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Multifunctional Tin Dioxide Materials: Advances in Preparation Strategies, Microstructure, and Performance

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Abstract

Tin oxide materials are a class of unique semiconductor materials with widespread technological applications because of their valuable semiconducting, gas sensing, electrical and optical properties in the fields of macro/mesoscopic materials and micro/nanodevices. In this review, we describe the efforts toward understanding the synthetic strategies and formation mechanisms of the micro/nanostructures of various tin dioxide thin films prepared by pulsed laser ablation, highlighting contributions from our laboratory. First, we present the preparation and formation processes of tetragonal-phase tin dioxide thin films with interesting fractal clusters. In addition, the quantum-dot formation and dynamic scaling behavior in tetragonal-phase tin dioxide thin films induced by pulsed delivery will be discussed experimentally and theoretically. Finally, we emphasize the fabrication, properties and formation mechanism of orthorhombic-phase tin dioxide thin films by using pulsed laser deposition. This research may provide a novel approach to modulate their competent performance and promote rational design of micro/nanodevices. Once mastered, tin dioxide thin films with a variety of fascinating micro/nanostructures will offer vast and unforeseen opportunities in semiconductor industry as well as in other fields of science and technology.

Keywords: Tin Oxides; Thin Films; Preparation Strategies; Microstructure; Performance
1. Introduction

The key scientific issues of semiconductor micro/nanodevices and optoelectronics components in application and development have been driven scientists to explore in depth the design, preparation, micro/nanostructure and performance of semiconductor materials.\(^1\)\(^-\)\(^5\) Semiconductor oxides are fundamental to the development of smart and functional materials, devices, and systems. Tin oxide materials have two unique structural features: mixed cation valences and an adjustable oxygen deficiency, which are the bases for creating and tuning many novel material properties, from chemical to physical. Tin oxide micro/nanostructures have garnered considerable attention in recent years for their potential to facilitate both the fundamental research and practical applications through their advantageous chemical and physical properties.\(^6\)\(^-\)\(^8\) An integrated device for semiconductor industry is highly desirable for versatile advanced applications.\(^9\)\(^-\)\(^11\) The prospect of using pulsed laser deposition processes to fabricate semiconductor oxide thin films continues to drive research towards improving the performance of the semiconducting materials utilized in these devices. Since the properties of materials strongly depend on its micro/nanostructures, which all result from the fabrication processes, the influence of micro/nanostructural evolution on material properties is especially remarkable for materials science and engineering.\(^12\)\(^,\)\(^13\) However, challenges remain to further improve the material fabrication processes for various advanced applications. This optimization requires a clear understanding of the relationship between micro/nanostructures and thin film morphologies.\(^14\)\(^,\)\(^15\)

Tin oxide micro/nanostructures provide a versatile, multifaceted platform for a broad range of advanced applications.\(^16\) Recent studies have validated their use in many fields of science and technology that integrate the areas of chemistry, physics, materials science and nanotechnology. For example, they can function as semiconductors for a number of applications in microelectronic devices, optoelectronic components, and solar-thermal converter, they can serve as gas-sensors for the detection and forecasting of a variety of combustible gases, environmental pollution gases, industrial emissions
and hazardous gases, they can be used as electrodes for melting optical glass and electrolytic aluminum industry, they can act as catalysts for the active phase of many heterogeneous catalysis in hydrocarbon oxidation, they can also serve as varistor for the arrester used in power systems, and so on.

Tin dioxide (SnO$_2$) thin films are essential components of several modern technologies. For instance, SnO$_2$ thin films represent an unsurpassed material in the design of metal oxide gas-sensors, and the microelectronic revolution would have not been the same without the excellent properties of SnO$_2$ thin films. However, SnO$_2$ thin films with fascinating micro/nanostructures are often used in many sundry devices and systems. For example, it is used as the lithium-ion battery anode materials, gas-sensing materials, negative temperature coefficient thermistor materials, doped SnO$_2$ varistor materials, resistance-type humidity-sensing materials, catalyst materials, optical and electrical materials, etc. the possibility to grow micro/nanostructures is therefore essential to improve the performance of SnO$_2$ thin films. Several synthetic strategies have been developed to grow the SnO$_2$ thin films and study their chemistry. In fact, significant advances have been done in the understanding of the micro/nanostructural evolution of SnO$_2$ thin films. However, it is only in the past few years that it became evident that besides SnO$_2$ thin films that closely resemble the corresponding bulk materials, also new systems exist, sometimes with unexpected properties either related to the morphologies of SnO$_2$ thin films or to their micro/nanostructural flexibility. Presumably, the most exciting developments are related to the possibility to modify in a desired manner the chemical properties of molecules or deposited SnO$_2$ thin films with fascinating micro/nanostructures. Most of above applications are based upon the novel micro/nanostructures known as derived from different synthetic strategies and processing. Pulsed laser deposition (PLD) technique is considered to be one of the effective methods for the preparation of SnO$_2$ thin films with fascinating micro/nanostructures.

PLD is a useful growth tool in which photonic energy is coupled to the bulk starting material via electronic processes. Laser ablation for thin film growth has many advantages: (i) energy source
(laser) is outside the vacuum chamber, in contrast to vacuum-installed devices, which provides a much greater degree of flexibility in materials used and geometrical arrangements; (ii) almost any condensed matter material can be ablated; (iii) pulsed nature means that thin film growth rates may be finely controlled; (iv) amount of evaporated source material is localized only to that area defined by the laser focus; (v) under optimal conditions, the ratios of the elemental components of the bulk and thin films are the same, even for chemically complex systems; (vi) kinetic energies of the ablated species lie mainly in a range that promotes surface mobility while avoiding bulk displacements; and (vii) ability to produce species with electronic states far from chemical equilibrium opens up the potential to produce novel or metastable materials that would be unattainable under thermal conditions. Above growth processes may be supplemented by an inert or reactive gas or ion source, which may affect the ablation plume species in the gas phase or surface reaction. The diversity of thin films grown by using PLD is enormous and perhaps recommends its flexibility more persuasively than anything else.

During the past ten years or so, we and our collaborators have actively devoted in the investigations of the micro/nanostructures of tin oxide thin films that related to the synthesis methods, technological improvements, characterizations, properties and applications. This review only covers some of the most recent studies, with a focus on their synthetic strategies and formation mechanisms. We start with a detailed investigation of the preparation and formation processes of tetragonal-phase SnO$_2$ thin films with interesting fractal clusters. We then describe experimentally and theoretically the quantum dot formation and dynamic scaling behavior in tetragonal-phase SnO$_2$ thin films induced by pulsed delivery. Finally, we elaborate on the fabrication, properties and formation mechanism of orthorhombic-phase SnO$_2$ thin films. Fig. 1 shows schematic illustrating the morphological changes involved in the tetragonal SnO$_2$ fractal thin films, tetragonal SnO$_2$ quantum dots and orthorhombic SnO$_2$ thin films prepared by laser ablation.
Fig. 1 Schematic illustrating the morphological changes involved in the tetragonal SnO$_2$ fractal thin films, tetragonal SnO$_2$ quantum dots and orthorhombic SnO$_2$ thin films prepared by laser ablation.

2. Tin dioxide fractal thin films

With the advent of advanced thin film technology more cost-effective, reproducible devices can be constructed with a reduction in device size and a concomitant increase in the response speed by using SnO$_2$ thin films. Since gas sensing is based on adsorption mechanism on the SnO$_2$ grain surface, a small grain size is desirable in order to achieve a high specific area for high sensitivity.$^{31,32}$ Structural properties, such as grain size, grain geometry as well as specific surface area, can significantly affect the gas sensing properties of SnO$_2$ thin films. In order to control these structural characteristics, the micro/nanostructural evolution of SnO$_2$ thin films should be understood. Micro/nanostructural
variations should inevitably change their chemical and physical properties. Thus, the study of the micro/nanostructures of SnO$_2$ grains can help us to reveal some peculiar micro/nanoscale features and to explain the corresponding experimental results.

Fractal theory is a potentially powerful technique to characterize micro/nanostructures. We and our collaborators have successfully applied this technique to the fractal assessment of SnO$_2$ thin films.$^{33,34}$ Besides showing some examples of geometric structures of SnO$_2$ thin films, here we will discuss the applicability and relevance of fractal theory to studying the micro/nanostructure and formation mechanism of SnO$_2$ thin films. Fig. 2 shows the scanning electron microscopy (SEM) images of SnO$_2$ thin films prepared on Si (100) substrate at temperatures of (A) 300, (B) 350, (C) 400, and (D) 450°C, respectively. SEM observation indicated that all thin films produced under different substrate temperatures exhibited self-similar fractal patterns. It can be seen that the fractal patterns are open and loose structure with increasing substrate temperature. The average size and fractal dimension ($D$) of the fractal clusters for four thin films were estimated by measurement on the fractal regions and using conventional box-counting method,$^{35-37}$ respectively, which were decided to be about 0.307 µm (Fig. 3A) with $D = 1.896$, 0.906 µm (Fig. 3B) with $D = 1.844$, 1.202 µm (Fig. 3C) with $D = 1.865$, and 1.608 µm (Fig. 3D) with $D = 1.818$. It was found that the average size of the fractal clusters increased and the fractal dimension decreased with increasing substrate temperature. The smaller fractal dimension means that the SnO$_2$ thin films are composed of the open and loose fractal structure with finer branches. This fractal structure may lead to improvement in the design of gas sensors for the monitoring of environmental pollutants.
Fig. 2 SEM images of SnO$_2$ thin films prepared on Si (100) substrate at temperatures of (A) 300; (B) 350; (C) 400; and (D) 450$^\circ$C.$^{33}$

On the basis of experimental observation, the formation process of SnO$_2$ nanocrystals and fractal clusters could be reasonably described by a novel model proposed by us.$^{33}$ It was separated into eight steps, which illustrated in detail in Fig. 3: (i) operation of the KrF excimer laser at a repetition rate of 10 Hz at an incident angle of 45$^\circ$ to the polished sintered cassiterite SnO$_2$ target rotating at a rate of 15 rpm to avoid drilling; (ii) production of the high-temperature and high-pressure SnO$_2$ plasma at the solid-liquid interface quickly after the interaction between the pulsed laser and SnO$_2$ target; (iii) subsequent expansion of the high-temperature and high-pressure SnO$_2$ plasma leading to cooling of the SnO$_2$ plumes.$^{38,39}$ In this case, the interval between two successive pulses is much longer than the life
of the plasma. Therefore, the next laser pulse had no interaction with the former plasma; (iv) deposition of the SnO$_2$ plume on Si (100) substrate after the disappearance of the plasma, inducing the initial nucleation of SnO$_2$ nanocrystals; (v) grain rotation culminating in a low-energy configuration. This process is directly related to the reduction of surface energy, aimed at minimizing the area of high-energy interfaces;\textsuperscript{40} (vi) possible formation of a coherent boundary between grains due to grain rotation, with the consequence of removing the common grain boundary and culminating in a single larger SnO$_2$ nanocrystal. This is the coalescence process; (vii) growth of SnO$_2$ nanocrystals along preferred crystallographic directions which could be predicted by an analysis of the surface energy in several crystallographic orientations; (viii) formation of the fractal structure as SnO$_2$ crystallizes and nucleates at high energy interfaces such as grains boundaries. According to the fractal theory, the heat released by crystallization leads to a local temperature rise in surrounding area and this temperature field can propagate quickly and stimulate new nuclei appearing randomly in nearby regions. The stimulated nuclei of the next generation can also cause a local temperature rise and repeat the above process many times until SnO$_2$ fractal patterns are formed.\textsuperscript{41,42} Based on the above proposed formation mechanism, we characterized the formation processes of SnO$_2$ fractal clusters as shown in Fig. 3A~I. We believe that the laser ablation technique is an appropriate method to synthesize a series of fractal clusters with controlled composition, morphology and nanocrystal size, which are of important in the study of the sensitivity of SnO$_2$ thin films.
Fig. 3 The formation processes of SnO$_2$ nanocrystals and fractal clusters: (A) laser; (B) target; (C) plasma; (D) plume; (E) nucleation; (F) grain rotation; (G) coalescence; (H) growth; and (I) fractal.$^{33}$

3. Tin dioxide quantum dots

In a variety of nonequilibrium growth processes, such as gelation, aggregation, coagulation, and condensation, the formation of size-distributed clusters is a very commonly encountered phenomenon. Therefore, understanding the related dynamics is a problem of considerable interest. Many studies on
this subject have revealed the scale invariance of the cluster size distribution. Among the various processes involving cluster/droplet growth and coalescence, the process of vapor deposition has been most widely investigated, a few examples being the role of condensate patterns in heat transfer, breath-figure formation, and thin film growth. We have successfully demonstrated experimentally and theoretically the quantum dot formation and dynamic scaling behavior of SnO$_2$ nanocrystals induced by pulsed delivery.$^{43}$ Fig. 4 shows a high-resolution transmission electron microscopy (HRTEM) image of the as-deposited SnO$_2$ thin films prepared by PLD method. It can be seen that the clear-cut crystalline features inside the SnO$_2$ thin films. On closer inspection, recurrent values of separation distance between lattice layers were found (in particular, 0.33 nm, evidenced in the bottom left-hand corner inset of Fig. 4), corresponding to lattice parameters of the rutile structure of SnO$_2$ cassiterite phase (arising from $\langle 110 \rangle$ reflection). HRTEM investigation can give useful information about local composition at dislocation cores. As can clearly be seen in Fig. 4, the grain cluster is composed of several primary nanocrystallites without grain boundaries. This is strong evidence that the coalescence occurs when two or more neighbor grains assume the same orientation, resulting in a single nanocrystal. When nanocrystalline materials grow by oriented attachment at crystallographically specific surfaces, there is a small misorientation at the interface. Spiral growth at two or more closely spaced screw dislocations provides a mechanism for generating complex structures.$^{40}$ When the grains assume the same orientation, that is, a coherent grain-grain boundary, the grain boundary must migrate toward the smaller particle, resulting in a single larger nanocrystal.$^{42}$ We suggest that these nanocrystals are composed of isolated SnO$_2$ nanocrystals about from 4 to 10 nm in size that are besieged by amorphous phase. This structure should result in the quantum dots of SnO$_2$ nanocrystals. The local HRTEM image revealed that individual SnO$_2$ nanocrystal embedded isolatedly in an amorphous matrix, which confirmed that the existence of the quantum dots is due to the reduction of the grain size by pulsed delivery. It is reasonable to speculate that the crystalline quantum dots may
lead to further enhancement of the energy gap due to low-dimensional confinement. This quantum dot distribution is in agreement with previous simulations based on the kinetic Monte-Carlo model.\textsuperscript{43}

Fig. 4 HRTEM image of the as-prepared SnO$_2$ thin films shows the structural features of the crystalline nanophase; the bottom left-hand corner inset shows a magnification of the image of a single SnO$_2$ dot 5.5 nm in diameter in (110) plane with the measured lattice parameters.\textsuperscript{43}

Fig. 5 shows the kinetic Monte-Carlo simulations of pulsed-laser deposition (Fig. 5a) and molecular-beam epitaxy (MBE) (Fig. 5b) in the submonolayer regime. This model is controlled by three
parameters: the pulse intensity $I$, the diffusion constant $D$, and the average flux density of incoming particles $F$. In particular, the control parameter of PLD is the pulse intensity $I$, which is the number of particles deposited in one pulse per unit area, and the diffusion-to-deposition ratio $D/F$. The average deposition rate is given by $F = I / \Delta t$, where $\Delta t$ is the time interval between two pulses. The intensity is measured in monolayers (ML), and $D/F$ is dimensionless, as the lattice constant is set to unity. Performing Monte-Carlo simulations, we investigated the nucleation density for various pulse intensities using a system size of 400×400 square lattice and the island distance has been measured at 0.2 ML coverage, when the island density reaches its maximum but coalescence does not yet set in. For small intensities, we recover the well-known power law for the island distance in MBE:\textsuperscript{44}

\begin{equation}
I_D \propto (D/F)^\gamma,
\end{equation}

where the exponent $\gamma$ depending on the dimension of the surface, the island dimension, and the critical nucleus $i^*$, that is, the smallest stable island contains $i^*+1$ atoms. For a two-dimensional surface, compact islands and a critical nucleus of $i^* = 1$, one obtains $\gamma = 1/6$. Here, one should note that the islands are not compact but fractal patterns as shown in Fig. 5b. This is due to the fact that edge diffusion is not considered in the simulations. The exponent $\gamma$ can be determined from simulations such that one monitors the number of nucleation events in a layer ($\propto I_D^{-2}$) as a function of $D/F$. However, for PLD with large intensities, the island distance obeys a different power law:

\begin{equation}
I_D \propto I^{-\nu},
\end{equation}

where $\nu = \gamma/(1 - 2\gamma) = 1/(2 + d_f)$, and more generally $\gamma = 1/(4 + d_f)$, if they have the fractal dimension $d_f$. In this regime the island distance is independent of the parameter $D/F$, since the adatoms do not make use of their diffusion probability, as they find an island and attach to it in a much shorter time as the time they are allowed to diffuse between two depositions. Therefore, above two regimes
described by the formulae (1) and (2) are separated by a crossover at a certain intensity, where the number of deposited atoms is of the same order of magnitude as the adatom density. As the average adatom density \( n \) in MBE scales as \( n \propto (D/F)^{-1+2\gamma} \), the critical intensity has to show the same scaling behavior: \( I_c \propto (D/F)^{-1+2\gamma} \). The qualitative difference between PLD and MBE for \( I>I_c \) is shown in Fig. 5. As can be seen, there are many nucleations at an early stage, although the effective flux of incoming particles is the same in both cases. The scaling behavior, namely, the fractal dimension, is measured by using the box-counting method. The fractal dimension values for the PLD and MBE were decided to be 1.28±0.03 and 1.62±0.03, respectively. The scaling exponent was found to be significantly different as compared to the exponent for the same system under continuous vapor deposition such as MBE. The simulations revealed that this attractive difference could be pursued to the large fraction of multiple droplet coalescence under pulsed vapor delivery.
Fig. 5 The kinetic Monte-Carlo simulations of pulsed-laser deposition and molecular-beam epitaxy in the submonolayer regime. (a) A simulated PLD-grown surface with $D/F = 2 \times 10^8$ and $I = 0.01$ ML; (b) A simulated MBE-grown surface with $D/F = 2 \times 10^8$. The figure shows typical configurations after deposition of 0.05 ML.$^{43}$
4. Orthorhombic tin dioxide thin films

It has been known that the naturally occurring form of SnO$_2$ is cassiterite. Under normal conditions, SnO$_2$ exists in the most important form of a crystalline phase known as cassiterite. The cassiterite has a rutile tetragonal crystal structure and its optical, electrical and gas-sensing properties have been extensively studied.\textsuperscript{22,23} Sangaletti and co-workers have reported SnO$_2$ multilayer thin film grown by the rheotaxial growth and thermal oxidation method on Al$_2$O$_3$ substrates.\textsuperscript{45} Their results indicated that, in addition to the SnO$_2$ cassiterite phase, a contribution from another SnO$_2$ phase was present, which can be related to cassiterite by introducing micro-twinning effects. This SnO$_2$ multilayer thin film showed a higher sensitivity towards CO with respect to the conventional single layer SnO$_2$ sensors.

Another form of SnO$_2$ with an orthorhombic structure is known to be stable only at high pressures and temperatures. The formation of orthorhombic-phase SnO$_2$ is intimately tied to a number of important synthesis parameters such as high pressures and temperatures.\textsuperscript{46-48} Müller found an unknown epitaxial interface phase of SnO$_2$ on $\alpha$-quartz (10$\bar{1}$0), which indicated that different octahedra stacking in the case of SnO$_2$ may give rise to different orthorhombic possibilities.\textsuperscript{49} Several authors have claimed the “discovery” of this “high-pressure” phase under low-pressure conditions.\textsuperscript{50-53} Arbiol and co-workers have reported the synthesis of pure monocrystalline orthorhombic SnO$_2$ nanowires and pure monocrystalline orthorhombic SnO$_2$ nanowires decorated with cassiterite SnO$_2$ nanoclusters.\textsuperscript{54} In fact, when previous experiments are examined in detail, it is often difficult to rule out the possibility of the presence of high compressive stress. Here, we highlight our experimental results of orthorhombic SnO$_2$ thin film under low pressure and temperature by using pulsed laser deposition technique.\textsuperscript{55}

The X-ray diffraction (XRD) patterns of the as-prepared thin films (Fig. 6a-i) indicated that the major reflections can be indexed to the orthorhombic-phase SnO$_2$ (labeled O) referred to the International Center for Diffraction Data PDF file as shown in Fig. 6a-iii. Upon exposing the as-prepared thin films to ambient air for six months, the intensity and position of the XRD patterns remain...
unchanged (Fig. 6a-ii). This result revealed that the as-prepared thin films are stable and have an orthorhombic SnO$_2$ structure. However, it seems that some reflections can also be assigned to the tetragonal-phase SnO (labeled T). Above results proved that the as-prepared thin films may be a mixture matrix of the orthorhombic-phase SnO$_2$ and tetragonal-phase SnO. Further investigation of the phase purity of the as-prepared thin films is necessary. Fig. 6b shows the X-ray photoelectron spectra (XPS) taken from the tin and oxygen regions. The peaks at 495.0 and 486.5 eV are attributed to the Sn3$d_{3/2}$ and Sn3$d_{5/2}$, respectively, which are close to the data for Sn(3$d$) in SnO$_2$. The gap between the Sn3$d_{3/2}$ and Sn3$d_{5/2}$ levels is 8.5 eV which is approximately the same as that in the standard spectrum of Sn. The peak at 530.5 eV can be assigned to the O1s (the inset in Fig. 6b). Owing to the proximity of the XRD patterns and XPS peaks of SnO$_2$ and SnO, the valence states of tin species of the as-prepared thin films could not be satisfactorily determined from the XRD and XPS results. Fig. 7a represents the room-temperature experimental Mössbauer spectrum for the as-prepared thin films as well as its fitting curve. Clearly, only one absorbing peak appears here, with an isomer shift and a quadruple splitting being 0 and ~0.6 mm/s, respectively. From data analysis, it is concluded that the tin shows a Sn$^{4+}$ valence state. The energy-dispersive X-ray spectroscopy (EDXS) analysis revealed that the as-prepared thin films are composed of 33.4 at.% Sn and 66.6 at.% O (Fig. 7b), that is, Sn:O = 1:1.994, which is in good agreement with Sn:O = 1:2 of SnO$_2$ bulk. The above results indicated that the chemical composition of the as-prepared thin films is consistent with the SnO$_2$ form.
Fig. 6 (a) XRD patterns of (i) the as-prepared SnO$_2$ thin film (orthorhombic SnO$_2$ labeled O and tetragonal SnO labeled T); (ii) exposing the as-prepared SnO$_2$ thin film to ambient air for six months;
(iii) the standard SnO$_2$ bulk. (b) XPS of the as-prepared SnO$_2$ thin film, which was taken from the tin and oxygen regions.$^{55}$

Fig. 7 (a) Room-temperature experimental Mössbauer spectrum for the as-prepared SnO$_2$ thin film and its fitting curve. (b) EDXS of the as-prepared SnO$_2$ thin film.$^{55}$
Since the applications of SnO$_2$ are related to surface electronic properties, we further examined the electronic structure of the orthorhombic SnO$_2$ thin films using soft X-ray absorption near-edge structure (XANES) spectroscopy. A comparison of the Sn $M_{4,5}$-edge XANES spectrum of the orthorhombic SnO$_2$ thin films to those of the tetragonal SnO$_2$ and SnO reference samples is given in Fig. 8a. The Sn $M_{4,5}$-edge spectra reflected electron transitions from Sn3$d$ core level (spin-orbit split into 3$d_{3/2}$ and 3$d_{5/2}$ levels, giving rise to $M_4$ and $M_5$ edges, respectively) to unoccupied electronic states above the Fermi level. If the core hole and electron correlation effects are ignored, such spectra essentially depicted Sn-related $p$- and $f$-projected states in the conduction band. Nevertheless, it is important to note that the surface electronic structure of the orthorhombic SnO$_2$ is more similar to that of the tetragonal SnO$_2$ rather than the tetragonal SnO. The data in Fig. 8a show that undercoordinated surface atoms in the orthorhombic SnO$_2$ thin films introduce additional Sn-related electronic states, which are close to the conduction band minimum (~499 eV in Fig. 8a). This finding is surprising. It is consistent with the Mössbauer and EDXS analysis which revealed no evidence of the tetragonal-phase SnO, and rules out the existence of the tetragonal SnO in XRD. The evaluation of above all experimental data indicated that the as-prepared thin films are composed of a pure orthorhombic-phase SnO$_2$. Fig. 8b shows that the optical transmittance is measured in the wavelength range from 200-800 nm for the orthorhombic SnO$_2$ thin films and tetragonal SnO$_2$ reference sample at room temperature. We found that the transparency of the orthorhombic SnO$_2$ is superior to that of the tetragonal SnO$_2$. Fig. 8c shows the absorption coefficient versus the photon energy for the orthorhombic SnO$_2$ and tetragonal SnO$_2$ reference sample. A linear extrapolation towards zero absorption $E_g$ corresponds to direct allowed transitions. We obtained $E_g = 4.02$ eV for the orthorhombic SnO$_2$ and $E_g = 3.73$ eV for the tetragonal SnO$_2$ reference sample in energy. By comparing $E_g$ for the orthorhombic SnO$_2$ thin films with that of the tetragonal SnO$_2$ reference sample, it is evident that the band-gap widening occurs and hence the orthorhombic SnO$_2$ thin films becomes transparent.
Fig. 8 (a) Sn $M_{4,5}$-edge XANES spectrum of the orthorhombic SnO$_2$ [labeled SnO$_2$(O)] compared with the spectra from tetragonal SnO$_2$ [labeled SnO$_2$(T)] and SnO [labeled SnO(T)]. (b) Spectrophotometric transmittance measured in a wavelength range of 200-800 nm for the orthorhombic SnO$_2$ and tetragonal SnO$_2$. (c) Absorption coefficient vs photon energy obtained from Fig. 8b.$^{55}$
Further advancement of this approach to the synthesis of orthorhombic SnO\textsubscript{2} thin films requires a clear understanding of its formation mechanism. Fig. 9 shows the schematic diagram of the oxygen exchange reaction mechanism at the grain interfaces to explain the formation of this orthorhombic phase. It consisted of four different oxygen species (O\textsubscript{2}, O\textsubscript{2}\textsuperscript{-}, O\textsuperscript{-}, and O) coupled by the elementary reaction steps. Since the transported oxygen species is neutral atom, the availability of neutral oxygen atom at the surface of the deposition layer is a factor influencing the degree of exchange. The amount of available oxygen atom depends on the rate of the dissociation of O\textsubscript{2} and the amount of oxygen species at the surface of the deposition layer in the atmosphere of the laser ablated plume. A based explanation for the formation of orthorhombic-phase in the oxygen exchange reaction may come from ablated plume to deposition layer variation. Since the grain-boundary diffusion is fast, we expect oxygen exchange reaction at the grain interfaces in the deposition layer. The most significant development of this model is the incorporation of the neutral oxygen atoms, which can be considered to be a part of the lattice in the oxidized or stoichiometric form of the deposition layer, resulting in the atomic rearrangement and the formation of the orthorhombic-phase SnO\textsubscript{2}. In this model, the capture of an electron depends on the thermal velocity of electrons close to the substrate temperature and the density of electrons close to the surface of the deposition layer. Since the oxygen species (O\textsuperscript{-2} and O\textsuperscript{-}) continuously exchange electrons with the deposition layer and the neutral oxygen atoms may contribute to the lattice of the deposition layer via the faster diffusion of the grain boundary, which result in the reduction of the oxygen vacancies, the band-gap widening occurs and the orthorhombic SnO\textsubscript{2} thin films becomes transparent.\textsuperscript{56} The epiaxial strain in randomly oriented polycrystalline orthorhombic SnO\textsubscript{2} thin films should not attain substantial magnitude. We can speculate that the key factor for the synthesis of the orthorhombic SnO\textsubscript{2} thin films is not compressive stress in the thin films. Above results indicated that the orthorhombic SnO\textsubscript{2} thin films can be fabricated through processes at ambient or subambient pressures.
Fig. 9 Schematic diagram of oxygen exchange reaction mechanism at the grain interfaces to explain the formation and optical properties of the orthorhombic phase.⁵⁵

5. Concluding Remarks

Due to increasing interest in the SnO₂ nanomaterials, we carried out a series of studies investigating their micro/nanostructural evolution and related formation mechanisms. We examined the micro/nanostructures, functions, formation processes, and physicochemical characteristics of the SnO₂ thin films. Research on SnO₂ thin films will bring the innovations to technologies, such as micro/nanostructure and morphology associated technique, micro/nanostructure and characterization coupling technique, micro/nanostructure and advanced function simulation technique, and so forth. In order to achieve optimized functional performance with the SnO₂ micro/nanostructures, however,
several challenges still remain. Further investigation and additional effort are needed to tackle some important issues for promoting the practical applications of the SnO$_2$ micro/nanostructures.

This review has provided the synthetic strategies and formation mechanisms of the micro/nanostructures of various SnO$_2$ thin films prepared by pulsed laser ablation. We hope this review has given the reader a sense of the great potential of SnO$_2$ thin films with interesting micro/nanostructures. As we and others continue to explore this promising material, the unique micro/nanostructure features of SnO$_2$ thin films and numerous ways in which the properties can be tuned will likely lead to the development of further exciting techniques and powerful combinations of existing ones. It is expected that these SnO$_2$ thin films with fascinating micro/nanostructures may offer vast and unforeseen opportunities in oxide semiconductor devices as well as in other fields of science and technology.

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References


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