EXPERIMENTAL AND THEORETICAL STUDIES OF THE INDIUM OXIDE-BASED GAS SENSORS DEPOSITED BY SPRAY PYROLYSIS

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The correlation of surface structure and gas response properties of In_2O_3 polycrystalline films has been studied employing experimental methods of surface characterization (XRD, AFM and HRTEM) along with theoretical modeling of the In_2O_3 surface.

1. Characteristics of the In_2O_3 surface structure

The In_2O_3 films deposited by spray pyrolysis belong to cubic I*a*3 space group with *a*=1.0118 nm. The films deposited at T_{pyr}>350°C have a clearly pronounced columnar structure with characteristic grain size of ~30-40 nm in vertical direction. Such films are compactly packed and highly textured with predominant crystallite orientation in the (001) direction perpendicular to substrate.

The analysis of XPS spectra indicated that terminal (100) face of In_2O_3 films exhibit oxygen deficiency, corresponding to formula In_xO_y, where x, y→1. Notice, that such oxygen deficient surface state remains stable even after heat treatment in oxygen atmosphere and only annealing at T>1000°C restores the stoichiometry corresponding to the ideal In_2O_3 surface.

2. Peculiarities of In_2O_3 gas response properties

The study of gas sensing behavior of In_2O_3 films with different thickness and grain sizes permits to conclude that response to oxidizing gases is limited by chemisorption/diffusion type processes. In this case, the typical regularity was observed: the smaller grains size the higher sensor sensitivity. It was found, however, that the sensitivity of In_2O_3-based gas sensors to reducing gases has noticeable value even for crystallites size exceeding 80-100 nm. Basing on the analysis of gas response properties and ESR spectra it was concluded that sensing mechanisms to reducing gases include “redox” and chemisorption effects in the thin subsurface area. Such conclusion correlates with detected by XPS non-stoichiometry of the thin subsurface layer at (100) atomic face of In_2O_3 films.

3. Theoretical modeling of In_2O_3 (100) face

The modeling of the ideal (100) face of In_2O_3 displayed three types of bridging oxygen of the terminal layer distanced from the indium atomic plane on 1.43 Å, 1.31 Å and 0.95 Å. At that, metal ions have completely saturated bonds making “redox’ mechanism the only possible for such idealized structure. On the other hand, the metastability of the bridging oxygen atoms evaluated with semi-empirical (PM3) method amount to 2.97 eV, 1.6 eV and 0.95 eV, respectively. The reconstruction at the real (100) surface is connected with the symmetry breakdown of bridging oxygen atoms of the terminal layer. Such reconstruction leads to the partial unsaturation of the surface indium ions and appearance of the energetically stable oxygen deficient surface. The oxygen adatoms stabilized at the unsaturated indium ions provide the path for competitive realization of the chemisorption mechanism at the real surface of In_2O_3.

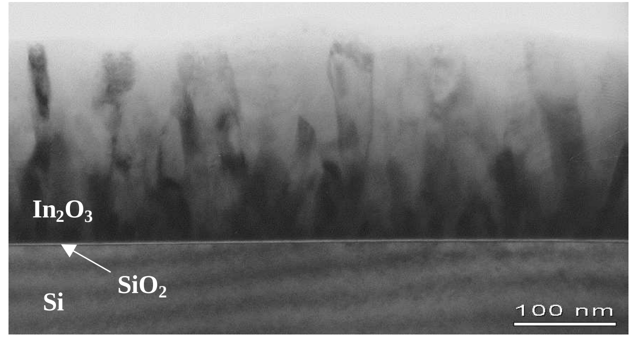

Fig.1. TEM micrograph of the In_2O_3 film (d~ 200 nm) cross-section demonstrating its columnar structure.

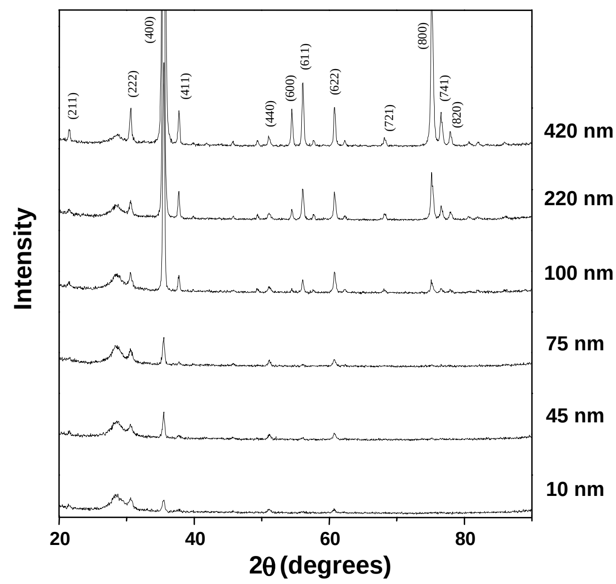

Fig. 2. XRD patterns of In_2O_3 films vs. film thickness. The (100) atomic plane corresponds to the terminal layer of In_2O_3 films deposited by spray pyrolysis.

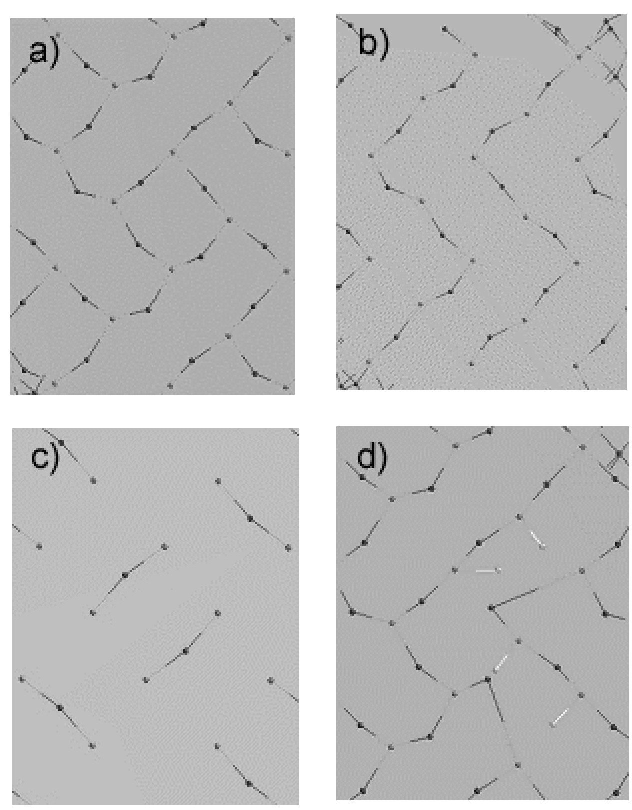

Fig. 3. Different patterns of gradually reduced (400) atomic face of In_2O_3 (a, b, c) and proposed “intermixed” reconstruction of In_2O_3 surface (d).