DOPING OF SnO_2 FILMS DURING SPRAY PYROLYSIS DEPOSITION: INFLUENCE ON GAS SENSING CHARACTERISTICS AND THERMAL STABILITY OF FILM STRUCTURE

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The study of additives' influence on both the gas sensing characteristics and thermal stability of SnO_2 films structure was the main goal of presented research. A conception of such approach is based on a statement that the appearance in gas sensing matrix of elements with different physical-chemical properties gives additional factors influencing the important parameters of metal oxide [1].

For SnO_2 films deposition we used spray pyrolysis from 0.2 M $SnCl_4$-water solutions. Peculiarities of this process were described earlier in Ref. [2]. Studied films were deposited on alumina ceramic and oxidized Si substrates at T_{pyr}= 350 ^oC and 450 ^oC. These T_{pyr} were selected as deposition parameters, providing the attainment of maximum gas response to reducing gases. Film thickness, estimated using laser elipsometry, was from 40 nm to 400 nm. Fe, Cu, Co, and Ni have been used as doping additives. Their selection was conditioned by the fact, that those impurities, at one hand, may influence film's structure, and at the other hand, may be used for optimization of metal oxide gas sensors and creation of nanocomposites, perspective for various gas sensing applications. Additives were added into sprayed solution in the form of chlorides. Concentration of doping elements in sprayed solution varied from 0 to 16 wt %. This concentration region is being used often for optimization of gas sensing characteristics of metal oxide sensors. Annealing at 600-1000 ^oC was carried out in the atmosphere of usual air.

XRD, SEM, and AFM methods were used for structural characterization. The size of the crystallites forming the film was evaluated by Scherrer's formula. Structural properties of undoped SnO_2 films were discussed in detail in [3]. Gas sensing characteristics were measured in steady-state temperature mode using special flow-type reactor with controlled relative humidity (~1-3 %RH or 45-55 %RH) and gas surrounding. Operating temperatures were varied between 25 and 450 ^oC.

Conducted research has shown that selected doping elements did not have pronounced effect on grains' growth inhibiting during spray pyrolysis deposition. Indicated effect takes place, however the decrease is not so considerable as it was expected, basing on the results of study, given for SnO_2 powders. The strongest doping influence was observed for Cu and Fe additives.

Gas sensing characterization showed that the doping could significantly improve both sensitivity and selectivity of gas sensors. However, the optimization of gas response takes place only for concentrations of additives in the range from 0.05-3 wt.%. The superfluous concentration of these additives sharply reduces the gas response. On the base of results of structural study of doped SnO_2 films it was concluded that observed worsening of gas sensing characteristics is a consequence of second metal oxide phase formation in SnO_2 matrix.

It was established that second oxide presents really in SnO_2 matrix. However, it presents in very fine dispersion phase, because even after thermal treatment at T_{an}~ 850 ^oC, the grain size of second metal oxide phase did not reach a critical size of 1-3 nm, at what on XRD patterns well-defined peaks should become apparent.

It was found also that doping does not improve high temperature stability of SnO_2 films' structure in studied range of temperatures 600-1000 ^oC. It's necessary to note that optimizing influence is not being observed for all additives. The nature of existent changes does not depend on doping. After annealing at T_{an}>900 ^oC the morphology of the SnO_2 films becomes similar**.** Both grains and agglomerates lose clearly defined cutting. And what is more, such additives as cooper and cobalt stimulate grain's growth during the process of high temperature annealing. Such ambiguous influence of additives on films' structure forces researchers to be careful during the elaboration of technologies of gas sensing layers' forming on the base of doped and multi-component materials. When choosing additives for film structure optimization or stabilization, one should take into account, that at changing of the conditions of synthesis, exploitation, or parameters of post-deposition thermal treatments, the consequences of doping could be fundamentally different from the ones, which we have been observing during initial experiments.

It was concluded that the most important consequence of SnO_2 doping is the increase of the content of SnO_2 fine dispersion phase in film's structure. It was found that the coalescence of this fine dispersion phase in SnO_2 is the main influencing factor on grain's growth during annealing at temperatures 600-850 ^oC.

References:

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