the values of R_ω and C_ω of the film can be evaluated from the real and imaginary parts of the impedance as [10]:

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

$$C_\omega = \frac{\mathrm{Im}(Z)}{\omega\left[\mathrm{Im}^2(Z) + \mathrm{Re}^2(Z)\right]} \tag{3}$$

Estimated by equations (2) and (3) the resistance R_ω and capacity C_ω of the film at characteristic frequency, i.e. R_m and C_m are listed in Table 1.

Table 1. Impedance and R-C values at characteristic frequency, by different environments

Environment	f_m kHz	Z kOhm	$\tau_m \cdot 10^{-7} s$	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
H_2 1% by volume	600	19,8	2,7	31,7	8,5
50ppm H_2S	400	29	4	44,5	9

3.2 Impedance behavior under mixture of dry air with NO_2, H_2 and H_2S

Fig.2 reports the complex impedance spectra of aged tellurium-based films upon exposure to different test gases that is NO_2, H_2 and H_2S. It is seen that addition of these gases to dry synthetic air does not change the general shape of curve, i.e. they influences all elements of the equivalent circuit. The values of characteristic frequency, impedance and time constant τ_m of the film at this frequency, by indicated concentrations of NO_2, H_2 and H_2S at room temperature, are summarized in table 1. Listed in this table values of R_m and C_m (the resistance and capacity at characteristic frequency) have been obtained from Eq. (2) and (3) applied to the data of Fig.2.

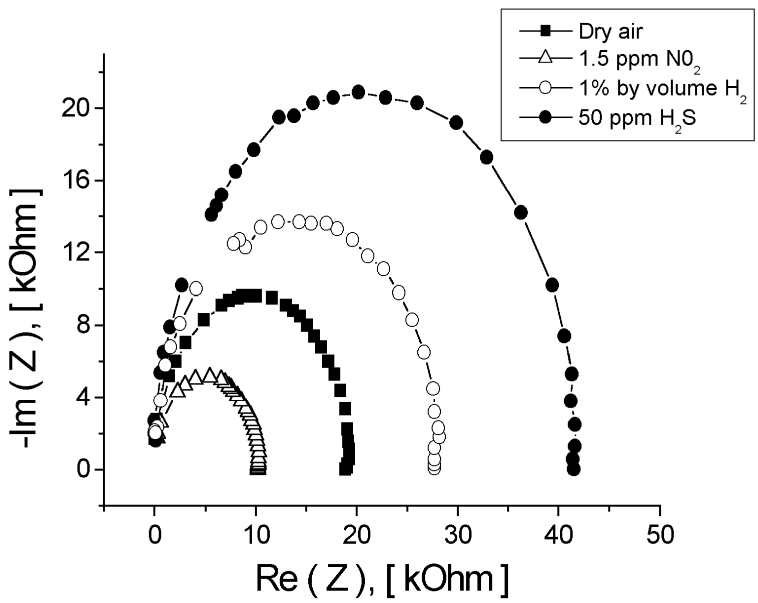

Fig.2. Nyquist diagrams of tellurium thin films in different environmental conditions.

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 vary 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_2 or H_2S increases these parameters. In this context it becomes interesting to analyze the frequency dependences of sensitivity to different target gases.

4. Discussion

4.1 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 [5]. 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.

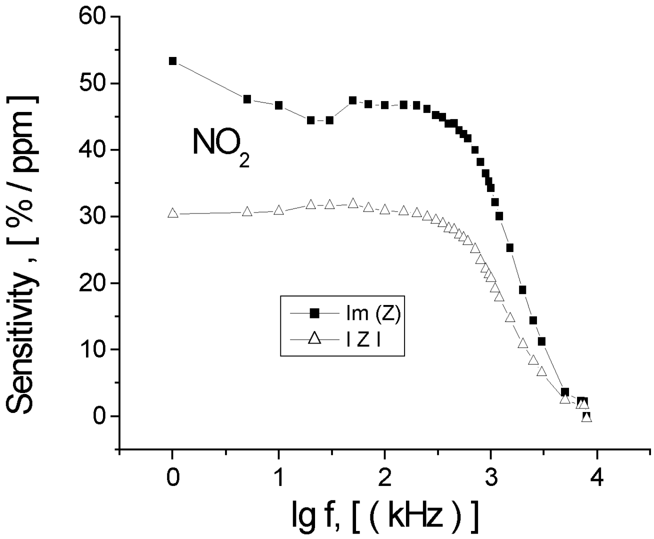

Fig.3. Sensitivity to NO_2 for impedance and its imaginary part as a function of frequency

Fig. 3 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 measurement 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. 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 [5], which involves the ″strong″ chemisorption due to interaction between the odd electrons of NO_2 molecules and lone – pair electrons of tellurium based chalcogenides.

4.2. Hydrogen

Fig. 4 shows the sensor sensitivity as a function of measurement frequency using the hydrogen as a test gas. It is observed that sensitivity to hydrogen is by four orders of magnitude smaller that to NO_2, but also cover a large range of frequencies and can be clearly detected.

Unlike exposure to NO_2 the impedance response spectra to hydrogen go down starting with approximately 150 kHz but at 1,0 MHz the sensitivity to H_2 practically disappears.

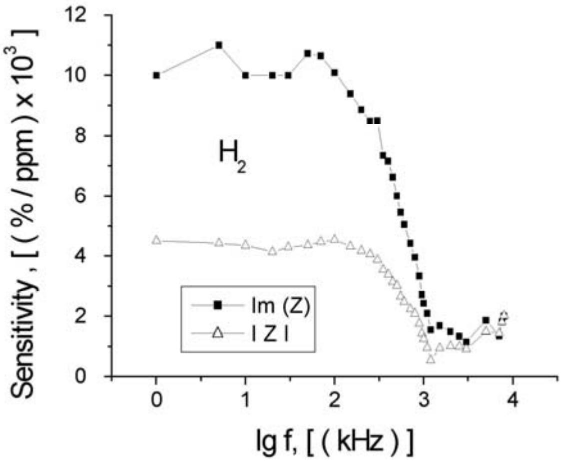

Fig.4. Sensitivity to H_2 for impedance and its imaginary part versus frequency.

The last is valid also for the imaginary part taken as a sensor response, although the resulting value of sensitivity in this case is more than twice higher. These peculiarities suggest that mechanism of hydrogen – tellurium film interaction essentially differs from interaction of these films with NO_2 .

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 tellurium film. Perhaps the sensitivity of tellurium films to H_2 arises because –of reducing effect of oxygen a priory absorbed on the surface of the film from carrier (dry air) gas. In our previous paper [5] was shown that the ″weak″ chemisorption of symmetric molecules of O_2 from carrier gas is accompanied by localization of holes near the surface, which results in decrease the film resistance. Besides, the high concentration of oxygen in carrier gas promotes formation of a catalytic gate [11], which can be removed by other gases. That is why, assuming that the molecular hydrogen removes a priory adsorbed oxygen, we can expect the decreasing of both, hole concentration and conductivity of the surface and intragrain regions of the film.

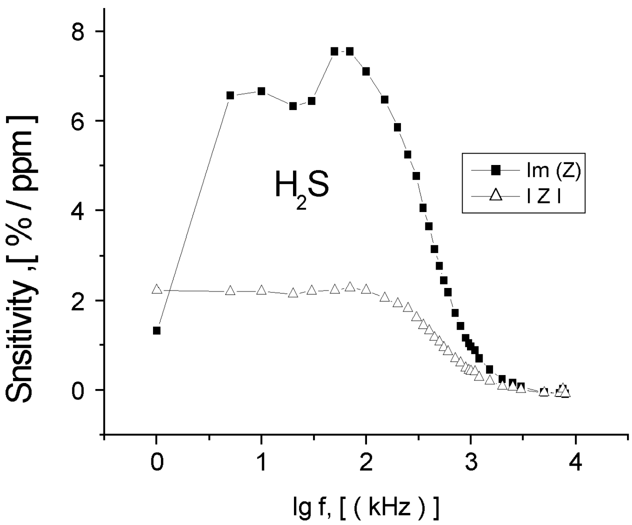

Fig.5. Sensitivity to H_2S for impedance and its imaginary part versus frequency.

The "weak" chemisorption of O_2 molecule on the semiconductor surface assumes an acquirement of a dipole moment (deformation polarization of a homopolar molecule). Therefore, a diminishing (or even absence) of such an adsorption at high frequencies can be expected, which explains the weak sensitivity of tellurium films to hydrogen at frequencies higher that 1 MHz.

4.3. Hydrogen sulphide

As sensing of hydrogen sulpfide by tellurium films has been investigated early [4], here we show only some peculiarities related to sensitivity of such a 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 based film. As have been pointed out (Fig. 2) hydrogen sulphide leads to increasing 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 frequency during exposure of 50 ppm H_2S .

Firstly, it is observed that sensitivity of tellurium films to H_2S is by three orders of magnitude higher then sensitivity to H_2, but remains nearly by ten times smaller then sensitivity to NO_2. Moreover, the substitution of sensor response from impedance to its imaginary part, results in an evident increase of sensitivity. The sensor sensitivity to H_2S , evaluated from the imaginary part of the impedance exhibits a maximum at frequency of around 100 kHz, being of about 8 % / ppm, which is nearly four times higher than sensitivity evaluated from the whole impedance.

Secondly, the high frequency edge of sensitivity to H_2S is shifted to 1 MHz, being the same as edge of sensitivity to hydrogen. These peculiarities indicate that interaction of H_2S with tellurium film can be attributed neither to "strong" chemisorbtion of H_2S molecules or to reducing of preliminary "weak" chemisorbed oxygen from carrier gas.

Taking into consideration that the electron configurations of water and hydrogen sulphide are similar the interaction of tellurium film with H_2S is likely, to take place similar as proposed early [5] mechanism of interaction of water vapor with these films. 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 weak 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. The last explains the high sensitivity of tellurium films to H_2S comparable with their sensitivity to H_2, which is due to removal of “weak» chemosorbed O_2.

5. Conclusions

Impedance spectra of tellurium thin films are strongly influenced by composition of gaseous environment. The effect of harmful gases on impedance is mainly due to variation of film’s resistance but capacitance does not vary essentially. Addition of NO_2 decreases impedance whereas addition of H_2 or H_2S increases it in a large range of frequencies.

The response curves (sensitivity) for either impedance or its imaginary part strongly depend on target gas NO_2, H_2 or H_2S and frequency, because of different mechanisms of interaction between these gases with tellurium based films.

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