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Conduction mechanism involved in sensing mechanism of $SnSe_2$

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Simple investigation of the electrical resistance does not permit to draw up the conduction mechanism of thin $SnSe_2$ layers. The presence of reducing gas atmospheres, respectively CH_4, CO and H_2O could change the concentration of the free charge carriers, beside electron affinity changes induced by the appearance of surface dipoles. Work function and electrical resistance were simultaneous investigated for thin $SnSe_2$ films. The experimental results permit the evaluation of electron affinity and band-bending behavior. Conduction mechanism can be discussed in terms of surface or bulk contribution.

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1. Introduction

Usually, the gas sensing properties are evaluated by simply monitoring the resistance variation of the active layer, which physically involves the variation of free charge carriers concentration, due to chemical interaction.

In our previous papers [1, 2] we showed the gas sensing effect of $SnSe_2$ to CH_4, CO and H_2O, considering also the influence of calcination temperature on the signal of the sensors and the relative selectivity. $SnSe_2$ thin films were prepared by pulsed laser deposition on alumina substrate provided with platinum interdigital electrodes and heater. The calcination temperature range was 600-650 °C in oxygen atmosphere. Methane sensitivity was pointed out at operating temperature of 600 °C. Relative to potential interfering gases, $SnSe_2$ presents selectivity even to high CO concentrations. At that moment, a possible explanation of the gas-sensing behavior was the bulk conduction mechanism which requires high activation energy, ensured by a relative high operating temperature.

Based on complex experimental investigations, in the present paper we propose a conduction mechanism of thin $SnSe_2$ layers.

2. Experimental

$SnSe_2$ thin films were prepared by Pulsed Laser Deposition (PLD) on alumina substrate provided with platinum interdigital electrodes and heater. The obtained have been calcinated at 635 °C in oxygen atmosphere.

For gas atmosphere simulation we used a computer controlled set-up consisting of a gas mixing station which had the possibility of switching between 6 channels directly to the test gas bottles. The relative variation of the Contact Potential Difference (CPD) at $SnSe_2$ surface was measured by a Kelvin probe system, which basically is a vibrating capacitor, consists of a reference metallic grid in electrical contact with the sample. Due to the electrical contact an electron transfer takes place until the Fermi levels of both materials are equilibrated. Results the so-called Contact Potential Difference (CPD) witch permits to evaluate the relative variation $\Delta\Phi$ as $\Delta CPD^{*}q_e$, in respect with distinct situations Φ_F and Φ_I (Φ_F corresponds to test gas atmosphere and the initial Φ_I corresponds to synthetic air). The electrical resistance was measured with a digital Keithley 2000 multimeter.

Electrical properties of $SnSe_2$ thin films were reported by D.A. Hady et al. [3] which suggest semiconductor properties and indicate that the electrons are the majority carriers in $SnSe_2$. The surface work function Φ of the considering n-type $SnSe_2$ semiconductor contains three contributions: energy difference between Fermi level and conduction band in the bulk $(E_C\text{-}E_F)_{bulk}$, band bending qV_S and electronic affinity χ. All three contributions may change upon to gas exposure [4-6].

$$\Phi = \left(E_C - E_F\right)_{bulk} + qV_S + \chi \qquad (1)$$

The conductance of the semiconductor may be described by equation (2).

$$G = G_0 \exp\left\{\frac{(E_F - E_C)_{bulk} - qV_S}{k_B T}\right\} = G_0 \exp\left\{\frac{(\chi - \Phi)}{k_B T}\right\} \qquad (2)$$

It follows $$k_B T \ln\left(G_I / G_F\right) = \chi - \Phi \qquad (3)$$

Where, G_I is the initial conductance and G_F is the final conductance (test gas)
Hence, using (3):

$$\Delta\Phi = \Phi_F - \Phi_I = k_B T \ln\left(G_I / G_F\right) + \chi_F - \chi_I = k_B T \ln\left(R_F / R_I\right) + \Delta\chi \qquad (4)$$

where R_I is the initial resistance and R_F is the final resistance.

3. Results and discussion

The data plots corresponding to the experimental results are presented in figures 1-3.

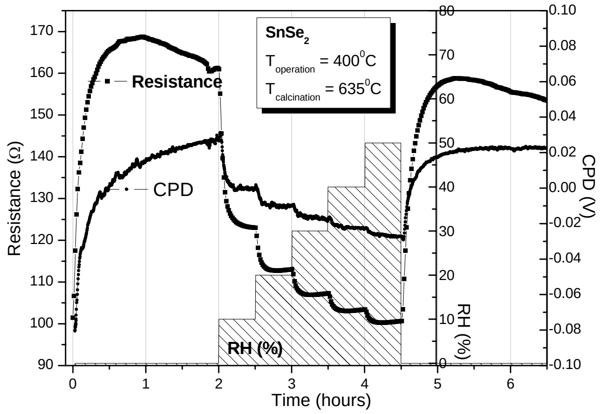

Fig. 1. CPD and electrical resistance changes induced by H_2O.

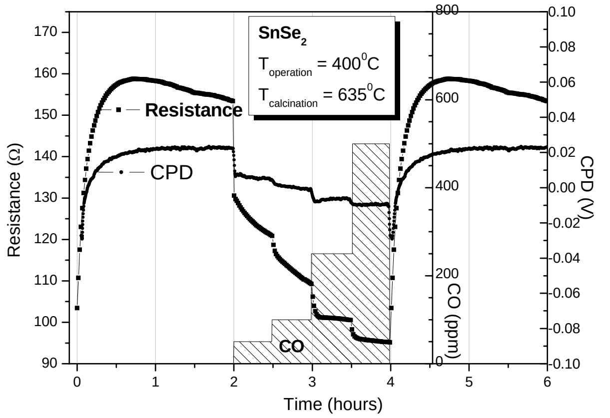

Fig. 2. CPD and electrical resistance changes induced by CO.

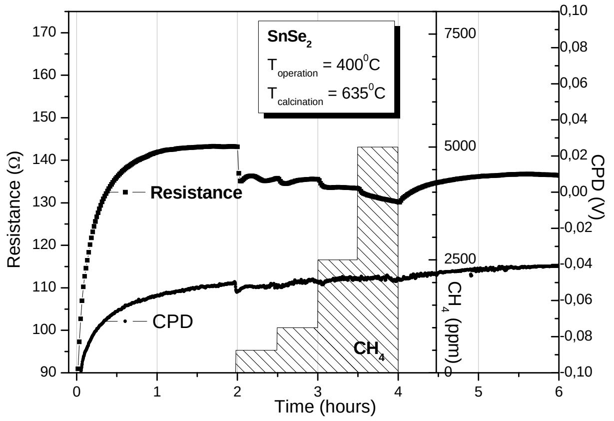

Fig. 3. CPD and electrical resistance changes induced by CH_4

Based on equation (4), the obtained Figs. 4-6 illustrate the changes induced by H_2O, CO and CH_4 on the surface work function, band bending and electron affinity respectively.

In the presence of humidity, the surface work function decreases due to the potential barriers and also to the electronic affinity.

Surface potential barriers vary due to the chemical interactions between $SnSe_2$ and water molecules dissociated as H^+-OH^-. H^+ forms chemical bonds with previous adsorbed oxygen and decrease the electric charge (electrons) accumulated on surface states and the band bending respectively. The terminal hydroxyl group OH^- forms dipolar bonds with lattice Sn^+, which affects the electronic affinity of $SnSe_2$ surface. Surface work function decreases when the relative humidity increase, as a result of its component decreasing.

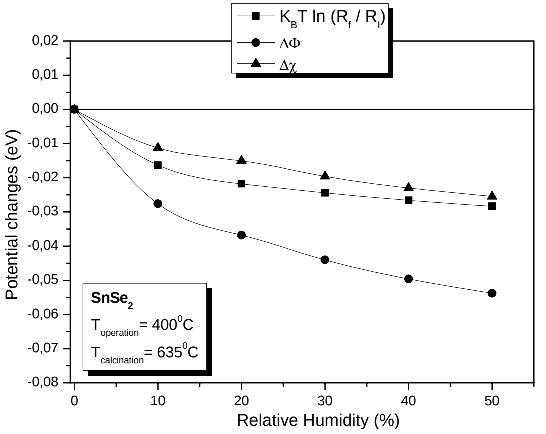

Fig. 4. Work function, band bending and electron affinity changes induced by H_2O

In the case of CO, the surface work function decrease is a result of band bending decrease due to the chemical interaction with previous adsorbed oxygen. The electronic affinity of $SnSe_2$ is practically unaffected by the CO presence on the sample surface.

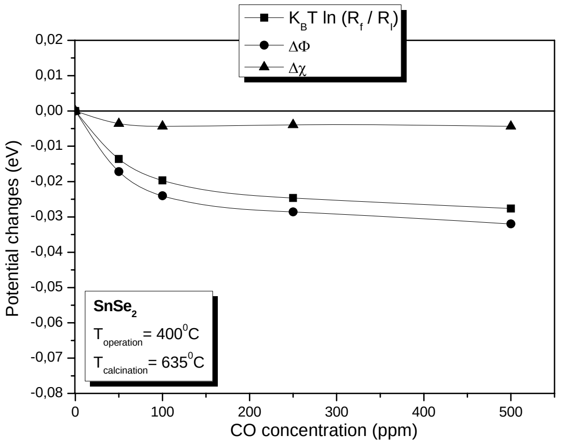

Fig. 5. Work function, band bending and electron affinity changes induced by CO.

Opposite to H_2O and CO atmospheres, the presence of CH_4 insignificant affects the surface band-bending and work function, which permits to conclude that $SnSe_2$ presents bulk conduction in methane detection.

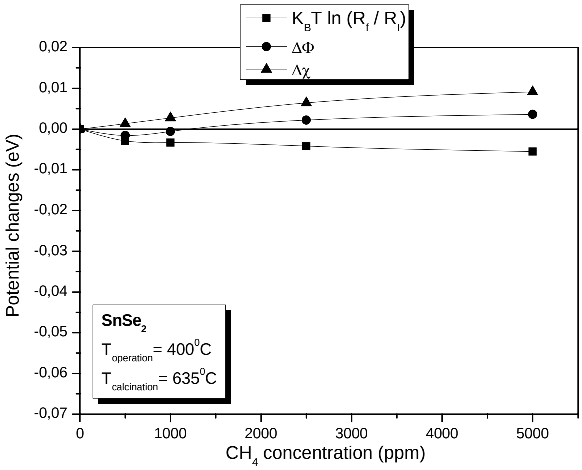

Fig. 3. Work function, band bending and electron affinity changes induced by CH_4.

4. Conclusions

Simple monitoring of the variation in resistance of the surface layer does not completely illustrate the surface interactions. A complex investigation of gas-sensing properties of thin $SnSe_2$ films was carried out by means of simultaneous monitoring of two physical parameters: electrical conductance (resistance) and work function (CPD). In this way we could experimentally demonstrate the hypothesis that methane interact with the bulk of $SnSe_2$ and the other two gases (CO and H_2O) interact with the $SnSe_2$ surface [2]. Chemical interactions based on methane dissociation and bulk defects apparition by thermal removal of Se, requires higher temperatures than 400 ºC.

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