Kinetic characteristics of SnO_2 thin film gas sensors for environmental monitoring

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ABSTRACT

In this report we presented results of gas sensitivity' kinetics analysis for undoped SnO_2 thin films, deposited by spray pyrolysis method, using $SnCl_4x5H_2O$ alcohol solution. The comparison of gas sensitivity's kinetics in measurement cycles air⇒{air+(0.08-1.7%)CO}⇒air and air⇒{N_2+0.5%O_2}⇒air for different thickness of SnO_2 films (d=40-200 nm) and operating temperature (T=150-400°C) was carried out. We have determined the kinetic parameters (τ and E_{act}) and made a conclusion that kinetics of gas sensitivity is limited by the rate of SnO_2 surface refilling by oxygen.

Key words: SnO_2; thin films; gas sensitivity; transient curves.

1. INTRODUCTION

Analyzing numerous publications dedicated to semiconductor gas sensors design [1-5], we have to mention that empirical approach to searching of optimal decisions is predominated in these articles. As a result, absolute gas sensitivity becomes main and the only parameter, which is controlling during experimental research of gas sensors. Such situation doesn't promote both more deep understanding of the nature of detection reaction, and adequate description of itself mechanism of gas sensitivity[6]. For this purpose we are need of the information about energetic parameters of the processes, responsible for gas sensitivity of semiconductor oxides and we have to know how these parameters depend on conditions of ambient atmosphere, and on operating modes of gas sensors. Many of these parameters and regularities could be determined on the base of analysis of gas sensitivity's kinetics. However, because of experimental difficulties of carrying out these experiments, such research doesn't became systematic, and they are realized too rare[7-12]. In this report we made the attempt to liquidate such blank for thin film gas sensors on the base of SnO_2.

2. EXPERIMENT

Undoped SnO_2 thin films (d=40-200 nm) were deposited by spray pyrolysis method(SPM), using $SnCl_4x5H_2O$ ethyl alcohol solution. Peculiarities of used SPM and modes of SnO_2 thin films deposition were described earlier in[13-15].

The transient characteristics of gas sensitivity have been measured by monitoring the conductivity of SnO_2 films versus time, upon exchange composition of ambient atmosphere. For these purposes we used measurement cycles: air⇒(0.07-1.7%CO)+air⇒air; air⇒1%H_2+air⇒air or air⇒0.5%O_2+N_2⇒air. For carrying out of these experiments the measurement cell was modified, and special method of measurement was elaborated. In particularly, volume of the cell and diameter of gas pipes were decreased as much as possible. Additional source of control gas was put in gas system, and optimal gas flow was determined. These technical and methodical decisions promoted to decrease the time of changing of ambient atmosphere's composition in measurement cell to 2-10 seconds in dependence of used type of gas sensors.

3. RESULTS AND DISCUSSION

3.1. GENERAL REGULARITIES

Typical of isothermal transient curves of SnO_2 films' sheet conductance in the conditions of step changing of partial pressure of reducing gas (CO) are shown in Fig.1 and 2. One can see that transient curves in the shape $\ln([G(\infty)-G(t)]/[G(\infty)-G(0)])=f(t)$ are linear. It means that the kinetic characteristics of gas sensors (GS) are well described by standard relationship for recharging of surface states, i.e. $G(t)=G(\infty)-[G(\infty)-G(0)]\exp(-t/\tau)$, where τ - time constant of transient curves. It's necessary to note, that such shape of G(t) dependencies is typical enough for semiconductor gas sensors. Analogous transient curves were observed earlier both for thick[7,12] and thin film[8] semiconductor gas sensors.

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For response characteristics we observe the presence of only one exponential component. For recovery characteristics one can see the presence, in the majority cases, of second, more fast component. The contribution of this fast component to total changing of G(t) on dependence on operating temperature is shown in Fig.3. One can see, that influence of the fast component increases with increasing of operating temperature and gas concentration. More than that, we have determined that this component $\Delta G(t)$ has linear dependence on measurement time [27].

As follows from our experiments, similar regularities of transient characteristics of GS observed for experiments based on measurement cycle air⇒(N_2+0.5%O_2)⇒air, also (Fig.4). Difference consists in only values of τ_{res} and τ_{rec} , and in correlation between these values. If for cycle air⇒(CO+air)⇒air $\tau_{res} \geq \tau_{rec}$, for the cycle air⇒(N_2+0.5%O_2)⇒air $\tau_{res} >> \tau_{rec}$. More than that, τ_{res}(N_2+0.5%O_2)>>τ_{res}(CO+air) and τ_{rec}[(air+CO)⇒air]=τ_{rec}[(N_2+0.5%O2)⇒air].

We have to emphasize that such correlation for response and recovery times ($\tau_{res} \geq \tau_{rec}$) for reaction of CO detection allows us to conclude that for description of kinetics of SnO_2 films' gas sensitivity it's necessary to use the detection reactions of second order, but not first one. For such conclusion we used the results of the analysis carried out by Lundstrem[10]. For first order reactions of gas detection $\tau_{res} << \tau_{rec}$. This conclusion is quite lawful, from our point of view, as reaction of CO detection includes the process of dissociative oxygen adsorption (4). How important this process for the reaction of gas detection one can judge on the base of correlation, which we observed for our SnO_2 films. If the sensitivity to O_2 was higher, the sensitivity to CO was higher too.

As it's known,[10,16,17] the kinetics of gas sensitivity can be determined both physical-chemical phenomena (adsorption/desorption and chemical reactions on the oxide surface), and physical phenomena, connected with charge transfer between surface chemisorptional particles and semiconductor bulk. Results of experiments, described in[18] have shown that the influence of another physical phenomena can be neglected for used operating temperature (T<400°C). For these temperature diffusion of oxygen vacancies (V_O) in SnO_2 is too slow. More than that, in according with results received in [18], i.e $G \sim 1/4\ln P_O$, the changing of G can not be more than by 1.5 times, when P_{O2} changes more than by 10^2 times. However, our experiment has showed that for such conditions G of our films can change by more than 10 times.

Due to small thickness and high solidity of our films effects connected with diffusion and diffusion distribution of detected gas along the thickness of the sensing SnO_2 films[19] can be neglected too.

Charge transfer between surface and semiconductor bulk is controlled by surface potential.[21,28] Surface potential is higher, the time of surface recharging is longer. Gas sensitivity is a result of surface potential changing.[20] Therefore, if we have physical limitations, the time constant of transient curves of gas-sensing parameters should change during of itself act of gas detection. As a result, the transient curves must have a complicated shape, and constant times of response and recovery characteristics have to depend on concentration of detected gas. However, we have been observed sufficient simple transient curves with single value of τ, and τ_{res} for CO detection does not depend on the concentration of gas (see section 3.2).

These results allowed us to make assumption that the physical limitation doesn't realize itself in our real situation ($U_S \leq 1.0$ eV; T>150°C)). That is, the interchanging of charge between surface and bulk of semiconductor oxide has time over changing of surface condition. Therefore, kinetics of SnO_2 gas sensitivity is limited by the physical-chemical processes, taking place at the surface of semiconductor oxides, and τ doesn't depend on U_S.

This conclusion proves to be true by the results of following experiment. Studying the influence of preliminary short thermal annealing ($T_{an} \sim$ 400-600°C) on the parameters of SnO_2 films, we determined that such treatment results in increasing of both gas sensitivity, and resistance of these films. The increasing of U_S is the main factor influencing on the increasing of R for used conditions of annealing and operating. Therefore, in the case of physical limitation of gas sensitivity's kinetics, we could wait the τ increasing. However, our experiment shown contrary feature. After annealing, when R increased, the τ_{res} sharply decreased.

If physical limitation of gas sensitivity' kinetics would take place, we would have of another shape of experimental τ(d) dependencies (see section 3.4) also. For small d in the conditions of limited amount of charge carriers in the nanorcystallites there is the effect of "Fermi level shift" [22,23] and in that case the surface potential is larger than without such limitation. Therefore, in this situation we have to observe increasing, but not decreasing of time constants for transient curves.

For more deep understanding of the nature of the processes determining the kinetics of undoped thin films' gas sensitivity, we carried out in [24,25] the theoretical simulation of these processes. For analysis of gas sensitivity kinetics we used the model of thin film gas sensors, which was described earlier in [26].