Cu, Fe, Co, AND Mn SILD TECHNOLOGY FOR SURFACE MODIFICATION OF SnO_2 GAS SENSITIVE FILMS

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In this report we discuss possibilities of SILD (successive ionic layer deposition) technology for surface modification of nano-scalled SnO_2 films by nano-clusters of Cu, Fe, Mn, and Co oxides. These elements are widely used for improvement of gas sensing characteristics of metal oxide gas sensors. Samples of SnO_2 films with thickness (30-50 nm) were deposited by spray pyrolysis [1].

Method of SILD consists essentially in repeated successive treatments of the substrate surface with solutions of various salts, anions and cations, which form poorly soluble compounds [2]. Then samples were washed with distilled water, which removed excess of salt; treated with the H_2O_2 (OH-) solution, and again washed. The duration of each treatment was varied from 0,25 to 2 min. One such treatment comprised one deposition cycle. The ellipsometry method has shown that after each cycle we can deposit the layer of peroxicomplexes of metals with thickness 0,6-1,5 nm. During our experiments we used from 1 to 8 deposition cycles. The aqueous of 0,01-0,001M solutions of $Fe(NH_3)_2SO_4$, $CoSO_4$, $CuAc_2$, and $MnCl_2$ ($KMnO_4$) were used as a precursors for synthesis of FeOOH, CoOOH, $Cu(OH)_x(OOH)_{2-x}$, and MnO_2xH_2O correspondingly. On relatively weak heating (100-400^oC), hydroxides, peroxides and peroxide hydrates release water and transform into corresponding oxides. Gas response to CO, O_3 and H_2 was tested in steady state and transient modes in the range of operating temperatures equaled 50-500^oC.

It was established that the influence of surface deposition of indicated oxides on both the electro-physical, and gas sensing characteristics of SnO_2 films takes place. I.e. this method of surface modification by SILD can be used for improvement of sensitivity, selectivity, and rate of SnO_2 gas response. This influence depends on the nature of metal oxide, size of cluster, and operating temperature. Surface modification by Cu, Co, Mn, and Fe increases SnO_2 film resistance. Addition of Cu depresses gas response to ozone. Modification by Co improves both the gas response to H_2 in the range of low operating temperatures, and the rate of gas response. Fe can be used for improvement of both gas response to CO, and selectivity. Surface modification by Mn depresses gas response to both CO, and H_2.

The comparison of gas sensing properties of SnO_2 films with bulk and surface modification by Co, Mn, Cu, and Co was conducted. The origin of surface modification influence on SnO_2 gas response is discussed.

References.

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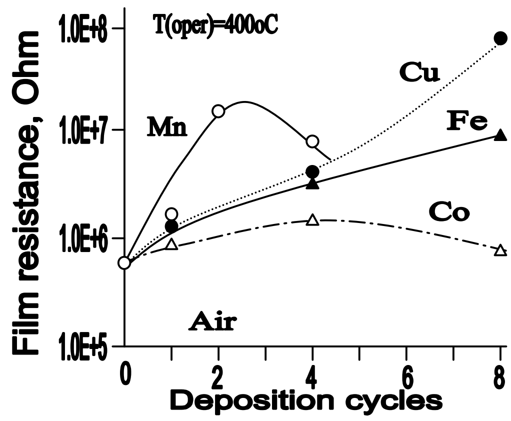
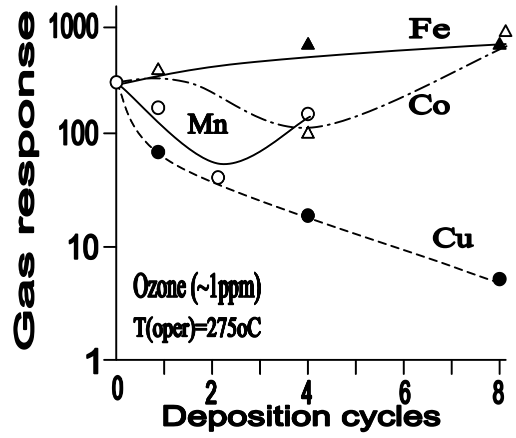


Fig.1. Surface modification influence on SnO_2 film resistance.



Fi.g.2. SnO_2 gas response to ozone vs. surface modification.

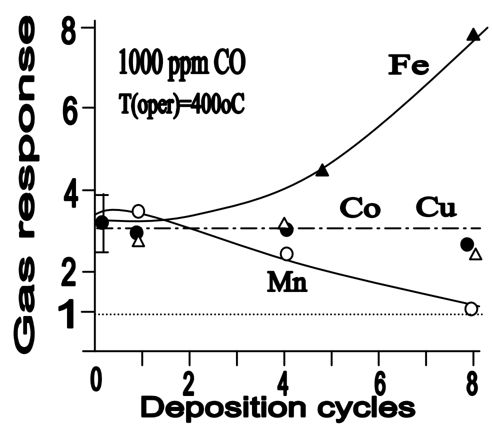


Fig.3. Influence of surface modification on gas response to CO

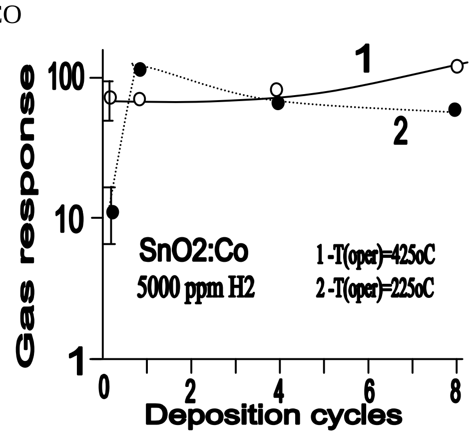


Fig.4. Gas response to H_2 in dependence on operating temperatures