EFFECT OF CONTACTS AND THICKNESS ON THE NO_2 SENSING PROPERTIES OF TELLURIUM BASED FILMS

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Abstract

The influence of contacting materials, and thickness of the tellurium based films on their electrical conductivity and sensitivity to NO_2 is given. It is shown that until thickness is below 100 nm the conductivity increases with the increase of the layer thickness but becomes almost constant at thicknesses more than100nm. Scanning electron microscopy analyses indicates that grown films are compact, i.e. two-channel mechanism of current flow occurs.

The sensitivity toward NO_2, being controlled by gas concentration, decreases with film thickness increase but is nearly independent on contacts work function.

The results are discussed taking into consideration the contributions of grain boundary as well as grain bulk and surface resistance to the total conductivity. Chemisorption of NO_2 molecules is accompanied by hole enrichment of the surface and grain boundary region, due to interaction of these molecules with lone-pair electrons.

Keywords: Gas sensors; Tellurium chalcogenides, NO_2

1. INTRODUCTION

The detection and emission control of nitrogen dioxide, released by combustion, plants and automobiles is of great importance. Therefore, much effort is made to develop sensors for monitoring the concentration of this pollutant in our environment. So far the SnO_2 based nitrogen dioxide sensors were the mainly investigated and also of commercial value [1]. They are, however not very selective and usually operate at temperatures above 300 °C.

Only recently a novel class of gas sensors, based on chalcogenide materials was proposed for monitoring pollutants in ambient air [2 -3]. Most attractive in this respect were thin films based on pure tellurium or its alloys from the As-Ge-Te system. These films show remarkable sensing properties to NO_2 at even room temperature, with the response time of only several minutes and the sensitivity being especially high at concentrations less than 1 ppm.

The mechanism of gas detection of these materials is, however, still not completely understood, because of the lack of sufficient experimental data. In particular there are no reports on the influence of the contact materials and film thickness, on the electrical and sensing properties of the films. In the present study the dependence of the NO2 sensing properties of tellurium-based films on these process parameters have been investigated. The possible mechanism of gas sensing is also discussed.

2. EXPERIMENTAL

Tellurium alloys based thin films of different thicknesses were deposited onto Pyrex glass substrates with thermal vacuum evaporation. The evaporation was performed from a quartz crucible at the working pressure of $\approx 10^{-4}$ Pa. Rectangular samples of different (20, 60, 110 and 190 nm) thicknesses were prepared by a variation of the distance between the evaporation crucible, while the evaporation time has been kept the same. The surface morphology of the films was investigated, using a scanning electron microscope (SEM) TESLA BS 340.

In order to investigate the possible effect of film contacting, the electrode materials with greater work function (gold, ~ 5,3 eV) or lower work function (indium, 4,12 eV) than tellurium work function (4,95 eV [4]) have been tested. Gold electrodes were deposited onto the film surface through thermal vacuum evaporation. Copper wires were then attached to the electrodes by silver paste. Indium contacts have been made with two "indium pillows", which were pressed on top of the tellurium film.

NO_2 vapor with a concentration of 0,75 to 18 ppm was obtained by using the experimental set up described in [5]. Gaseous NO_2 media was obtained by using a calibrated permeation tube (Vici Metronics, USA), which was introduced into the experimental set-up. Ambient air was used as the carrier, as well as the reference gas. The data was processed, using a PC and a data acquisition board manufactured by National Instruments Inc.

Current / voltage characteristics have been carried out with different gas concentrations at room temperatures.

The sensor sensitivity was defined as the relative resistance variation expressed in percent:

$$S = 100\,(|R_a - R_g|) / C \cdot R_a \qquad (1)$$

where R_a and R_g are the electrical resistances of the film in air and in the presence of NO_2 respectively. C is the gas concentration.

2. RESULTS AND DISCUSSION

Figure1 shows the current / voltage characteristic of tellurium alloys based films with Au electrodes in the air and in the presence of NO_2 vapor. The devices with In electrodes exhibit the same characteristics. In all cases the I / U characteristics are linear and follow the Ohm' s law but the electrical conductivity of the sensitive layer depends on the layer thickness.

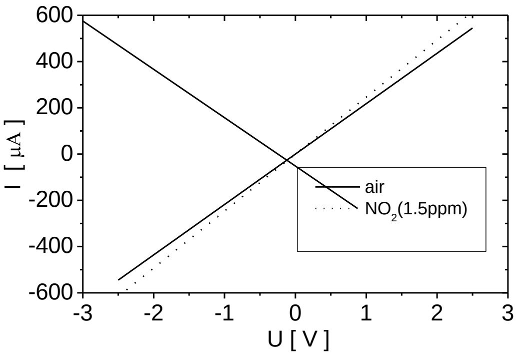

Fig.1. I /U characteristics of the films with Au electrodes in air and in presence of 1,5 ppm of NO_2

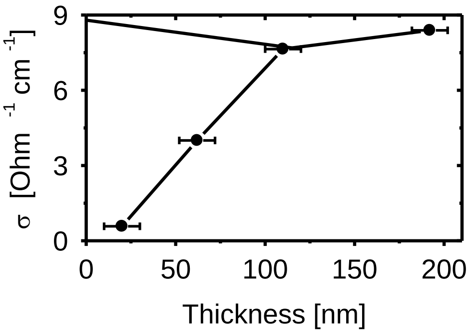

Fig.3. Electrical conductivity of the films vs. their thickness

Figure 2 shows the conductivity vs. layer thickness at room temperature. It is seen that until thickness is below 100 nm the conductivity increases with the increase of the layer thickness, then when thickness reaches 100nm, the conductivity becomes almost constant.

The influence of NO_2 vapor leads to an increase of the current independently of the direction of the bias voltage. Note the high value of the gas-induced current, which is in the range of dozens of microamperes, depending on the film' s thickness and bias voltage.

The sensor sensitivity as a function of film thickness is shown in Figure3. As can be seen the film sensitivity strongly increases with thickness decrease. Such behavior can be expected in the case of a compact layer [6].

Figure 4 shows the SEM view of an as-deposited sensitive film. It can be seen that the morphology of the film shows a compact layer. In the case of a compact layer [6], the current flows through two parallel channels, one of them being the surface channel, which is affected by the gas reaction, and the other is the gas-unaffected bulk. Because the surface part of the grains can be oxidized under interaction with atmospheric oxygen, the appearance of a grain boundary resistance occurs, which is put in series with a resistance of the surface cannel of current flow.

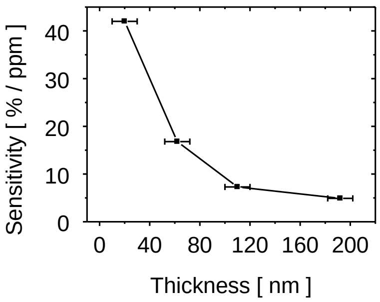

Fig.3 Effect of thickness on sensitivity to 1,5 ppm of NO_2 at room temperature.

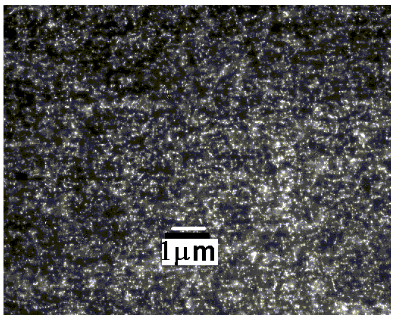

Fig. 4 SEM micrograph of an as-grown film

Decreasing the layer thickness leads to enhancing the influence of the surface grain boundary resistance and removing the bulk, gas-unaffected parallel resistance. That is why the film conductivity decreases, while its sensitivity strongly increases with the thickness decrease.

CONCLUSIONS

The electrical conductivity and the sensitivity to NO_2 of tellurium alloys based films are strongly dependant on the thickness of the films when the thickness is less than 100 nm.

Such behavior is due to existence of two parallel conducting channels: the surface, affected by the gas reaction channel and the gas-unaffected bulk one.

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