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Hydrogen sensing behavior of tellurium thin films studied by A.C. measurements

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. The hydrogen gas sensing performance of tellurium thin films was investigated by method of impedance spectroscopy. The impedance spectra are strongly influenced by gaseous environment but the effect of target gas is mainly due to variation of resistance of the film. It is assumed that the sensitivity of tellurium films to H_2 arises because – of reducing effect of oxygen priory absorbed on the surface of the film from carrier (dry air) gas. The high concentration of oxygen in carrier gas promotes the formation of a catalytic gate, which can be removed by other gases including hydrogen. Removing of the priory-adsorbed oxygen results in decreasing of both, hole concentration and conductivity of the surface and intragrain regions of tellurium film. Due to impedance change in different direction, reducing H_2 may be distinguished from oxidizing NO_2, hence the effective, operating at room temperature H_2 sensors can be manufactured using tellurium-based films.

Key words: *Gas sensing, Tellurium, Hydrogen, A.C. measurements*

1. INTRODUCTION

Hydrogen (H_2) gas is a clean, naturally abundant energy resource and presently it has been widely implanted in household and transportation applications. To avoid damage to human life and infrastructures, a reliable sensor with accurate and fast H_2 gas detection is essential to safe H_2 gas production, storage and utilizations.

The development of hydrogen sensors concerns the research into the new materials that provide advanced sensitivity, selectivity, stability and low power consumption. So far, the metal oxide semiconductors, such as tin oxide [1] or tungsten trioxide [2] are the most studied materials for the H_2 gas detection. Although these materials exhibit good hydrogen sensing characteristic they require evaluated (100 - 600 ^{0}C) operable temperature. In the present study we rapport the possibility to detect H_2 at room temperature using tellurium thin films. It is known that a number of gases may be easily detected at room temperature using these films. First this possibility has been pointed out for NO_2 [3], then have been reported sensors operable at room temperature based on tellurium thin films to detected CO and propylamine [4] as well as NH_3 [5]. 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]. More over, 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 [8].

In the present paper the impedance spectra of tellurium based thin films with interdigital electrodes have been investigated in gaseous media H_2 as well as NO_2 for comparison.

2. EXPERIMENTAL

Tellurium based thin films of $\approx 100 nm$ thickness, were prepared by thermal vacuum evaporation of pure tellurium from tantalum boat onto ceramic substrates with a priory deposited platinum interdigital electrodes (Figure 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 investigated, using a

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VEGA TESCAN TS 5130 MM scanning electron microscope (SEM).

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.

Hydrogen gaseous media, with concentration 1% by volume was obtained from cylinders (Linde, Germania). Nitrogen dioxide (NO_2) vapors with concentrations of *1,5 ppm* 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.

Impedance measurements were carried out in frequency range of $5Hz$ to $13MHz$ using a HP 4192 A impedance analyzer.

3. 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.

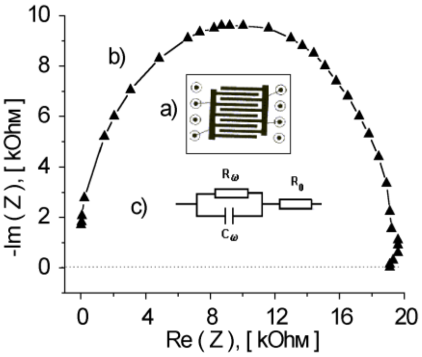

Figure 1 - a) Interdigital electrode structure used to measure the a.c. conductivity; b) Nyquist diagram of an aged at 22°C tellurium thin film in pure synthetic dry air; c) Suggested equivalent circuit

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]. 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_0 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 $R\omega$ 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 $R_r \approx 20kOhm$.

For a parallel $R_\omega\ C_\omega$ 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, that is the frequency at which the imaginary part -$I_m(Z)$ reaches its maximum value. 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:

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

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 (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.

Table 1 - Characteristic frequency, impedance and R-C values at different environments.

Environment	$f_m\,(kHz)$	$Z\,(kOhm)$	$\tau_m \cdot 10^{-7}\,s$	$R_\omega\,(kOhm)$	C_ω (pF)
Dry air	900	13,3	1,8	19,2	9,6
H_2 1% by vol.	600	19,8	2.7	31,7	8,5
1,5 ppm NO_2	1500	7,5	1,1	11,8	9,3

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

Figure 2 reports the complex impedance spectra of aged tellurium-based films upon exposure to different test gases that is NO_2 and H_2. 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 and H_2 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 Figure 2.

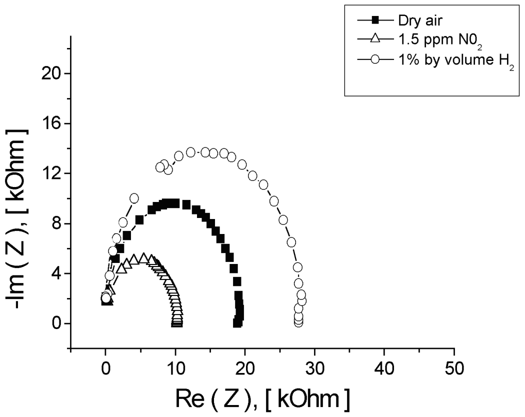

Figure 2 - Nyquist diagrams of tellurium thin films in different environmental conditions

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 very essentially. 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 increases these parameters.

3.3. Real and imaginary parts of impedance for Te films in H_2 and NO_2 gaseous media.

Figure 3 reports the spectra of the real part of impedance of tellurium films upon exposure to different test gases. 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 1 % of volume of H_2 to dry synthetic air enhances the real part of impedance by ~7,0 kOhm in the much shorter frequency range: 1,0 – 100 kHz.

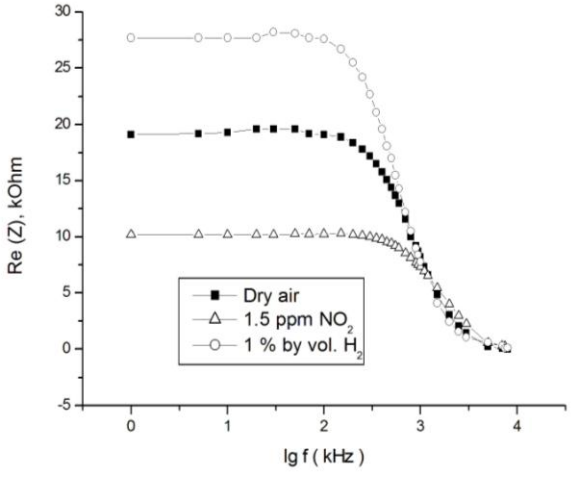

Figure 3 - Effect of target gas on the real part of impedance

The spectra of imaginary part of impedance exhibits the maximums strongly influenced by harmful gases species (Fig.4). The NO_2 vapors diminish the peak of imaginary part of impedance shifting it to higher frequencies but the addition of H_2 vapors results in a vice-versa behavior. Analysis of these spectra help determining the influence of tested harmful gases on all elements of the equivalent circuit of the sample showed above in the Table 1.

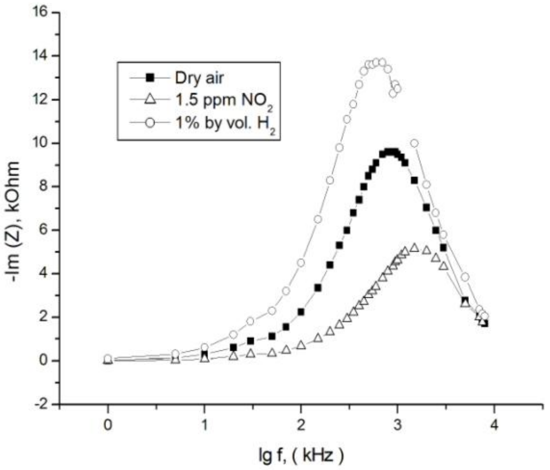

Figure 4 - Spectra of imaginary part of impedance upon exposure to different test gases

As the response to different gases strongly depends of applied frequency, it becomes interesting to analyze the frequency dependences of sensitivity to different target gases.

3.4. Sensor sensitivity versus applied frequency

3.4.1. 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 [9]. Apparently, by changing from d.c. to a.c. technique the mechanism of interaction cannot be modified but the sensitivity (or selectivity) can be increased.

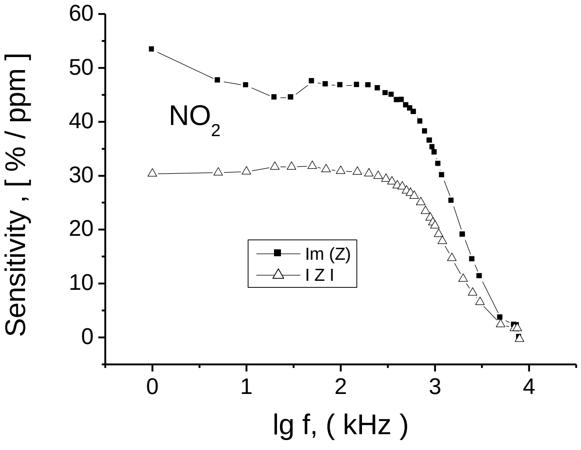

Figure 5 - Sensitivity to NO_2 for impedance and its imaginary part as a function of frequency

Figure 5 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 [9], which involves ″strong″ chemisorption due to interaction between odd electrons of NO_2 molecules and lone – pair electrons of tellurium based chalcogenides.

3.4.2. Hydrogen

Figure 6 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.

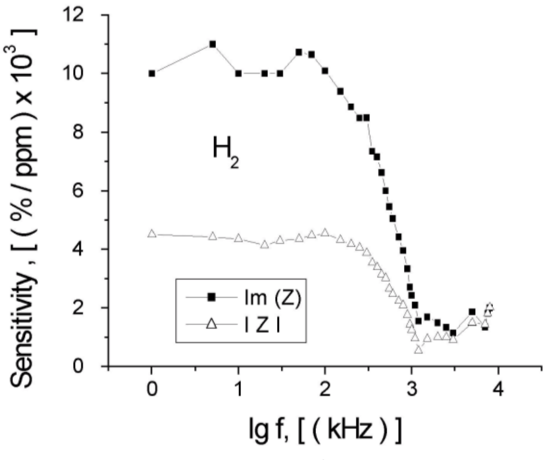

Figure 6 - Sensitivity to H_2 for impedance and its imaginary part versus frequency.

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 comprises unpaired (dangling) electrons, i.e. cannot be expected the strong chemisorptions of hydrogen on the surface or within the tellurium film. Perhaps the sensitivity of tellurium films to H_2 arise because – of reducing effect of oxygen priory absorbed on the surface of the film from carrier (dry air) gas. In our previous paper [9] was shown that ″weak″ chemisorptions of symmetric molecules of O_2 from carrier gas is accompanied by localization of holes near the surface, which results in decreasing the film resistance. Besides, the high concentration of oxygen in carrier gas promotes formation of a catalytic gate [10], which can be removed by other gases. That is why, assuming that 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 tellurium film.

4. 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 very essentially. Addition of H_2 increases impedance whereas addition of NO_2 decreases it in a large range of frequencies.

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

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IZVOD

PROUČAVANJE PONAŠANJA VODONIKA NA OSETLJIVIM TANKIM FILMOVIMA OD TELURA POMOĆU AC MERENJA

Po prvi put je pokazano da su Telurovi tanki filmovi osetljivost na H_2 na sobnoj temperaturi uz osetljivost na NO_2. Reagovanje vodonika na Telurove tanke filmove ispitan je metodom spektroskopske impedanse. Spektri impedanse su pod jakim uticajem gasovitog okruženju, ali je efekat ciljanog gasa uglavnom zbog varijacija otpora filma. Pretpostavlja se da osetljivost Telurovih tankih filmova za H_2 nastaje zato - da se smanji dejstvo kiseonika apsorbovanog na površini filma od provodnog gasa (suv vazduh). Visoka koncentracija kiseonika u nosećem gasu podstiče formiranje katalitičkog kapije, koja može ukloniti druge gasove, uključujući i vodonik.

Uklanjanje apriori apsorbovanog kiseonika smanjenjuje koncentracije i provodljivosti na površinskim i intrgranularnim regionima Telurovih tankih filmova. Zbog promene impedanse u drugom pravcu, redukcija H_2 može se razlikovati od oksidacije NO_2, stoga efikasno, rad na sobnoj temperaturi H_2 senzora mogu biti proizvedeni pomoću telur osnovnih filmova.

***Ključne reči:** vodonik, osetljivi tanki filmovi, telur, AC merenja*

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