Involvement of Contact and Surface Phenomena in Nanolayered Amorphous Te Films for Toxic Gas Detection at Room Temperature

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Abstract. A fast responding NO_2 sensitive device operating at room temperature has been realized using the nanolayered amorphous Te (a-Te) grown onto insulating wafer of silicon dioxide (SiO_2) between Pt contact electrodes with larger thickness in a planar arrangement. The structure of the fabricated sensor has been investigated by AFM and SEM but its characterization was realized via studying the current - voltage characteristics, dynamic response, long – term stability and effect of humidity. Explanation of obtained results is given in terms of a model based on simultaneous involvement of contact and surface phenomena for the gas sensing. As the Pt electrode work function (5.43 eV) exceeds the respective value of a-Te (5.03 eV) the ohmic contacts are formed and the current flow is controlled exclusively by bulk resistance of a-Te nanolayer that is known to be controlled by type and concentration of toxic gas of the ambiance. Wherein, as the energetic forbidden gap of a-Te (0.33 eV) is less than the work function difference between contacting materials, at the contacts can arise the degenerate regions of p-type metallic Te, as well as geometric contact gaps originated from microscopically roughness. The gas adsorption inside these contacts gaps leads to increasing the portion of the semiconducting a-Te nanolayer turned into metal of p-type Te and consequently to a fast increasing of the current.

Keywords: Nanolayers · a-Te · Contacts · Gas sorption

1 Introduction

Tellurium thin films can be successfully used for the detection of nitrogen dioxide and hydrogen sulfide at room temperature [1, 2]. The high sensitivity of Te films to nitrogen dioxide attracted special attention because it is a very toxic gas, released by combustion, plants and automobiles and its monitoring in the environment is of great importance. Exemption from stoichiometry problems allowed using of different methods of sensor fabrication including the thermal evaporation, sputtering, chemical precipitation etc. that allowed strongly modifying the film's microstructure. In order to increase the performances in detection of NO_2 at room temperature the new technologies of fabrication were developed allowing the shortening of dimensionalities of Te microcrstallites to nanoscales and further until their total disappearance, accompanied by transition of

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films into an amorphous state. For example, the growing of Te nanotubes by direct vapor phase process in an inert atmosphere [3] has allowed enlarging of dynamic range of room temperature operating gas sensitive devices from 1.0 to 400 ppm NO_2, alongside with increasing of the concentration dependent gas sensitivity. Growing of nanocrystalline Te films via rf sputtering in an ultra-high-purity argon onto glass or alumina substrates, [4] or amorphous tellurium one onto pre-nanostructured (porous) dielectric substrates [5] allowed diminishing the response time to approximately 30 and 15 s respectively, maintaining the sensitivity toward NO_2 at ~40% per ppm. The further improvement of the performances of Te based gas sensors can be achieved via utilizing the contact phenomena in the form of Schottky diodes, MOS capacitors or FETs [6]. Recently [7] was find out that the capacitance spectra of glassy tellurium chalcogenide based Pt - $As_2Te_{13}Ge_8S_3$ – Pt structure gives evidence that both surface and contact phenomena being interdependent are controlled by interaction with gases from ambiance. The present work is conducted to show a possibility of enhancing the performance of toxic gas sensing, using the features of Pt/a-Te junction that can comprise a region with p-type metallic conductivity adjacent to contact.

2 Experimental

Pt/a-Te/Pt functional structures, schematically represented on Fig. 1, were realized on thermally oxidized p-type silicon wafers (10 Ω cm) having a size 3 × 8 mm. Two platinum contact lines have been photo lithographically patterned on top of the insulating silicon oxide layer, whereupon the active ultrathin amorphous tellurium film was deposited between them. The last has been grown via thermal evaporation of polycrystalline tellurium (purity 99.999%) in vacuum of 10^{-4} Pa from a tantalum boat without cooling or heating the substrate. Gaseous media with different concentration of NO_2 was obtained by using the calibrated permeation tubes (Vici Metronics, USA), which was introduced into the experimental set-up described elsewhere. Ambient air or dry synthetic air was used as the carrier and reference gas.

The sensing devices were put into a test cell (of 10 ml volume) but the gases were injected with a flow rate of 100 ml/min, parallel to the film surface. Humidity cross-sensitivity to NO_2 was studied via humidification of the carrier gas that was accomplished using different saturated solutions of the salts in water.

I-U characteristics have been carried out in ambient air and its mixture with 1.0 ppm NO_2 at room temperature. The applied voltage varied between −5 V and +5 V in steps, increasing by 20 mV at each step, while the respective values of the current were measured. The delay time between successive measurements was 2 s. Current - transient characteristics have been carried out at a constant (1 V) applied voltage in condition to successive injection of rectangular pulses of 1.0 ppm NO_2 into test cell. Delay time between successive measurements was 40 ms. Data were processed, using a PC and a data acquisition board manufactured by National Instruments Inc. The sensor sensitivity was defined as the relative resistance variation expressed in percent:

$$S = 100\left(R_a - R_g\right)/R_a \tag{1}$$

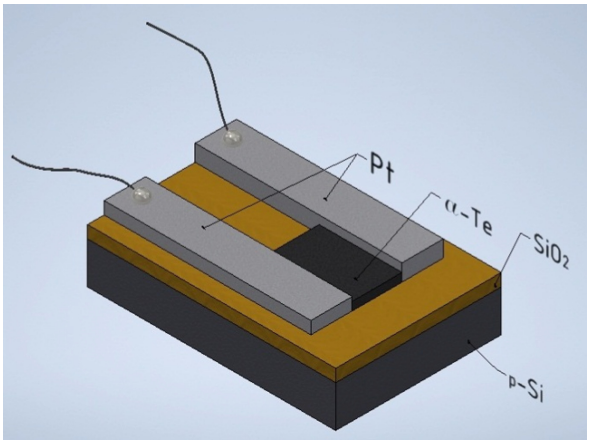

Fig. 1. Schematic of the sensor design

where R_a and R_g are the sensor's resistances in the air and in the presence of NO_2. The response and recovery time were defined as the times taken to reach or to lose the 90% of maximum values of the current respectively.

3 Results

3.1 Morphology and Design Details

The surface morphology of the films was investigated using the scanning electron microscope VEGA TESCAN TS 5130 MM but the design details of the sensor have been studied using an Atomic Force Microscope (AFM) SIS SCAN Control C. Figure 2 shows the AFM scanned profiles of Pt electrodes and Te film, alongside with its SEM image. It can be observed that the thickness of Pt electrodes is around 100 nm but the thickness of Te film is about 30 nm. The SEM image of Te film (Fig. 3c) shows a uniform surface without of morphological structure that confirms its amorphous state.

3.2 Gas Sensing Characterization

a) *Current – voltage characteristics*:

Figure 3 shows the typical I –U characteristic of Pt/a-Te/Pt functional structures in air and in the presence of NO_2 vapor in a semi-logarithmic scale. The influence of NO_2 vapor at bias higher than 0.1 V leads to an increase of the current independently of the direction of the bias voltage.

Alongside at bias less than 0.1 V, the gas induced current increases much stronger, which results in an intersection of I-V curves measured in air and in its mixture with NO_2.

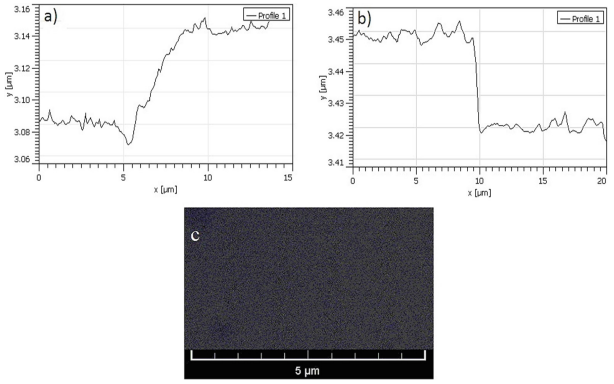

Fig. 2. AFM profiles of Pt electrodes (a); Te film (b) and SEM image of tellurium film (c).

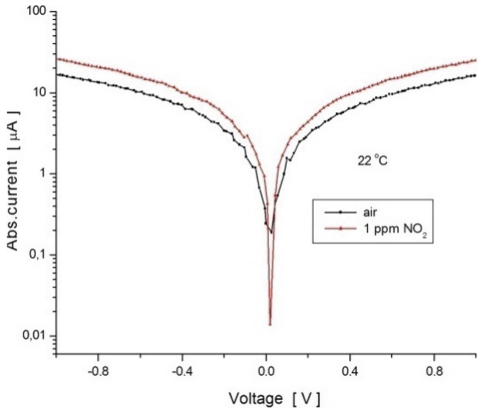

Fig. 3. Current/voltage characteristic of Pt/a-Te/Pt functional structure in air and in the presence of 1.0 ppm of NO_2

b) *Dynamic response, long – term stability and effect of humidity:*

Figure 4 shows the current flow through a sensor under repeated switching on-off of the NO_2 gas mixture at constant bias voltage. Squared pulses of NO_2 vapor with concentration of 1.0 ppm were applied. The dotted line shows the switching schedule. It is seen that the current follows the schedule; the response is fast and consists of around 3–5 s but and the recovery one is longer and is ~60 s. It is significant that there is no baseline drift or noticeable drift of the gas induced current.

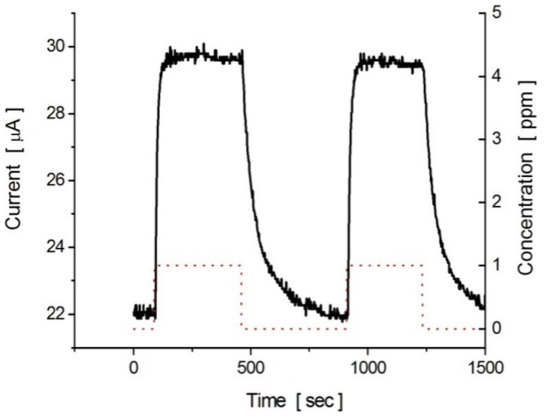

Fig. 4. Transient characteristics by exposure to NO_2 at 22 °C

b) *Long – term stability and effect of humidity*

The long –term stability of the sensor tested by operating it for three months is reported on Fig. 5(a). It is seen that in both air and its mixture with NO_2 vapors there no appreciable changes in its gas sensing characteristics.

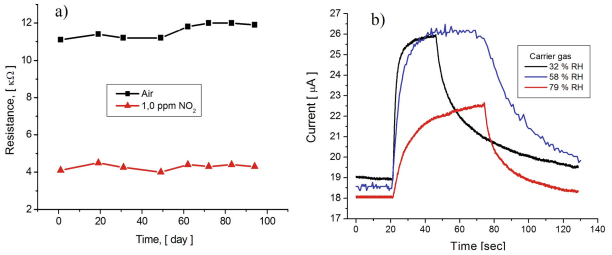

Fig. 5. Long –term stability (a) and effect of humidity (b) by NO_2 sensing at room (22 °C) temperature

The interfering effect of humidity on NO_2 detection with a developed sensor was assessed at room temperature (22 °C). Figure 5(b) illustrates the response of the sensor towards a pulse of 1.0 ppm NO_2 in humid air with 32%, 58% and 79% RH. The effect of NO_2 is to increase the current in the sensor independently on humidity of the carrier gas, but the baseline current, magnitude and velocity of response and recovery times are influenced by water vapor concentration. Increasing the RH diminishes both baseline current and response signal but enlarges the response time, which nevertheless remains in the range of seconds.

4 Model

Figure 6(a) illustrates the possible band diagram of Pt/a-Te junction in normal conditions sketched using the following parameters of contacting materials: Pt and Te work function $\varphi_{Pt} = 5.45$ eV and $\varphi_{Te} = 5.03$ eV respectively [8]; Forbidden gap of a-Te $E_g \approx 0.33$ eV [9]; a-Te electron affinity $\chi \approx 2$ eV [10]; Fermi level position $\eta \approx E_g/2$.

The diagram is sketched according to Schottky - Mott barrier, which assumes that the contact comprises a thin insulating layer (several Angstroms), formed during electrode deposition process [11]. The region between the electrode and semiconducting layer, called the "transition region" serves as a gap where both platinum clusters formed and gas molecules chemisorbed [12]. The diagram given in Fig. 6 shows also that the Pt/Te junction belongs to an extreme one, when the adjacent to contacts regions of p-type Te become degenerate, with the Fermi level E_f lying below the valence band edge E_v. Such an unusual situation can occur because the band bending exceeds the Te forbidden gap $\varphi_{Pt} - \varphi_{Te} > E_g$ [13].

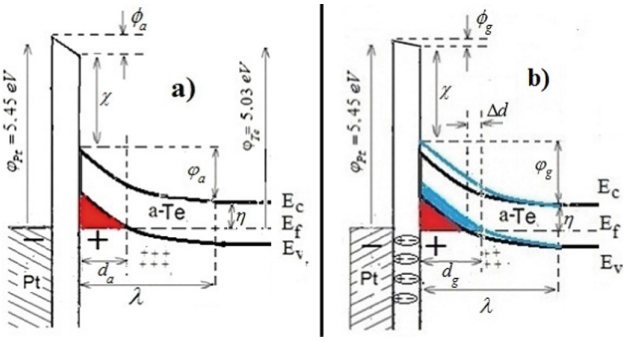

Fig. 6. Possible band diagram of the nonbiased Pt/a-Te junction in air (a) and NO_2 (b) ambiance (see the explanation in the text)

The band diagram shows the relation:

$$\varphi_{Pt} = \phi_a + \chi + \varphi_a + \eta \tag{2}$$

where ϕ_a is the potential drop from the Pt to the a-Te in the interface gap and φ_a is the band bending, both in air.

Let us assume that the examined Pt/a-Te junction is introduced into NO_2 environment and the chemical adsorption of gas molecules occurs both on the surface of the bulk region and contact gaps. Due to peculiarities of NO_2 molecules [14] such simultaneous adsorption leads to different consequences:

1. Absorption on the surface of bulk leads to increase the majority carrier's density in the adjacent surface of the bulk region of Te film, which results in increasing its conductivity, so a parallel shift-up of the linear part of the I-U characteristic should occur.

2. Penetration (adsorption) of polarized NO_2 molecules into contact gaps has to change the potential drop in the interface gap: they will align in the direction controlled by direction of gap field, created as a result of work function difference of contacting materials [12], leading to modulation of both potential drop at the surface and work function of the a-Te. Figure 6 (b) illustrates the effect of NO_2 adsorption into gap of contact transition regions. It is seen that for this case the Eq. (2) can be expressed as:

$$\varphi_{Pt} = \phi_g + \chi + \varphi_g + \eta \tag{3}$$

where ϕ_g and φ_g is the potential drop at the gap and band bending respectively, at exposure to NO_2.

Assuming that the φ_{Pt},χ and a η stay unchanged it can be concluded that the gas molecules modify only the value and curvature of the bands bending due injection of holes from Pt electrodes to restore the electrical neutrality:

$$\Delta\varphi = \varphi_g - \varphi_a = \phi_g - \phi_a = -\Delta\phi \tag{4}$$

The last leads to increasing the portion of the semiconducting Te nanolayer turned into metal of p-type Te, such that the width of metallic p-type Te adjacent to contacts increases as $\Delta d = d_g - d_a$. In the closed – circuit condition supported by voltage application, this partial semiconductor-metal transition should be observed as a sharp increasing of the current.

5 Conclusions

A rapidly – responding NO_2 sensor operating at room temperature based on nanolayered a-Te films grown between Pt electrodes was developed. As the work function difference between contacting materials exceeds the forbidden gap of a-Te at contacts can arise the degenerate (metallic) regions of p-type Te. Gas induced modulation of the width of these regions is assumed to be the reason for the essential diminishing of both response and recovery time.

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Conflict of Interest. The authors declare no conflict of interest.

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