GAS SENSING CHARACTERIZATION OF TELLURIUM THIN FILMS BY THE KELVIN PROBE TECHNIQUE

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Abstract

The sensing behavior of tellurium films at room temperature was tested with environmental pollutant gases, such as NO_2, CO, O_3, and water vapor, using the Kelvin probe technique. A significant sensitivity was observed for nitrogen dioxide. The detection range for NO_2 was between 0.5–5.0 ppm in air with controlled humidity. The response and the recovery time are rapid with good reproducibility and high sensibility. The work function measurements showed that chalcogenide semiconductors in question are well-suited materials for the detection of not only small concentrations of NO_2, but also for humidity sensing. The relative humidity of 45% induces the work function change $\Delta\phi$ of approximately 200 mV at room temperature. It is shown that the "strong" chemisorption of nitrogen dioxide results in an increase in both work function change $\Delta\Phi > 0$ and electrical conductivity $\Delta\varsigma > 0$ because of the additional charging of the surface and band bending. The effect of water vapor is due to a simple physical adsorption of polar water molecules oriented perpendicular to the surface with a negative pole inward. As a result, the dipole component of the work function increases, i.e., $\Delta\Phi > 0$, but the free lattice holes become more localized at the surface and the conductivity of the p-type chalcogenide layer decreases $\Delta\varsigma < 0$.

1. Introduction

In recent years, a considerable attention has been given to the possibility of using chalcogenide glassy semiconductors as the sensitive layer in chemical sensors for the analysis of industrial solutions [1] and pollutant gases [2]. Usually, the changes of the conductivity of these layers as sensitive parameter have been studied. A significant progress in investigating the sensing properties of these materials can be achieved by means of Kelvin probe (KP) measurements. The piezoelectrically driven Kelvin probe is a simple and fast technique to monitor the variation of surface potential during adsorption and desorption of gases from environment [3, 4]. In addition, the work function setup exhibits a good stability, because the sensitive layer is not electrically treated; that is, in contrast to conduction sensors, electromigration, which is a serious limiting factor for conductive thin film sensors, cannot appear. The KP equipment provides the possibility to measure the relative change of work function $\Delta\Phi$ of the chalcogenide layer in the presence of a carrier gas and during the exposure to a gas mixture of interest. The work function measurements by the KP method have been used in the present work for characterization of the interaction between Te based thin films and some harmful gases as well as water vapor at room temperature.

2. Experimental

For the work function measurements, a commercial Kelvin probe (Besocke GmbH, Julich, Germany) was used. It consists of a gold grid reference electrode, oscillating via piezoelectric transducer normally to the sample surface at a frequency of about 170 Hz. By use of this technique, the relative change of work function $\Delta\Phi$ of the chalcogenide film was measured in the presence of the carrier gas (ambient air with different degree of humidification) and during exposure to a vapor with different concentration of pollutants:

$$\Delta\Phi = \Phi_{vapour} - \Phi_{air}, \tag{1}$$

where Φ_{air} and Φ_{vapour} are the work function of sensitive film measured in air and in the presence of vapor of interest, respectively.

The measurement gas composition was controlled by a gas flow system, which controls the humidity, the flow of the carrier gas (dry ambient air, $< 1\%$ humidity) and the specific sample gas as load. Sample gases can be introduced into the system using gas sources of known concentration or permeation tubes. All measurement data were recorded with a computer controlled setup.

Tellurium (purity 99.999 %) based thin films were deposited by thermal vacuum evaporation from tantalum boats onto Pyrex glass substrates. The evaporation was performed at the working pressure of $\approx 10^{-4}$ Pa. The growth rate of the films was on the order of 10 nm/s and the area of deposition was around 50 mm^2. The film thickness determined using a MII-4 microinterferometer was about 60 nm. X-ray analyses and scanning electron microscopy (SEM) were used for structural investigations.

3. Results

Figure 1 shows the work function variation ($\Delta\Phi$) exposing a Te polycrystalline thin film at different concentrations of nitrogen dioxide. The measurements were performed at repeated on /off switching of the NO_2 gas mixture. The dotted line gives the switching schedule.

It is seen that in effect of NO_2 vapor the work function of the tellurium film increases, but after switching off the pollutant gas, the $\Delta\Phi$ curves return to their initial position. NO_2 gas concentrations like 1.9 ppm lead to a variation of work function by around 120 mV. The contact potential difference (CPD) measured in the present work vs. a vibrating gold grid reference electrode is

$$CPD = (\Phi - \Phi_{Au})/e, \tag{2}$$

where Φ is the work function of sample, Φ_{Au} is the work function of gold grid reference electrode, and e is the elemental charge. On the other hand, the work function value in a semiconductor material is the sum of several terms:

$$\Phi = \mu + \phi_0 + \varphi, \tag{3}$$

where μ is a bulk chemical potential, ϕ_0 is the surface dipole potential and φ is the eventual band bending.
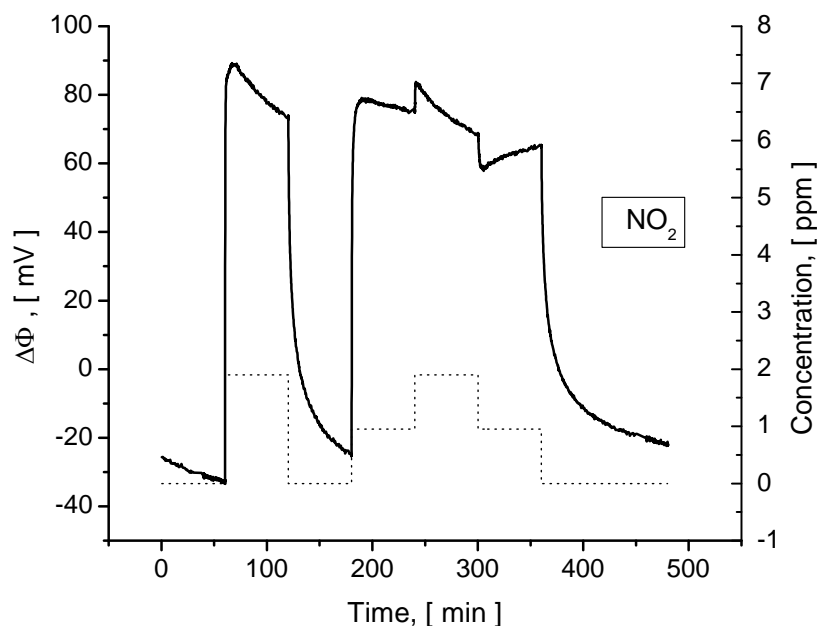
Fig. 1. Work function variation of a tellurium layer exposed to NO_2 according to the profiles shown at the bottom.

Considering the gold as a inert reference material, the work function variation $\Delta\Phi$ due to gas adsorption can be caused by variation of ϕ_0 or /and φ of ChS, which depend on nature and number of adsorbed particles, whiles μ is independent on adsorption, being determined by the nature and state (nature and concentration of impurities, temperature, etc.) of semiconductor; that is,

$$\Delta\Phi = \Delta\phi_0 + \Delta\varphi \tag{4}$$

Consequently, it is necessary to additionally investigate the presence of either ϕ_0 or /and φ contributions in work function variation caused by gas adsorptions.

In the present work, the influence of nitrogen dioxide, carbon oxide, ozone, and water vapor adsorption on the electrical conduction of thin tellurium films was studied to determine the possible contribution of band bending or of the surface dipole potential in change of $\Delta\Phi$, which cause the CPD variation. Figure 2 shows the current flow though the tellurium film under repeated switching on/off the NO_2 gas mixture at a constant bias voltage. The dotted line gives the switching schedule that is the same as in Fig. 1. It can be observed that the current follows the schedule: increases when the gas is applied and depends on its concentration. Thus, the adsorption of NO_2 results in an increase in both the work function difference ($\Delta\Phi > 0$) and electrical conductivity ($\Delta\epsilon > 0$) of the films in question.
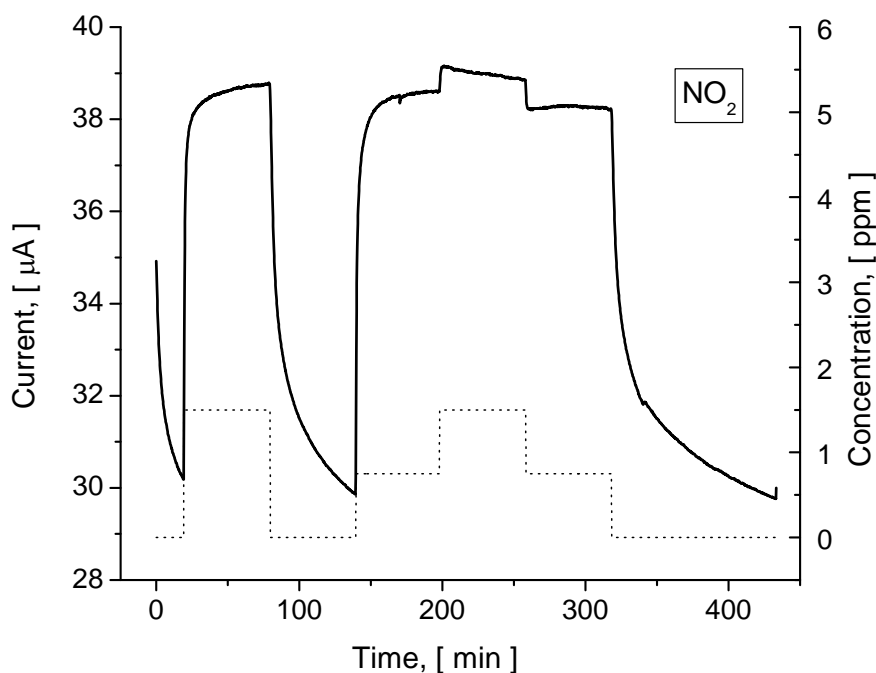
Fig. 2. Current flow though the tellurium film exposed to NO_2 at room temperature and a voltage bias of 4 V. The dotted line shows the switching schedule.

As far as the influence of water vapor is concerned, the film's behavior is particular.

Figure 3 shows the temporal evolution of the work function as the surface of a Te layer is exposed to air with different relative humidity. An increase in the relative humidity of the carrier gas (air) leads to a nonmonotonic increase in the work function variation ($\Delta\Phi > 0$). The saturation occurs at an applied relative humidity higher than 45%. The work function change $\Delta\Phi$ is very high with approximately 200 mV. The response and the recovery time (τ_{90}) is only a few minutes. On the other hand, the humidity diminishes the electrical conductivity of the film.

Figure 4 shows the typical response of a tellurium thin film to an impulse of humid (58% RH) air at 23 and 70°C. Dry (1-2% RH) synthetic air was used as reference gas. Switching from dry to wet synthetic air makes the current of the film slightly decrease and achieve a steady state at room temperature in approximately 45 min. The relative resistance of the film increases in this process by ~ 15%.

Thus, the effect of water vapor on electrical conductivity appears to be opposite from that of nitrogen dioxide: the adsorption of water vapor leads also to an increase in the work function change ($\Delta\Phi > 0$) but diminishes the electrical conductivity of the film ($\Delta\varepsilon < 0$). Note that, as follows from Fig. 4, the humidity response of the sensor heated to 70°C becomes unessential. RH of 58% leads to an increase in relative resistance only by 3–4% at this temperature. This range of $\Delta R / R_0$ variation remained nearly constant during heating to higher temperatures.
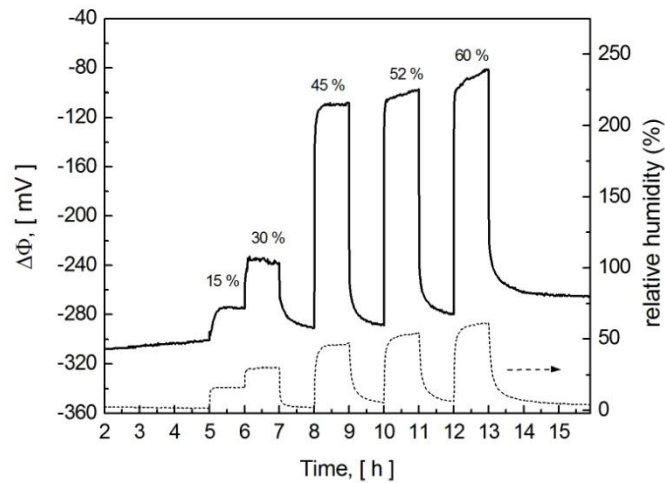
Fig. 3. Response of a Te film towards the humid (15, 30, 45, 52, and 60% RH) air pulse sequence at an operating temperature of 23^0C.
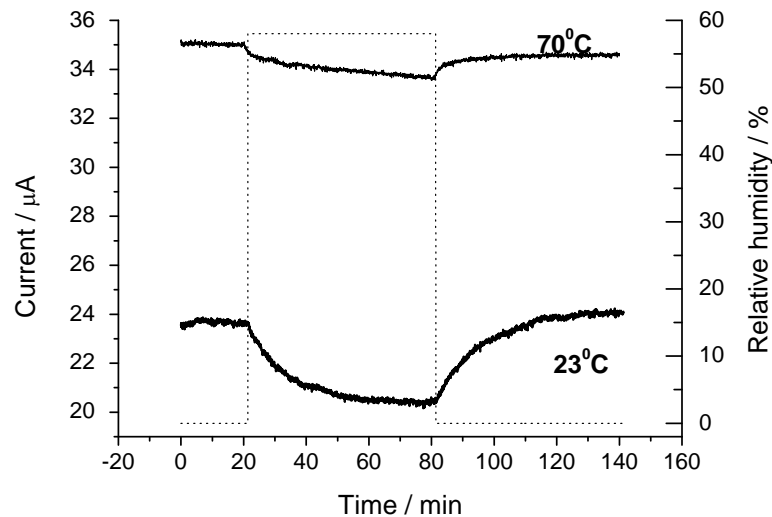

Fig. 4. Response of a tellurium based thin film to an impulse of humid (58 % RH) air at 23 and 70^0C.

4. Discussion

Tellurium and its alloys belong to so-called lone-pair (LP) semiconductor materials [5]. The main feature of lone-pair semiconductors is that the upper part of the valence band is formed from p-state lone-pair electrons. If the network of a LP glassy or crystalline semiconductor contains defects, such as unsaturated chemical bonds (dangling bonds), the interaction between these defects and lone-pair electrons occurs. The dangling bond interacts with neighboring lone-pair, bonding with it by distorting its environment (Fig. 5a). This interaction results in the formation of lattice defects and release of about 10^{13}-10^{15} holes/cm^3, which causes the p-type of conductivity. Since the maximum concentration of dangling bonds takes place namely on the

surface, the hole enriched (accumulation) region is formed at the surface; that is, the bands bend up (Fig. 5b). This region includes also the grain boundary.
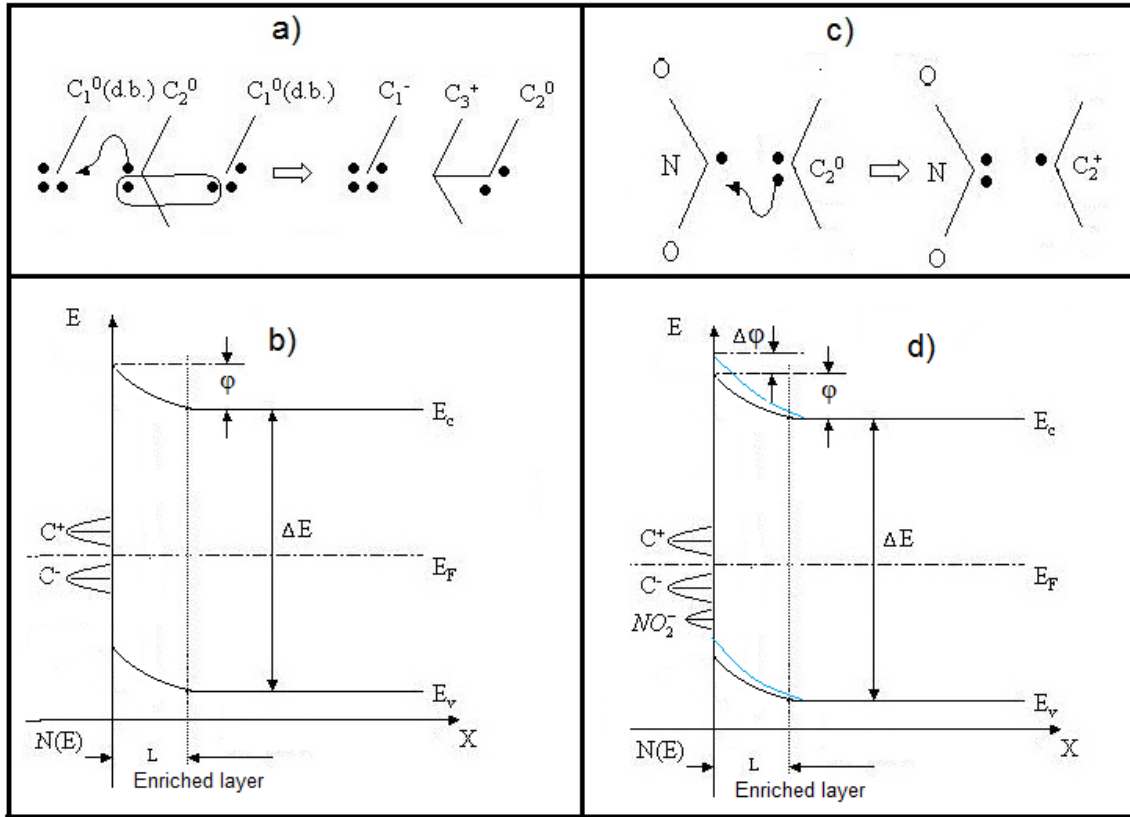
Fig. 5. Model of the dangling bonds - lone pair electrons interactions and the surface state bands at the chalcogenide semiconductor's surface before (a and b) and after (c and d) adsorption of acceptor like (NO_2) gas molecules.

In this respect, the gas sensing is due to variation of hole density or / and their mobility in the accumulation (surface and grain boundary) region in the presence of gaseous media.

When the chalcogenide semiconductor is introduced into a gaseous environment the adsorption of gas molecules occurs, which can produce either donor or acceptor levels. As far as the adsorption of nitrogen dioxide is concerned, its molecule comprises an odd electron [6]; that is, after covalently bonding of nitrogen to oxygen, one of the atoms remains with a single unpaired electron. Being adsorbed on the surface of the Te (grain) surface, the NO_2 molecule acts as a dangling bond (Fig. 5c) which can accept a LP electron to form an electron pair via the reaction:

$$NO_2 + e^- \rightarrow NO_2^- + h \tag{5}$$

Thus, the capture of a LP electron, i.e., the transition of an electron from the upper part of the valence band to a NO_2 acceptor level, is accompanied by the releasing of an additional hole at the surface. As a result, both the band bending (φ) and electrical conductivity (ε) increase (Fig. 5d), which gives rise to an increase in work function ($\Delta\Phi > 0$) and DC current really observed in

experiments. It is obvious that chemisorption of others gases implies other surface reactions, which can lead either to an increase or a decrease in the majority carrier density in the grain boundary region and hence to an increase or a decrease in the work function and conductivity of the film. In fact, the response of tellurium based films to ammonia was shown [7] to arise from reduction of tellurium oxide atoms present on the surface and intergrain regions, which also act as acceptors. Note that, in this experiment, the influence of dipole component of the work function, which can arise from the existence of a double electric layer on the surface layer, does not manifest itself evidently. Therefore, the potential drop across such a possible double charged layer is omitted in Fig. 5d.
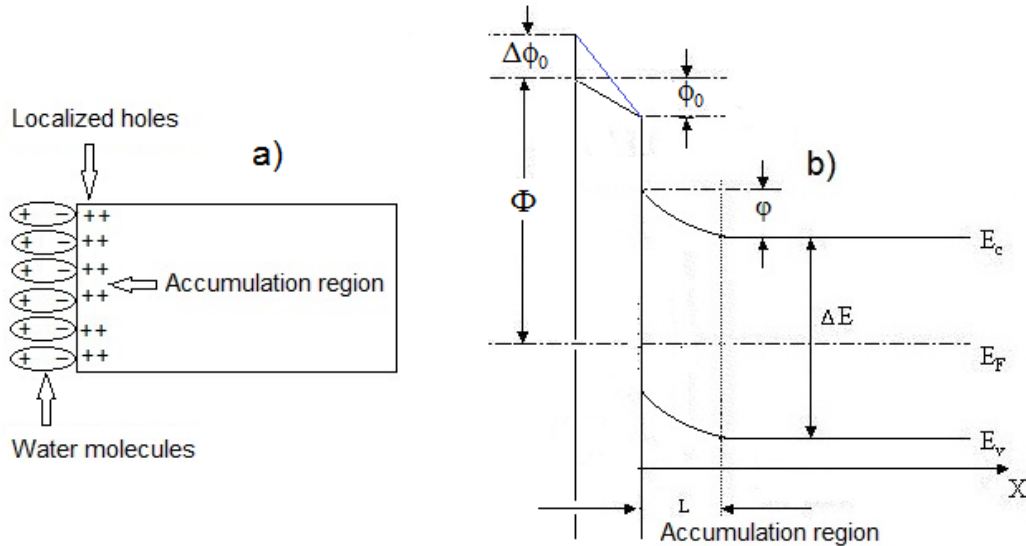
Fig. 6. Formation of an electric double layer by water physisorbtion (a) and its effect on work function of chalcogenide semiconductor (b).

On the other hand, a double electric layer can be easily created and controlled by the adsorption of dipole molecules, such as water one. The water increases the work function change ($\Delta\Phi > 0$) but diminishes the electrical conductivity of the film ($\Delta\varsigma < 0$) that could be related to peculiarities of water molecules. It is well known that a water molecule is an unusual molecule. Being threefold coordinated, it exhibits a high ($15 \cdot 10^{-30} C \cdot m$) dipole moment. As the molecule of H_2O approaches the surface of a positively charged Te film, it rotates and orientates its dipole moment perpendicular to this surface with a negative pole inward. At the same time, the free lattice hole becomes more and more localized at the point of the surface that water molecule approaches, and a very weak bond due to forces of electrostatic polarization is formed. Localization of the same free holes diminishes the electrical conductivity of the film; that is, the opposite of NO$_2$ response can be observed. Figures 6a and 6b schematically illustrate how a decrease in conductivity and an increase in work function are produced by surface hole localization resulting from the preferential alignment of the water dipoles.

Hence, the effect of water vapor is due to the orientation polarization of H_2O molecules on the surface and the formation of week bonds with an electrostatic origin. Confirmed by experiment, these bonds can be easy removed by heating (Fig. 4), while the effect of water vapor

does not disappear completely. This means the orientation polarization of the same physisorbed H_2O molecules is accompanied by their stretching along the dipole, which can result in a "weak" form of chemisorptions. In the "weak" bond, the chemisorbed H_2O molecule forms [8] a valence-saturated and electrically neutral structure, but requires a higher temperature to be removed.

5. Conclusions

• Tellurium thin films can be used in the development of effective work function gas sensitive devices. The sensors can operate at room temperature and show considerably short response times as well as sensitivity in the ppm and sub-ppm concentration range.

• The NO$_2$ sensing mechanism involves the "strong" chemisorptions, which results in an increase in band bending, work function, and electrical conductivity of the films.

•The effect of water vapor is due to a simple physical adsorption of dipole H_2O molecules accompanied by an increase in potential drop across the electric dipole layer, which results in an increase in work function. Simultaneously, the electrical conductivity of the film decreases due to hole localization resulting from the preferential alignment of the water dipoles with a negative pole inward.

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