THE ROLE OF WATER AND OXYGEN ADSORPTION/DESORPTION PROCESSES IN KINETICS OF In$_2$O$_3$ GAS RESPONSE

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1. INTRODUCTION

Kinetics of gas response is a important parameter of chemical sensor determining its adaptability for various applications. Therefore the definition of the nature of processes controlling the rate of both gas response and recovery is one of the crucial tasks on the stage of any chemical sensor design.

2. EXPERIMENTAL DETAILS

In$_2$O$_3$ films for research were deposited by spray pyrolysis. Structural parameters and gas sensing properties of these films were presented earlier in [1-5]. Methodology of film deposition and gas sensing characteristics measurement have been described in [6-8].

3. RESULTS AND DISCUSSIONS

As it is follows from the results presented in [2,4,5] the processes of ozone and reducing gas (CO, H$_2$) detection have essential distinctions in their behavior. In principle, such difference is predictable due to the difference in the nature of processes controlling In$_2$O$_3$ gas response to reducing and oxidizing gases. If in the reaction of O$_3$ detection only oxygen and water from surrounding atmosphere participate, during CO and H$_2$ detection these gases (CO and H$_2$) participate in indicated reactions in addition to oxygen and water.

During the last years it was proposed [2,9-12] that the In$_2$O$_3$ response to reducing gases at T$_{oper}$ >300ºC runs through "redox" (reduction/reoxidation) mechanism, and gas response to oxidizing gases at T$_{oper}$<300ºC has adsorption/desorption nature. It means, that for adsorption/desorption mechanism of gas detection we should take into account the processes such as adsorption/desorption of O$_3$, O$_2$, H$_2$O and detected gases; dissociation of adsorbed particles; surface oxygen diffusion; surface reaction between detected gas and adsorbed species; and

desorption of the products of surface reactions. For "redox" mechanism, besides the indicated above processes, we also have to take into account such processes as reactions of O_2, H_2O and detected gas with In_2O_3 lattice (reduction/reoxidation); surface reconstruction, and bulk diffusion of both oxygen, and oxygen vacancies (V_O). We need to mention that all indicated processes have their own time constants. It means that even recovery processes during detection of reducing and oxidizing gases must have different nature. If in the case of CO and H_2 detection the recovery process is a reaction of In_2O_3 reoxidation, in the case of O_3 detection the recovery process is a reaction of oxygen desorption from In_2O_3 surface. According to the experimental data the relation $\tau_{res} \sim \tau_{rec}$ is observed usually for "redox" mechanism. For adsorption/desorption mechanism of gas detection the ratio $\tau_{res} \ll \tau_{rec}$ as a rule takes place [13]. As it follows from the results presented in [2,4,5], exactly indicated correlation between τ_{res} and τ_{rec} was observed during reducing and oxidizing gases detection correspondingly.

However, detail analysis testifies that in the kinetics of In_2O_3 gas response to reducing and oxidizing gases we have been observing more similarities than differences. When we conducted the measurement of recovery times for CO, H_2, and O_3 detection at the same operating temperatures, very important regularity was established. Independently of the nature of detected gase, the following correlation between time constants of gas response has taken place:

$$\mathbf{\tau_{res}(CO, H_2) \approx \tau_{rec}(CO, H_2) \approx \tau_{rec}(O_3)} \tag{1}$$

Moreover, all regularities of In_2O_3 film's deposition parameters influence on the τ_{rec} during detection of both reducing and oxidizing gases are congruent [2,4,5]. In wet atmosphere indicated likeness is getting stronger. As it was indicated in [4], during O_3 detection in wet atmosphere $\tau_{res} \rightarrow \tau_{rec}$. It means that in wet atmosphere the mentioned above correlation (1) is effective also for τ_{res}, i.e.

$$\mathbf{\tau_{res}(CO, H_2) \approx \tau_{rec}(CO, H_2) \approx \tau_{rec}(O_3) \approx \tau_{res}(O_3)} \tag{2}$$

Taking into account a different nature of detected gases, the indicated similarity in gas response kinetics is possible only in the case when detected gas does not control this kinetics. According to common ideas such situation is possible only in the case, when processes, which are common for reducing and oxidizing gases detection, control the kinetics of gas response. If we compare the analyzed reactions of O_3, CO and H_2 detection, it can be found that only processes with water and oxygen participation (adsorption/desorption and diffusion) are common part of these reactions. Therefore, on the base of conducted analysis, we can conclude that the (1) and (2) corelations are possible only in the case, when these very processes with oxygen and water participation limit the kinetics of gas response. It means according to [8,14] that at partial oxygen and water vapor pressures stability in the surrounding atmosphere, the recovery times for reaction of both ozone and reducing gas detection will be identical.

Earlier, analyzing the kinetics of SnO_2 gas response [7,8], we have made the same conclusion. On the base of both experimental study and theoretical simulation of SnO_2 gas response to reducing gases in dry air we have shown that kinetics of gas response was controlled by oxygen adsorption/desorption. According to [8], the time constants of response and recovery transient characteristics over the temperature range of dissociative oxygen adsorption are determined by an expression

$$\tau^* = \frac{1}{(\alpha_o \beta_o P_{O_2})^{1/2} N^*} \sim \exp\left(\frac{E_{ads} + q_o}{2kT}\right), \qquad (3)$$

where α_o, β_o -coefficients of oxygen adsorption and desorption, E_{ads}, q_o - activation energies of oxygen adsorption and desorption correspondingly, P_{O_2} -partial oxygen pressure, and N^* - the concentration of oxygen adsorption centers.

The same equation could be written also for time constant of water adsorption/desorption process:

$$\tau^* = \frac{1}{(\alpha_{OH} \cdot \beta_{OH} \cdot P_{H_2O})^{1/2} N^*}, \qquad (4)$$

where α_{OH}, β_{OH} -coefficients of water adsorption and desorption, and P_{H_2O} -partial water pressure in the surrounding atmosphere, and N^* - the concentration of water adsorption centers. It is necessary to note that this equation (4) was received for the case of H_2O dissociative adsorption.

Suggested explanation that the detected gas does not control the kinetics of gas response, does not contain any contradiction. It's well known that gas detection process is a dynamic one. Even the "redox" mechanism of gas detection includes two stages: reduction, and reoxidation. The reduction proceeds with the participation of the detected gas. Only oxygen from the surrounding air participates in reoxidation. Between reduction and reoxidation some dynamic equilibrium is being established, i.e. under steady-state conditions the rates of these two processes are the same [15]. The absence of a detected gas influence on gas response kinetics just means that interaction reaction between reducing gas and In_2O_3 lattice is fast, comparing with process, controlling reoxidation of In_2O_3 lattice and recharging of In_2O_3 surface.

Apparently, the process of chemisorbed oxygen incorporation in reduced In_2O_3 lattice is fast as well. Only in this case the process of oxygen incorporation in In_2O_3 lattice, which is a part of reoxidation reaction, will not retard the transient process, to compare with a standard desorption process, running while a steady state in the system air-In_2O_3 is established after interaction with ozone. As it is known, recovery process of ozone detection does not contain the phase of In_2O_3 reoxidation. This conclusion is in accordance with the results of independent research, presented in [16]. According to [16], the reduced InO_x surface has been converted in In_2O_3 already at room

temperatures after oxygen exposition with a dose <10000L. This dose corresponds to an exposure during 10^{-2} s at normal atmosphere pressure.

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