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Influence of calcination temperature on the electrical signal of $SnSe_2$ sensors

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The effect induced by the calcination temperature on gas sensing properties of thin $SnSe_2$ layers exposed to reducing gas species, respectively CH_4, CO and H_2O, has been investigated. The sensor signal defined as the ratio between the electrical resistance in air and that in the test gas atmosphere has been used as monitoring parameter.

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1. Introduction

The detection of gaseous species in the surrounding atmosphere deserves a large-scale application, for both industrial and residential monitoring and protection. As an example, the methane leak should be avoided because the concentration of methane in air exceeding 5 % are easily flammable and highly explosive. Consequently, detection and monitoring of this gas in the vicinity of methane pipes, in coal mines or in houses is very important.

Chemoresistive sensors are devices for gas detection. They are simple and inexpensive devices based on metal oxide active layer deposited on a substrate provided with interdigital electrodes and heater. Despite the huge interest in developing gas sensors, the relatively lack of selectivity is still one of their disadvantages. Metal oxide semiconductor gas sensors have been largely used for the detection of toxic or explosive gases. Among the metal oxides, tin oxide (SnO_2) seems to play a leading role in the construction of chemical gas sensor due to its high sensitivity at relatively low operating temperatures. It was shown that the nanoparticle phase of SnO_2 improves the sensitivity to different gases [1-5].

The system Sn-Se is poorly studied and its interest consists in the special properties related to the presence of a metal (Sn) and a chalcogen (Se), with different valences and ionicities that govern the behaviour of the material. $SnSe_2$ belongs to the class of Group IV dichalcogenides having a crystal structure of CdI_2 type C6 [6]. The compound it is composed of planes of Se atoms hexagonally close packed alternating with planes of Sn atoms. The $SnSe_2$ films have been investigated in several papers. Optical and electrical properties have been studied by Evans and Hazelwood [7]. Bhatt and Gireesan [8] investigated the influence of heat treatment on electrical properties of thermally evaporated tin diselenide thin films. The electrical properties of $SnSe_2$ thin films reported by D.A. Hady et al. [9] suggest semiconductor properties and an activation energy of conduction of around E_g = 1.2 eV, above 400 K.

In a previous paper [10] we have remarked the gas sensing effect of $SnSe_2$ to methane, for 0 – 5000 ppm concentration.

In the present paper we report the results obtained during the investigation of the influence of calcination temperature on the signal of $SnSe_2$ sensor and also the relative selectivity to carbon monoxide and water vapors.

2. Results and discussion

$SnSe_2$ thin films were prepared by Pulsed Laser Deposition (PLD) on alumina substrate provided with platinum interdigital electrodes and heater. The pulsed laser deposition was carried out with a KrF* excimer laser (λ = 248 nm) with pulse duration t_{FWHM} > 7 ns and 1Hz repetition rate. The laser spot was set within 3 mm^2. The maximum output energy was 110 mJ/pulse corresponding to a fluency of ~3.6 J/cm^2. The obtained have been heat treated at several steps, from 600 up to 650 °C in oxygen atmosphere.

The $SnSe_2$ based samples were tested for gas sensors applications by electrical resistance measurements, under dynamic conditions ensured by a Gas Mixing Station whose flow system is computer controlled. The Station has two channels for generating the carrier gas with adjustable humidity (0-80% relative humidity). Other two channels were used with test gases (CH_4, CO), every channel operating with gas of purity 5N provided by special recipients.

The sensor signal S is defined as: $R_{air}/R_{test\ gas}$, where R_{air} is the electrical resistance of the active film in synthetic air atmosphere (reference atmosphere) and $R_{test\ gas}$ is the electrical resistance of the active film in synthetic air atmosphere with different concentration of reducing gases.

The sensor selectivity is defined as the ratio S_{CH4}/S_{CO}, respectively S_{CH4}/S_{H2O}, where letter S denotes the sensor signal.

The influence of calcination temperature on $SnSe_2$ gas-sensing properties was investigated by sensor signal evolution. The operation temperature (280÷600 °C) of the active films was ensured by the voltage applied on the heater. Methane concentration was chosen as 5000 ppm, corresponding to the Low Detection Limit - LDL of the gas, i.e. the danger threshold (Fig. 1).

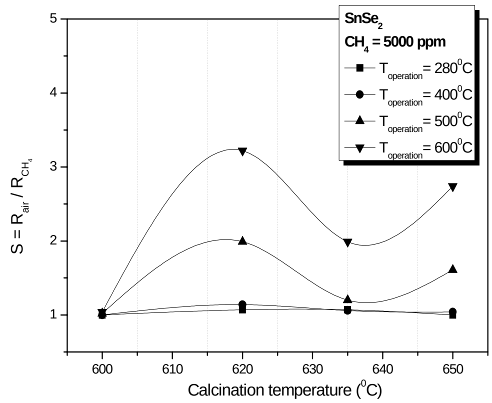

Fig. 1. The sensor signal for 5000 ppm CH_4 as a function of calcination / operation temperature.

Fig. 1 shows that both temperatures ($T_{calcination}$ and $T_{operation}$) influence the sensor signal, the higher sensitivity to CH_4 being obtained for $SnSe_2$ calcinated at 620 °C and operating at 600 °C. A special attention was focused on the influence of RH, which is not negligible for in-field applications and also for carbon monoxide. This potential interfering gas results from incomplete burning of methane, due to the lack of oxygen. The interest was focused both on Safe Limit – SL (50 ppm) and Detection Limit - DL (500 ppm) relative to methane signal already reported [10].

In order to explore the selectivity with respect to CO and RH, we have carried out experimental investigations in the same temperature conditions (Fig. 2, 3). At the beginning a concentration of 500 ppm CO and RH=50% (specific for in-field ambient conditions) has been considered.

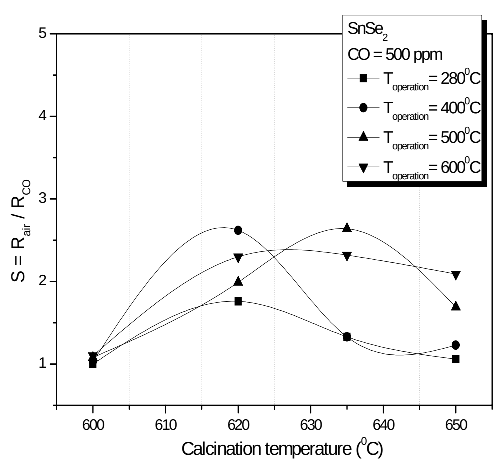

Fig. 2. The sensor signal for 500 ppm CO as a function of calcination / operation temperature.

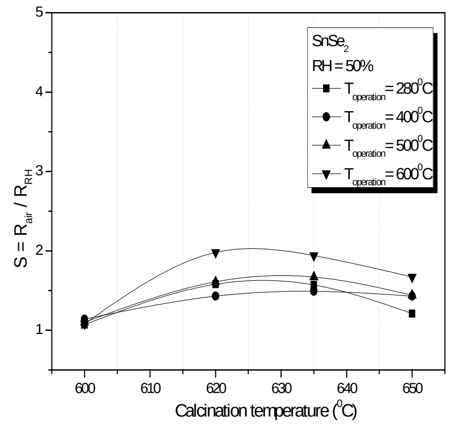

Fig. 3. The sensor signal for 50% RH as a function of calcination / operation temperature.

Our experimental investigations evidence that $SnSe_2$ ($T_{calcination}$=620 °C, $T_{operation}$=600 °C) presents selectivity for methane detection, even in wet atmosphere or high CO concentration conditions (Fig. 4).

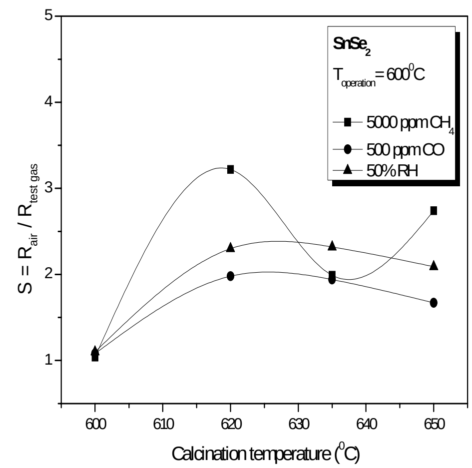

Fig. 4. The sensor signal for $SnSe_2$ as a function of calcination temperature and gas type.

A possible explanation can be the dominant component of bulk conduction mechanism, which requires higher activation energy, corresponding to the desorbtion of CO and water vapours. According to this explanation, the lower calcination temperature does not permit the appearance of bulk defects by thermal removal of Se.

The CO sensitivity of $SnSe_2$ (T_{calcin} = 620 °C) at T_{operat} = 400 °C has been investigated.

Qualitative investigations have been done at optimum temperature of CO detection (Fig. 2). The sensor signal was checked for a large range of concentrations, for all three gases. Comparisons in terms of sensor signal are presented in Fig. 5 (a, b and c). A special attention was focused on CO safe limit, respectively 50 ppm.

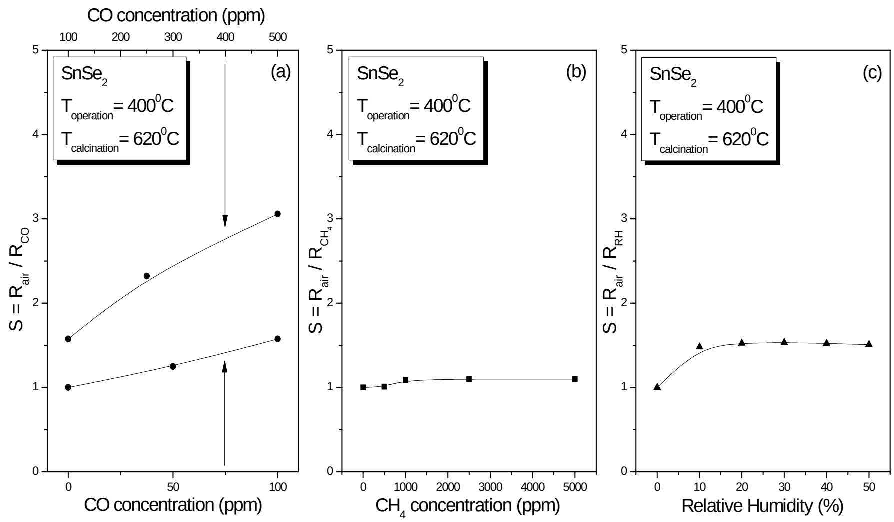

Fig. 5. The sensor signal for a) CO (0 – 100 ppm; 100 – 500 ppm) relative to: b) CH_4 (0 – 5000 ppm); c) RH (0 - 50%).

Based on experimental results, it was concluded that that $SnSe_2$ ($T_{calcination}$ = 620 °C, $T_{operation}$ = 400 °C) exhibits a significant CO selectivity relative to CH_4 and RH, only for CO concentrations higher than 100 ppm. For lower CO concentrations, the signal of $SnSe_2$ is around 1-1.5 for all test gases. Regarding the sensitivity to water vapours, there are differences only between dry and humid atmospheres, the level of RH being not important.

At $T_{operation}$ = 400 °C, $SnSe_2$ presents low and comparable sensitivity to CH_4, RH and low CO concentrations (0 – 100 ppm), for all calcination temperatures (Fig. 6).

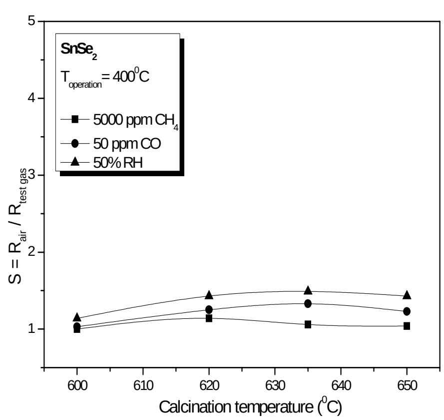

Fig. 6. The sensor signal for $SnSe_2$ as a function of calcination temperature and gas type.

From the point of view of gas-sensing properties, the operation temperature of 400 °C does not ensure the activation energy for bulk defects contribution to electrical conductivity of the active layer. In our opinion, higher operation temperatures ensure the sensitivity of $SnSe_2$ to methane and relative selectivity to other reducing gases possibly present in the environment atmosphere.

3. Conclusions

The $SnSe_2$ thin films prepared by pulsed laser deposition on alumina substrate provided with platinum interdigital electrodes and heater, calcinated at 620 °C, exhibit strong sensitivity to methane at the operating temperature of 600 °C. As regarding the potential interfering gases, $SnSe_2$ shows selectivity even to high CO concentrations. A possible explanation of the gas-sensing behavior can be the bulk conduction mechanism which requires high activation energy, ensured by a relatively high operating temperature.

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