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# Catalytic behaviour of ultrafine Pt on the gas sensor performances of ZnO nanoparticles

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**Abstract**

**Gas-sensing experiments on Pt-functionalized ZnO nanoparticles exhibited larger response to ethanol gas at lower operating temperature, attributed to the sensitization and spillover effects. The faster recovery time of Pt-decorated ZnO is associated with the catalyst effect of Pt. The maximum sensitivity of Pt-decorated ZnO is more than twice compared to that of bare ZnO nanoparticles. At 400°C, the response time of Pt-decorated ZnO to 13 ppm ethanol gas is 150 s, while that of bare ZnO is of about 1200 s**.

**1 Introduction** Recently, the potential of noble metals used as additive catalyst to metal-oxides has been investigated in order to improve the performances of metal-oxide gas sensors [1]. There are some possible hypotheses which may explain the phenomena occurring in gas sensors, such as the effect of the catalyst on the rate of a reaction, the production of new chemical species, and changing of the electronic interaction behavior of metal-oxide semiconductors, but the fundamentals of the influence of the noble metal additives on these sensors are still not fully understood [2, 3].In this report, Pt is used as the catalyst deposited on the surface of a ZnO nanoparticle (NP) layer. The gas sensing performance of a ZnO NP layer before and after Pt decoration is evaluated with a standard procedure using ethanol vapor.

**2 Experimental** The ZnO NP layer is fabricated using an original and purely physical method: the low energy cluster beam deposition [4]. The gas sensing characteristics of the fabricated ZnO NP layers were characterized with the experimental setup presented in Figure 1. All the experimental gas responses were acquired with the same concentration of 13 ppm ethanol. The response to ethanol of the ZnO NPs layer was measured for ZnO NP layer temperature of 300, 350 and 400°C. In this report, we particularly focus on the effect of Pt addition onto the surface of the ZnO NPs. For this purpose, a small amount of Pt was sputtered onto the ZnO NPs layer. The thickness of the deposited Pt on the ZnO NPs is of about 2 Å.

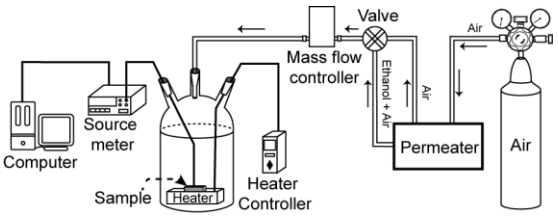


Figure 1 Schematic of the experimental setup used to measure the response of the ZnO NPs layer to ethanol vapor.

**3 Results and discussion** The responses of the ZnO NPs layer before and after Pt deposition are shown in Figure 2 for an operating temperature of 400˚C. Here, the response $S$ is defined as: $S=R_a/R_g$.

where $R_a$ and $R_g$ are the resistances of the sample under air and in the presence of the ethanol vapor, respectively. It is found that Pt decoration on the surface of the ZnO NPs layer enhances the response to ethanol vapor and at the same time drastically shortens the recovery time. The recovery time after the Pt decoration was almost equal to 150 s, as compared to 1200 s before Pt decoration.

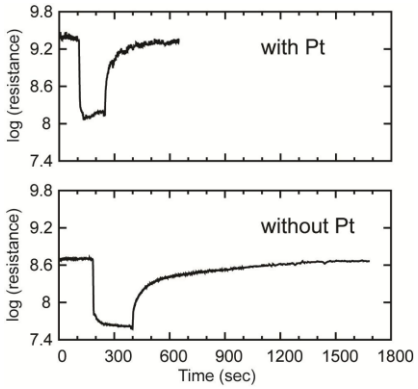


Figure 2 ZnO NPs layer responses to ethanol vapor at a concentration of 13 ppm before and after coating with Pt. The layer temperature was set to 400˚C.

The responses to ethanol at different temperatures with and without Pt decoration are reported in Figure 3. The variation of the response with the temperature reveals a maximum value at 350˚C for the ZnO NPs sample decorated with Pt. It is also found that all samples with Pt decoration exhibit a larger response to ethanol than those without Pt decoration.

To understand the effect of Pt deposition on the ethanol response of the ZnO NPs layer, we first explain the sensing mechanism of the ZnO NPs without Pt decoration. It is known that the depletion layer plays a key role in the sensing mechanism. The formation of the depletion layer occurs according to the following steps. ZnO possesses oxygen vacancies which are suitable to trap oxygen molecules. After adsorption, further chemisorption of oxygen molecules on the surface of ZnO (n-type metal oxide semiconductor) occurs by trapping free electrons from oxygen species such as $O^{2-}$, $O^-$, $O_2^-$ [2]. As a result of the electron trapping, the depletion layer is created.

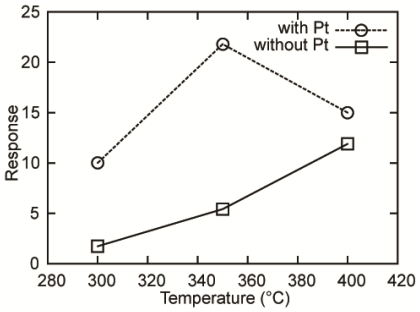


Figure 3 Response to ethanol as a function of the operating temperature for the ZnO NP layer without and with Pt decoration. The ethanol vapor concentration was kept constant at 13 ppm.

Generally, an increase in the thickness of the depletion layer leads to an increase in the resistance of the ZnO layer. To enhance the response of the ZnO NPS to a reductive gas such as ethanol, one way is to increase the number of trapped electrons from adsorbed oxygen species and thus obtain a large depletion layer and consequently maximize the variation of the layer resistance.

In the case of ethanol vapor, the adsorbed ethanol molecules can be decomposed via two chemical routes, namely, the dehydration and the dehydrogenation. The dehydrogenation is the dominant reaction, since ZnO has a basic surface favoring the formation of acetaldehyde ($CH_3CHO$). The chemical reactions are given as follows [5]:

$$CH_3CH_2OH(gas) \rightarrow CH_3CHO(ads) + H_2 \qquad (2)$$

(dehydrogenation)

$$CH_3CHO(ads) + 5O^{2-} \rightarrow 2CO_2 + 2H_2O + 10e^- \qquad (3)$$

(oxidation)

where the abbreviation (ads) stands for "adsorbed".

According to the reaction (2), a large number of electrons is released upon the ethanol oxidation, resulting in a decrease in the ZnO NPs layer resistance [6].

The observed enhancement of the ZnO NPs response to ethanol is likely caused by the combination of the two effects, namely the electronic sensitization and the spillover effect of Pt on the surface of metal oxide semiconductors.

The sensitization is caused by the difference of the work function between the Pt decorated region and the ZnO NPs. In comparison to ZnO, Pt has a higher value for the work function. It means that the ZnO NPs Fermi energy level is lower than that of the Pt, leading to the transfer of some free electrons from the ZnO NPs to the Pt particles, since the two systems attain a thermodynamic equilibrium and a new Fermi energy is created. The reduction of the number of free electrons in the ZnO NPs results in an increased depletion layer thickness as a raise of $R_a$ value (see Figure 2) is observed (and therefore an enhancement in the response is obtained). This effect is referred to as the electronic sensitization and its schematic diagram is given in Figure 4 (a) [7].

The spillover effect is explained by an enhanced dissociation of oxygen molecules into oxygen ions. In this mechanism, a weak bond is formed between an oxygen molecule and a Pt atom (a complex component). This complex component can be easily broken into oxygen ions (by trapping free electrons) that diffuse to the surface vacancies of the ZnO NPs. Therefore, more trapped electrons are created, leading to an increase in $R_a$ and consequently an improvement in the response of the ZnO NPs. Figure 4 (b) shows a schematic of the spillover mechanism [8]. These two phenomena are confirmed by the observation of an increase in the resistance of the ZnO NPs layer and its larger response to ethanol vapor upon Pt decoration in our experiments.

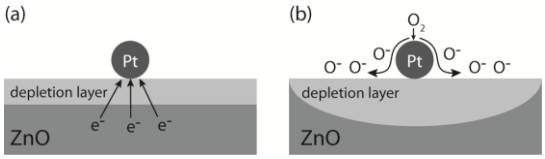


Figure 4 Schematic diagrams of (a) the electronic sensitization mechanism and (b) the spillover mechanism.

The observed fast recovery time of the Pt decorated sample (see Figure 2) is likely caused by a Pt-assisted decomposition of the adsorbed acetaldehyde formed in the reaction (3). Pt is well known to behave as a catalyst for breaking off the C-C bond, as reported in [9, 10]:

$$CH_3CHO(ads) \xrightarrow{Pt} CH_4(g) + CO(g) \qquad (4)$$

where the abbreviation (g) stands for "gas".

**4 Conclusion** The decoration with Pt of the ZnO NPs layer used in ethanol gas sensing experiments was found to enhance the response of the sensor in the presence of ethanol vapor. The response to ethanol was increased by 22 for an operating temperature of 350°C. The recovery time was decreased from 1200 s to 150 s at the operating temperature of 400°C. The enhanced response is attributed to the electronic sensitization and the spillover effect generated by the Pt decoration of the ZnO NPs. The shortening of the recovery time was explained by the catalytic effect of Pt in breaking the acetaldehyde molecule.

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