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Faceting characterization of tin dioxide nanocrystals deposited by spray pyrolysis from stannic chloride water solution

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Abstract

Tin dioxide (SnO_2) thin films grown by spray pyrolysis on Si substrates were studied. The evolution of the crystallographic orientation of these films (35–300 nm) with variation of the pyrolysis temperature (350–535 °C) is reported. Samples were characterized by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and High Resolution Transmission Electron Microscopy (HRTEM). Via digital image processing of the HRTEM micrographs, some crystallographic models of SnO_2 nanocrystals deposited at different pyrolysis temperatures are proposed. These models were tested by computer image simulation and compared with the experimental images. It was found that, in addition to the most stable plane (110), the external facets of SnO_2 nanocrystals can be formed by crystallographic planes with other structural and electronic configuration: planes (111), (200), (101), (011), (-1-12), and (210).
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1. Introduction

Comparing the gas sensing characteristics of SnO_2-based gas sensors manufactured in various groups, we had drawn attention that the gas response (S) dependencies on operating temperature [$S=f(T_{oper})$] vary greatly in terms of both the half-width and temperature position of gas response maximum even for undoped materials [1–4]. However, the causes of the behavior of these dependencies have not been studied in detail.

In our own research we have also found a considerable change in the shape of $S=f(T_{oper})$ curves depending on technological parameters of SnO_2 film deposition [3,5]. For different films, the temperature position of gas response maximum may shift more than 150 °C, while the response time for the same operating temperature (T_{oper}) may increase more than 10-fold.

To identify the reasons for this difference in gas sensing characteristics of SnO_2-based sensors, we carried out a detailed analysis of the influence of deposition parameter on the structure of films deposited by spray pyrolysis. We established that films with different behavior of $S=f(T_{oper})$ dependencies have different morphology [5,6]. Depending on pyrolysis temperature (T_{pyr}) and deposition parameters, the SnO_2 films deposited may consist of spherulites, agglomerates, nanocrystallites, and/or nanocrystals.

According to the generally accepted definitions, the term "crystallite" (or "nanocystallite") implies a monocrystalline formation without a visual crystallographic external shape (habit). The term "nanocrystal" means just the opposite, namely, the existence of a regular, macroscopically visible crystal habit in the nano-scaled range. We found that the formation of each structure is determined on pyrolysis temperature or substrate temperature during film deposition with relatively clear boundaries between temperature ranges of these structures existence. For example, the high T_{pyr} range (>400 °C) can be divided into three temperature intervals, which are characterized by needle, prismatic and bipyramidal types of growth in the grain structure. The low temperature range up to 400 °C, corresponding to crystallite (spherulite) and agglomeration growth with the prevalence of the (101) XRD peak up to 350 °C, was characterized by the appearance and development of the (110) reflection peak, and the almost complete

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suppression of other peaks. This peak was dominant up to 470 °C and then decreased, becoming comparable in terms of intensity with other XRD peaks like (200), (211), and (101). An alteration in this behavior was observed when the film thickness changed, and the main features mentioned above were maintained.

One should note that the agglomeration process has special features of its own that also depend on T_{pyr}. If in the low temperature range (≥ 360 °C) agglomerates are formed from randomly oriented crystallites in a sphere-like envelope, then at higher temperatures, close to the second boundary ($\sim 400-450$ °C), we observed the effect of mutual orientation of crystallites forming agglomerates. Furthermore, their envelope acquired the characteristic features of regular faceted nanocrystals.

These results persuaded us that the abovementioned effects of deposition parameters influence on gas sensing characteristics are connected with a change in crystallographic structure of the deposited films, not only with a change in crystallite sizes [3,4,6]. In many experiments, we observed considerable changes in gas response (S) and response time (τ) even for SnO_2 films with constant crystallite size (t) and film thickness (d).

At present, there is no doubt that the crystallographic structure of metal catalyst particles plays a key role in reactions of heterocatalysis [7–9]. From crystallography it is known that crystals from one crystallographic group can have various external shapes with different crystallographic faceting planes. However, during the design of gas sensors, the role of the crystallographic structure of metal oxide crystallites is not analyzed, and the possibility of modifying the crystallite shape to achieve better gas sensing characteristics is ignored. Only the dimension approach is usually used in this process. As is known, the decrease in grain size, forming a gas sensing matrix, is the universally recognized method for improving gas response in metal oxide gas sensors [10,11]. We believe that the «structural factor» of gas response is a more complicated concept, which includes not only grain size but also nanocrystal shape, structural stoichiometry, and the crystallographic orientation of external planes of nanocrystals. The external planes of nanocrystals participate in gas–solid interaction, and therefore these very planes determine the gas sensing properties of polycrystalline materials. This conclusion is based on the following theories [7,8,12–15]:

- Even within the same species, crystals can take a variety of shapes according to the combination and relative development of their faces. This phenomenon has attracted attention since the 17th century [16];
- Every crystallographic plane has its own definite set of electronic parameters, such as density of surface state (N_{ss}), surface position of Fermi level (E_{Fs}), energetic position of native point defects (E_t), etc.;
- Adsorption/desorption (A/D) processes [17] controlling the gas response have activation nature; and the parameters describing these processes are orientation-dependent [14,18]. This means that, depending on the external form, the crystallite will have different parameters of A/D processes, such as number of surface sites, A/D energies, position and distribution of local electronic levels in the band gap of the semiconductor due to chemisorption, etc.;
- The decrease in crystal size in the nanometer range notably increases the effect of the shape on the adsorption properties [15]. The shape and size of small crystals have a profound impact on the amount of adsorption that occurs and on the type of bonding to the surface that takes place. For example, according to [15], surface species with different types of bonding may have preferred adsorption on the edge/corner sites or on the flat planes.
- The shape and predominant orientation of crystallites determine the planes, forming intergrain contacts, the area, and gas permeability of gas sensing matrix.

In the light of these points we have formulated two questions: Do the crystallographic planes faceting SnO_2 nanocrystals change in real conditions when the crystal's shape changes? What is the real orientation of the external planes in the SnO_2 films analyzed?

We have found only a few studies of crystallographic plane faceting SnO_2 nanocrystals [4,19–23]. In fact most of the research in these studies was not connected with analysis of the grain habits of SnO_2 nanocrystals for gas sensor applications, but with the study of metal oxide nanowires, nanoribbons, nanotubes, whickers, and microcrystals with characteristic sizes of more than 10–100 Nm. Thus, despite the fact that most of the physical and chemical properties of nano-scaled materials are determined by the crystallographic characteristics of the grains forming this material, previous studies have largely ignored this problem. So, no clear link has been established between the crystallographic structure of metal oxide grains and thin-film deposition conditions.

In Ref. [6], we tried to answer these questions using Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD) measurements. However, our conclusions were only preliminary. The determination of crystallographic faceting planes in a nanocrystal using these standard XRD and SEM techniques is a very complex task. It is known that XRD patterns contain information on X-ray diffraction from all crystallographic planes presented in a crystal, but not from planes faceting this crystal. Nor is Scanning Electron Microscopy appropriate for these purposes, because the SEM images give only a top view of the films studied and do not determine the crystallographic orientation of the faces observed.

With the measurement capability of modern techniques, High Resolution Transmission Microscopy (HRTEM) obtains images of atomic structure of the materials studied, and can therefore be used for correct determination of crystallographic planes faceting SnO_2 grains.

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