DOI 10.5162/IMCS2012/1.3.5

Conduction Mechanism in Undoped and Antimony Doped SnO_2 Based FSP Gas Sensors

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Abstract:

The conduction mechanism in highly porous thick film SnO_2 sensing layers, obtained by a direct deposition technique using FSP (Flame Spray Pyrolysis), and the influence of different antimony (Sb) doping levels on the electrical properties of the host material is investigated by simultaneous DC electrical resistance and work function changes measurements in various ambient atmospheres. The situation in the case of the undoped FSP-sensors is very similar to the results obtained on polycrystalline thick film layers: we found a seamless transfer of the conduction mechanism from a depletion layer controlled one to the flat band situation and to an accumulation layer controlled one. The switch between these two models directly occurs in the absence of ambient oxygen, indicating that the depletion region is only determined by its adsorption. The degeneration of the semiconductor, in the case of the accumulation layer controlled conduction mechanism, is not observed. The addition of Sb influences the conduction mechanism dramatically due to its effect on the bulk concentration of free charge carriers. In contrast to the undoped FSP-SnO_2 sensor there is a direct switch from a conduction mechanism controlled by the depletion layer to the degenerate semiconductor situation that indicates a deep crossing of the Fermi level into the conduction band; moreover an initial upward band bending is observed.

Key words: conduction mechanism, depletion layer, accumulation layer, Sb doped SnO_2, band bending

1. Introduction

Although gas sensors based on semiconducting metal oxides have been used and studied since a long period, the exact way in which the full sensing procedure, including the surface chemistry, the charge transfer, the conduction and the transduction, is taking place is still not yet completely understood. In addition to the complex chemical reactions at the surface of the metal-oxide, the way in which the conduction in the sensing layer takes place is crucial for the magnitude of the sensor signal [1].

Recently, for undoped SnO_2 based polycrystalline thick film layers, it could be demonstrated that the conduction mechanism is depending on the surrounding conditions [2]. The decisive factors are the initial surface band bending (in the absence of atmospheric oxygen) and the position of the Fermi level in the bulk. In addition to the temperature, the position of the Fermi level is dependent on the concentration of donor or acceptor levels in the energy band gap [3]. Therefore the concentration of free charge carriers in the conduction band can be tuned by the nature and amount of the dopants.

In this contribution we are applying the same experimental and theoretical modeling tools in order to examine how the conduction mechanism for highly porous SnO_2 films prepared by FSP can be described. The main difference, when compared to the reference polycrystalline thick film SnO_2 layers realized by wet chemistry, is the small particle size of around 10 nm in case of sensors obtained by FSP (around 100-200 nm for the classical material) and the extremely high porosity. Besides ensuring an ultra fast diffusion of the target gases into the sensing layer, which is an advantage, the high porosity of the sensitive film has also a negative impact, namely a very large baseline sensor resistance. A possible remedy for this drawback is to change the electrical properties of the semiconducting material by the so called “bulk doping” method.

By replacing some of the tin sites in the lattice by an element having one electron more in the outer shell (Sb), we demonstrated that we can change the baseline resistance without having a negative impact on the sensing properties [4]. Here, we are examining the influence of Sb doping on the conduction mechanism of the host SnO_2 material.

2. Experimental

A direct sensing layer deposition method, using flame spray pyrolysis [5], onto alumina substrates - provided with interdigitated Pt electrodes for the read-out of the resistance and a Pt heater - was applied to prepare highly porous undoped and 0.1, 0.5 and 1wt. % Sb doped SnO_2 thick films. The conduction mechanism was investigated by simultaneously performing DC-resistance and work function changes measurements at a sensor operation temperature of 300°C [2]. To avoid changes in the electron affinity, very dry conditions were chosen. In this way the changes in the work function can be directly correlated with the changes in the band bending.

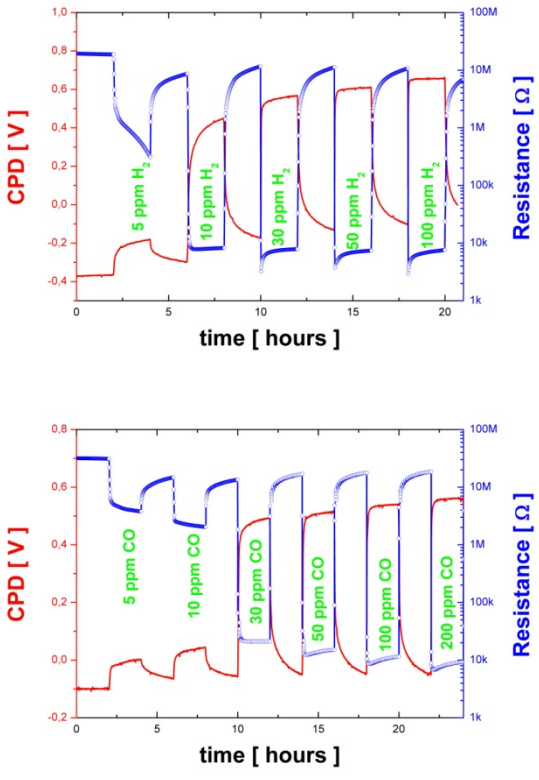

Fig. 1. Simultaneous contact potential differences (CPD) and electrical resistance changes of the undoped FSP-sensor during exposure to CO and H_2 in the absence of oxygen.

To cover a large range of band bending changes, the samples were exposed to CO and H_2 concentrations in different oxygen backgrounds: <12, 200 and 22000 ppm. An example representing the time dependence of the resistance and the CPD of an undoped SnO_2 sensor exposed to CO and H_2 in the presence of a very low oxygen background (<12 ppm) is shown in Fig. 1.

The presence of CO and H_2 determines a decrease in the resistance as well as in the work function ($\Delta\Phi=-\Delta CPD$). With increasing oxygen amount in the background, the relative changes are getting lower like it was also observed in our previous studies [2]. An overview of all the results obtained for the undoped SnO_2 sample is presented in Fig. 2 and the ones for the differently Sb doped samples in Fig. 3-5. There the resistances R as a function of the band bending changes $q\Delta V$ are plotted over the whole experimental range. The situation in N_2 is chosen as reference for the band bending changes ($q\Delta V=0$).

3. Results and discussion

In the case of the undoped FSP sample, there are two regions, where a linear fit - indicating an exponential dependency - can be clearly identified (Fig. 2): between 0.2 and 0 eV the experimental fit value is in good agreement with a conduction mechanism controlled by the depletion layer model (experimental dependency of $R \sim \exp(qV_s/1.19kT)$ compared . to the theoretical one of $R \sim \exp(qV_s/kT)$ [2]).

For values around 0 eV a transition into the accumulation layer controlled conduction mechanism, for which the Boltzmann statistic is valid, occurs. The underlying proportionality is described by $R \sim \exp(qV_s/2.34kT)$. The theoretical dependency in this case is: $R \sim \exp(qV_s/2kT)$ [2].

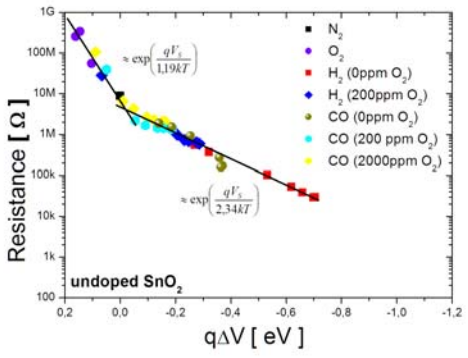

Fig. 2. Dependence of the resistance and the corresponding band bending for the undoped FSP sensor. A transition from the depletion layer model to the flat band situation and finally to the accumulation layer model is observed.

Due to the fact that the change between the conduction mechanism controlled by the

depletion and accumulation layer model takes place very close to 0 eV, the situation in the absence of oxygen at the surface of the grains is reflected by the flat band situation and therefore the upward band bending is only determined by chemisorbed oxygen.

Compared to the results obtained for the reference material, the only difference is that the degeneration of the semiconductor for the accumulation layer in case of the FSP samples is not observed in the applied concentration range for oxygen, H_2 and CO [2]. This indicates that the distance between the Fermi level and the conduction band edge in the bulk is larger in case of the FSP samples (at least 0,4 eV compared to 0,08 eV [6]).

The dependence of the resistance on the corresponding band bending for the different concentrations of Sb doping is presented in Fig. 3, 4 and 5. As a reference ($q\Delta V=0$) again the situation in N_2 atmosphere was chosen. The effect of Sb additives on the properties of the host can be summarized as followed:

- The baseline resistance is decreased proportionally to the amount of Sb;
- There are two regions where a reasonable exponential fit can be obtained;
- An initial upward band bending in N_2 is observed for all Sb concentrations;
- The conduction mechanism controlled by an accumulation layer model, where the Boltzmann statistics can be applied, is missing.

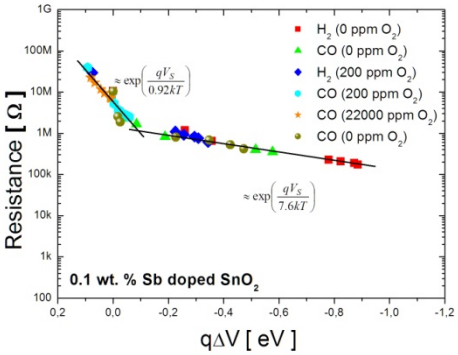

Fig. 3. Dependence of the resistance and the corresponding band bending for the 0.1 wt % Sb doped FSP sensor. In addition to the decrease of the resistance, the transition between the two models is shifted to the right.

In the case of the 0.1 wt. % Sb sensor the transition between the two conduction models occurs at around -0.1 eV, in the case of the 0.5 wt. % Sb at around -0.3 eV and in the case of 1 wt.% Sb at around -0.45 eV determining an initial band bending in N_2 of 0.1, 0.3 and 0.45 eV respectively. This surface band bending is caused by surface acceptor states acting as electron traps indicating that there is a surface effect due to the addition of Sb.

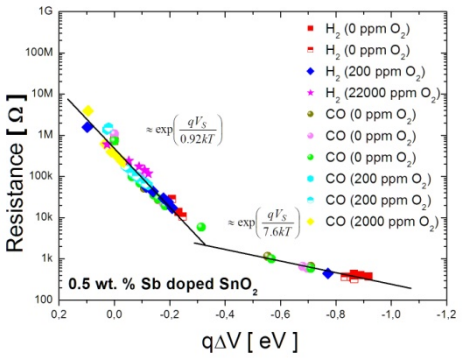

Fig. 4. Dependence of the resistance and the corresponding band bending for the 0.5 wt. % Sb doped FSP sensor. With increasing the Sb concentration the resistance is decreasing and the transition between the depletion layer model and the accumulation layer model is shifted to the right.

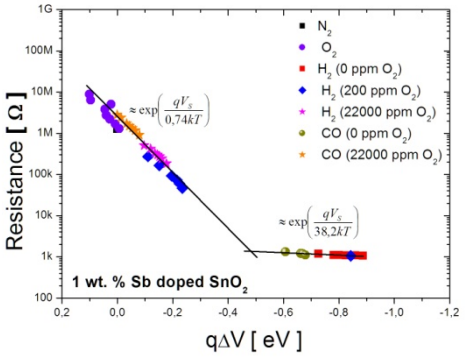

Fig. 5. Dependence of the resistance and the corresponding band bending for the 0.5 wt % Sb doped FSP sensor. As mentioned above, the effects are getting bigger with increasing the Sb concentration.

As mentioned in the introduction, the doping with Sb creates additional donor levels close to the conduction band edge. This leads to a higher concentration of free charge carriers and to the movement of the Fermi level position towards the conduction band (Fig. 6).

The increase in the free charge carrier concentration with increasing Sb amount is shown by a moving of the two conduction regions towards lower resistance values and is in line with DC-resistance measurements performed on similar samples [3].

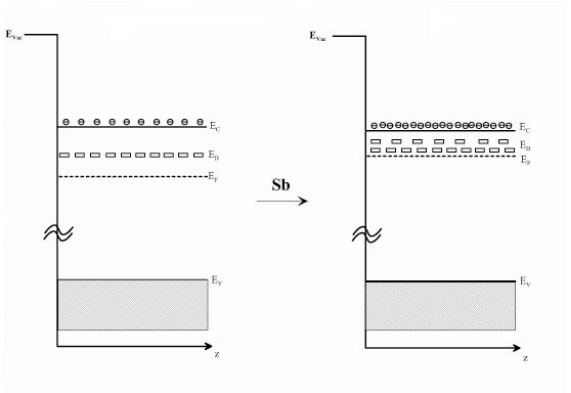

Fig. 6. Influence of the Sb doping on the energy band representation of SnO_2. The formation of donor levels in the bulk (E_D) shifts the Fermi level up towards the conduction band edge (the exact position of the additional donor levels and the new position of the Fermi level are not really known).

The remaining open question from the experiments is the absence of the accumulation layer region where one is allowed to use the Boltzmann statistics. For all Sb doped samples one observes a direct switch from the depletion layer model (theoretical dependence of $R \sim \exp(qV_s/kT)$) into the accumulation layer where the Boltzmann statistics cannot be applied anymore (theoretical dependence of $R \sim \exp(qV_s/mkT)$ with $m<2$). A region with a dependence of $R \sim \exp(qV_s/2kT)$ like it was found for the undoped SnO_2 sample does not appear. Consequently, due to the additional donor levels in the band gap and the moving of the Fermi level towards the conduction band edge, the degeneration of the accumulation layer already starts at a very small downward band bending. It seems that the Fermi level is located very close to the conduction band.

The expected effect of the Sb "bulk doping" is reflected by the resistance versus band bending plots. The decrease of the baseline and the moving of the Fermi level position towards the conduction band edge are observed. Interestingly, an additional surface effect in forms of surface acceptor levels is demonstrated which was not expected.

4. Conclusion and outlook

It could be demonstrated that the conduction mechanism of highly porous undoped SnO_2 based thick films prepared by FSP is almost similar to the one of the classical thick film layers. The only difference between both materials occurred in the position of Fermi level.

The conduction mechanism as well as the electrical properties of the host SnO_2 are largely influenced by the addition of Sb. Even at very small Sb concentrations a bulk and a surface effect are observed. The reason for these findings can be attributed to a shift of the Fermi level position due to the presence of additional donor levels in the band gap and to the appearance of surface acceptor levels.

Currently, the investigations will be extended to other dopants like Pt, Pd and Au for FSP sensors.

Acknowledgements

The authors would like to acknowledge the DFG through WE 3662/1-2 and MA 3333/2-1 support.

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