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FEATURES OF AMMONIA ADSORPTION ON SnO_2 THIN FILMS SURFACE

Ammonia adsorption processes on SnO_2 thin films under different conditions were investigated. It was researched temperature dependences of SnO_2 thin films conductivity. It was found that sensitivity depended on the sample operating temperatures and chemical state of the film surface. Ammonia adsorption mechanism was proposed. The main idea of adsorption mechanism was transformation of HN_3 to NO_x oxides with subsequent adsorption. Activation energies of adsorption were calculated and been in good comparison with activation energy of NO_x adsorption determined previously by the other authors.

1. INTRODUCTION

Sensitive properties of metal oxides to different toxic gases have been investigated since the sixties [1—4]. Deposition technologies and experimental methods to investigate metal oxide properties are highly developed [5, 6]. However, there are some problems which are still being developed: decreasing response time of sensors, declining selectivity and sensitivity to different gases and preventing water influence on sensor response.

In this paper the attention was paid to ammonia leakage detection. Ammonia sensors can be used for such applications as chemical plants, food technology, medical diagnosis and for environmental protection [7]. Recently their application in selective catalytic reduction (SCR) systems has gained importance [8, 9]. It was previously shown that sensitivity of SnO_2 depended on sample temperature and chemisorption state of film surface [10]. It was also pointed out that chemisorbed oxygen atoms O^- led to sensitivity to different organic vapours [10].

In this work temperature dependences of conductivity of SnO_2 thin films exposed to different atmospheres were researched, water and chemisorbed oxygen influence on sensitivity to ammonia were investigated. Reaction mechanism was proposed.

2. EXPERIMENTAL

The investigated samples were deposited by electro-spray pyrolisis method from $SnCl_4$ ethanol solution on alumina substrates. The substrate temperature was 420 °C and kept constant during all the deposition. Obtained samples were calcinated in air at 500 °C during 1 hour according to methods described in [10]. Figures 1, *a* and *b* shows SEM images of substrate and sensitive layer surface, correspondingly. Sensitive layer surface was formed with crystalline conglomerates with typical size 0,3—0,8 μm where-

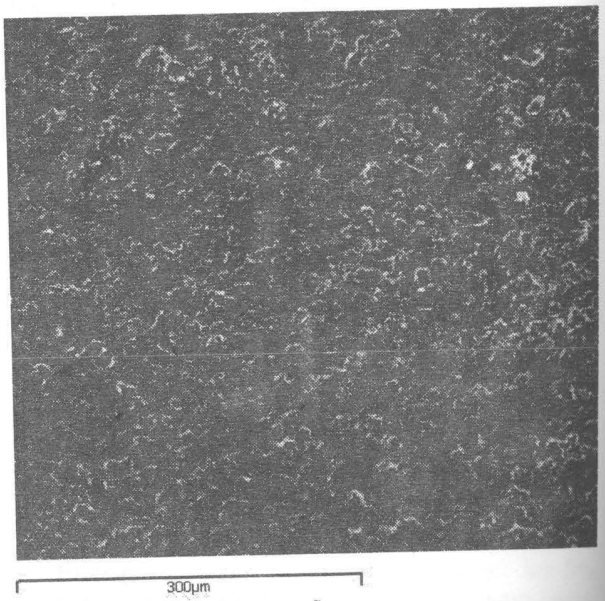

Fig. 1. SEM images of: *a* — substrate; *b* — thin SnO_2 film

as substrate surface consisted of conglomerates with typical size 1,3—2,8 μm. The film contained white areas which could be affected both by external structural defects and oxygen adsorption complexes.

The films were exposed in different atmospheres and temperature dependences of conductivity were measured. The heating rate was 5 K/min. During all the experimental cycles electrical voltage in additional resistance R was measured. The additional resistance was equal to $R = 2\,200\,000$ Ohm. According to Ohm's law:

$$I = \frac{U_r}{R}, \qquad (1)$$

where U_r — voltage in additional resistance R, I — current value. As to $I \propto \sigma$ where σ is conductivity, it is correctly to build in temperature dependences in $\ln I \sim 1/T$ coordinates. The above mentioned experimental cycle was also provided for clean uncovered substrates to determine its influence on SnO_2 film electrical properties.

Gas sensitivity measurements were provided in air—ammonia, air—water and Ar—ammonia atmospheres under different temperatures. Ammonia concentration was 80 ppm in all cases. Sensitivity value was calculating according to such formulas:

$$\gamma = \frac{R_{atm}}{R_{gas}} \text{ — for reducing gases;}$$

$$\gamma = \frac{R_{gas}}{R_{atm}} \text{ — for oxidizing gases.}$$

3. RESULTS AND DISCUSSION

Temperature dependences for conductivity of SnO_2 thin films are plotted on figure 2. One can see there are three regions (a, b, c) on these curves. For the samples exposed in Ar conductivity increased with heating at the temperature region of 10—160 °C (curve *1*, region *a*). Activation energy calculated for this part was $E_a = 0{,}18$ eV. In [11] it was mentioned that donors with activation energy $E_a = 0{,}12$—$0{,}2$ were corresponded with double ionized oxygen vacancies V_O^{2+}. Consequently one can verify that the films conductivity in neutral atmosphere at low temperatures is affected by oxygen vacancies V_O^{2+}.

At the temperatures from 170 °C to 250 °C shape of conductivity jump was observed (curve *1*, region *b*). Activation energy for this part equalled $E_a = 1{,}1$ eV. This phenomenon can be connected with structural changes inside the sensitive layer. At high temperatures following reaction is possible according to Kroger—Vink notation [12]:

$$O_{lat}^0 \leftrightarrow \frac{1}{2}O_2 + V_O^{2+} + 2e^-, \qquad (2)$$

where O_{lat}^0 — lattice oxygen atoms.

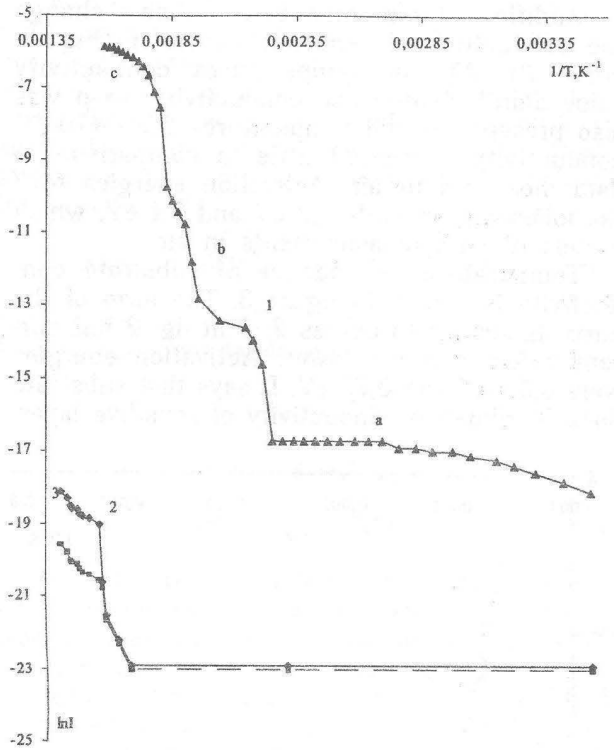

Fig. 2. Temperature dependence of conductivity of SnO_2 thin films exposed in different atmospheres:

1 — Ar; *2* — sintered air; 3 — air + ammonia

The activation energy value well correlates with activation energy of lattice oxygen which equals $E_a = 1{,}2$—$1{,}3$ eV [11].

Activation energy for region c was $E_a = 0{,}3$ eV which can correspond to thermally created defects [13].

Curve *2* in figure *2* represents temperature dependence for conductivity of sensors exposed in air. As one can see there's no conductivity changes at 10—250 °C. This feature can be connected with oxygen adsorption:

$$O_2 + V_O^{2+} + 2e^- \rightarrow 2O_{lat}^0, \qquad (3)$$

$$O_2^{ads} + e^- \rightarrow O_2^-, \qquad (4)$$

which leads to decreasing of free electron and oxygen vacancies concentration. Usually, it has been seen on $I \sim T$ curve as anomal temperature dependence of conductivity but in case of high resistive samples it was difficult to detect this process. At higher temperatures atomic oxygen forms:

$$O + e^- \rightarrow O^- \qquad (5)$$

and two competing processes take place on metal oxide surface described by equations (2) and (5). Where as probability of (5) is higher, therefore conductivity jump was also seen but much lower than on curve *1*. Activation energy of this part was $E_a = 1{,}2$ eV. At the highest temperatures, activation energy equaled $E_a = 0{,}37$ eV.

Addition of ammonia beams didn't change the conductivity dependence character (Fig. 2, curve *3*). At low temperatures conductivity value didn't change and conductivity jump was also present. At the temperatures 250—470 °C conductivity decreased little in comparison to data measured in air. Activation energies took the following amounts 1,2 eV and 0,4 eV, which correlated with measurements in air.

Temperature dependence of substrate conductivity is shown in figure 3. The form of the curve is similar to curves *2*, *3* in fig. 2 but current value is much lower. Activation energies were 0,59 eV and 0,79 eV. It says that substrate doesn't influence conductivity of sensitive layer.

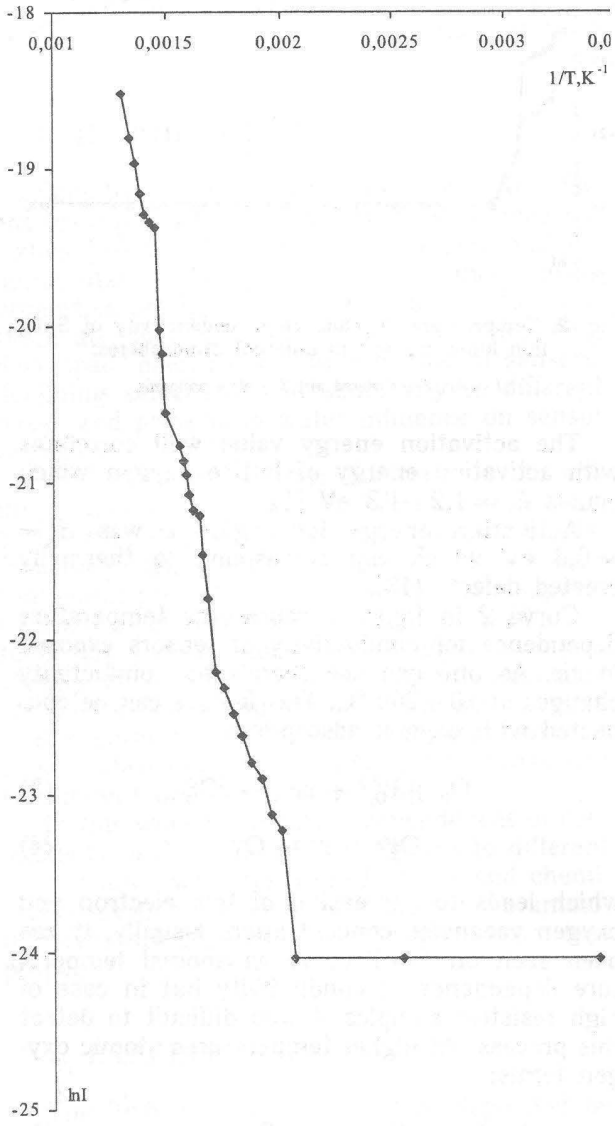

Fig. 3. Temperature dependence of conductivity of alumina substrates exposed in sintered air

Figure 4 illustrates sensors response to ammonia. In this case air was carrying gas. Response time was about 20—40 sec and recovery time was 3—5 minutes. It was determined that ammonia adsorption led to conductivity decline. Temperature dependence of SnO_2 thin films sensitivity is built in figure 5. Sensitive properties were observed at temperatures 250—470 °C. Sensitivity value changed from 2 to 11. Maximal sensitivity was reached at 430 °C.

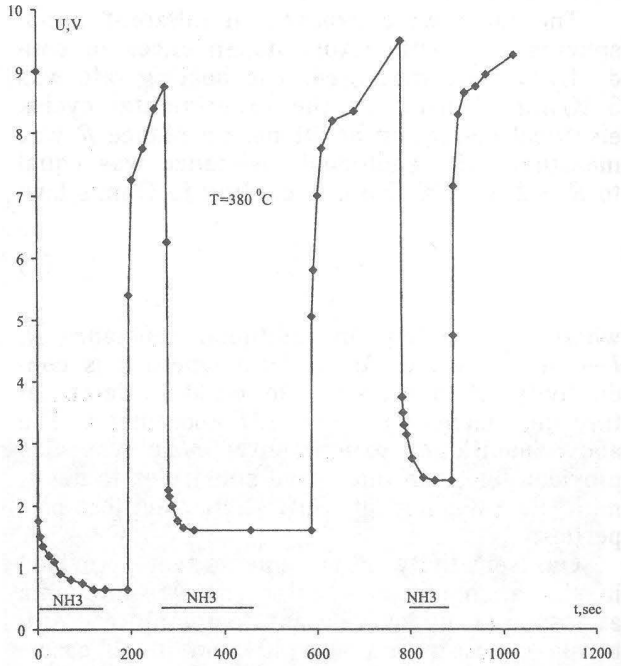

Fig. 4. Response of SnO_2 thin films to 80 ppm ammonia at different temperatures in presence of surface chemisorbed oxygen

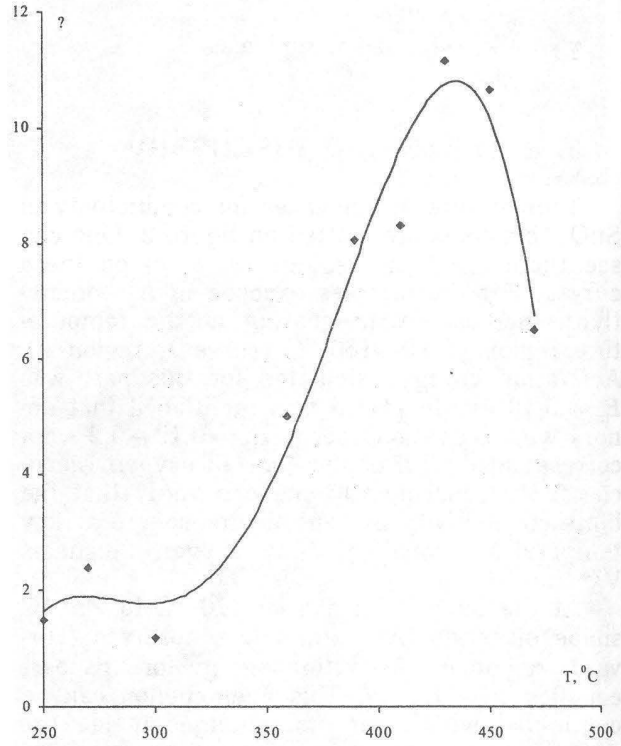

Fig. 5. Temperature dependence of sensitivity of SnO_2 thin films to 80 ppm ammonia in air + ammonia atmosphere

Sensitivity tests to ammonia in neutral atmosphere followed the film calcinations at 500 °C

in Ar. The sensors response to ammonia in such case is shown in fig. 6. Response time was higher than in previous case and evaluated by 60—80 seconds. Recovery time was 2—3 minutes. The sensor conductivity increased under ammonia adsorption. One can conclude that surface cleaning from chemisorbed oxygen led to changes of ammonia adsorption. Fig. 7 illustrates the sensor sensitivity to ammonia in Ar presence. Sensitivity value changed from 6 to 20. Maximal sensitivity was observed at 420 °C.

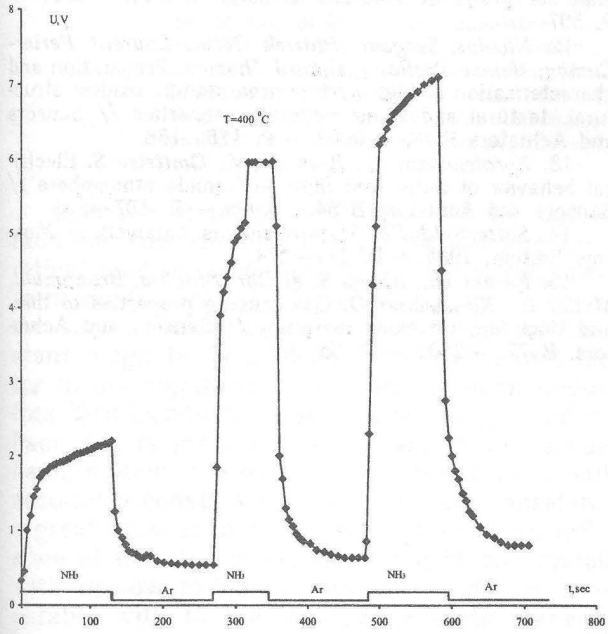

Fig. 6. Response of SnO_2 thin films to 80 ppm ammonia at different temperatures under absence of surface chemisorbed oxygen

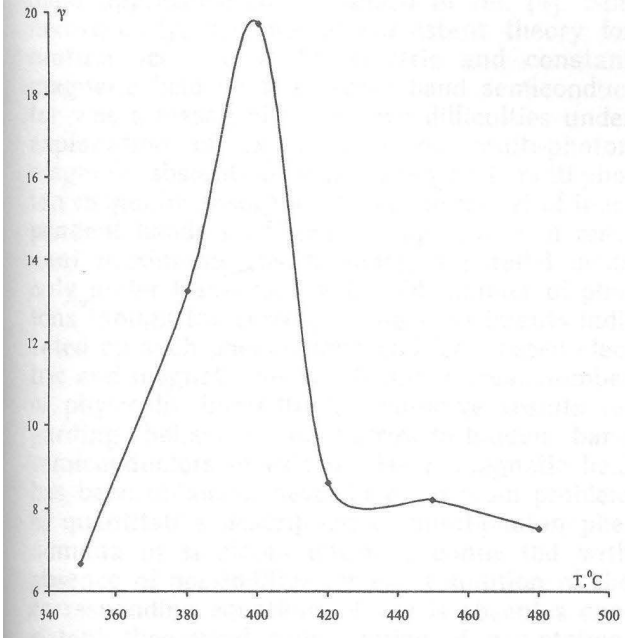

Fig. 7. Temperature dependence of sensitivity of SnO_2 thin films to 80 ppm ammonia in Ar + ammonia atmosphere

Investigations of conductivity at different temperatures and sensor response behavior allow us to verify that adsorption mechanism is affected by chemisorbed surface oxygen. In some cases chemisorbed oxygen atoms act as surface adsorption states. Ammonia molecules adsorbed at these states can be oxidized due to the following scheme [14]:

$$4NH_3^{ads} + 5O_2^{gas} \rightarrow 4NO^{ads} + 6H_2O\uparrow. \quad (6)$$

Consequent adsorption of nitrogen oxides can lead to conductivity decrease:

$$NO^{ads} + e \rightarrow NO^-, \quad (7)$$

$$NO^- + O_2^{gas} + e \rightarrow NO_2^- + O^-, \quad (8)$$

$$NO + O_{ads}^- \rightarrow NO_2^-. \quad (9)$$

In reality it's probable one of above mentioned mechanisms (7)—(9). However all of them lead to creating negative surface charge what restricts conductivity in *n*-type semiconductors.

Adsorption activation energies calculated from kinetic curves were 0,35 eV and 0,6 eV for the beginning and limiting phase of ammonia adsorption correspondently. The last one is compared with activation energy of NO_x adsorption 0,55—0,7 eV, published in [5].

In chemisorbed oxygen absence ammonia adsorption increased SnO_2 thin films conductivity. Adsorption scheme can be the following;

$$NH_3 \rightarrow NH_3^+ + e. \quad (10)$$

Activation energy of this process is equal to 0,32 eV which is in good correlation with activation energy determined for ammonia adsorption under surface oxygen presence.

CONCLUSION

We analyzed ammonia adsorption processes on SnO_2 thin films under different conditions. It was determined that at high temperatures structural properties took place inside the film what reflected on temperature dependence of conductivity of SnO_2 thin film as conductivity jump with the film heating. Ammonia adsorption mechanism was proposed. The last one depends on temperature and surface chemical state. Maximal sensitivity to ammonia reached at 420—440 °C. Surface adsorbed oxygen absence led to 'acceptor'-type reaction between ammonia molecules and SnO_2 surface whereas interaction of ammonia molecules with Ar-treated SnO_2 surface was 'donor'-type. The main idea of adsorption mechanism was transformation of HN_3 to NO_x oxides with subsequent adsorption. Activation energies of adsorption were calculated and been in good comparison with activation energy of NO_x adsorption determined previously by the other authors.

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