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Templated bicontinuous Tin oxide thin film fabrication and the NO_2 gas sensing

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ABSTRACT

Bicontinuous Tin oxide (SnO_2) thin films were fabricated by atomic layer deposition (ALD), annealing, and acid washing with nanoporous gold (NPG) structure serving as templates. The resultant SnO_2 films show high sensitivity on NO_2 gas. The detection limit is as low as 170 ppb in dry N_2 flow with a rapid response/recovery time of 40/130 s at the optimized working temperature of 300 °C. The performances dependence of the gas sensor on the working temperatures and the exposure environments reveal that the gas responses strongly rely on the dynamic balance of O_2, O_2^-, O^-, NO_2^-, and NO_3^-. Our study not only shows this bicontinuous SnO_2 films is promising for sensitive gas sensor but also provides insightful understanding on the NO_2 gas sensing mechanism.

1. Introduction

Gas sensors have attracted considerable research interests in both industry and academia because they are promising in various fields such as the environmental monitoring, the food industry, and the homeland security [1,2]. In particular, NO_2 gas sensing is an urgent need in that the oxidizing gas is the major cause for the ozone formation, the acid rain, and the smog in atmosphere [3–5]. Various metal oxides are used for gas sensing. Among them, SnO_2 has been widely utilized due to its high conductivity as well as good thermal stability from 200 to 400 °C [6–9]. It's generally accepted that SnO_2-based NO_2 gas sensors belong to the surface-control type [10–12]. The resistance response is dependent on the NO_2 and oxygen absorption/desorption on the oxide 'surfaces' which depth is generally determined by the Debye length L (L ~ 3 nm for SnO_2 [13]). The resistance changes dramatically as a result of the SnO_2 conduction band electron extractions from the depletion layer (smaller than $2L$) by oxidizing species like NO_2, O_2, O_2^-, O^-, and O^{2-} [10–12]. Although various works on the NO_2 gas sensing were explained by the above oxidizing reactions, however, whether such oxidizing processes competes or interplaits mutually upon different working temperatures or exposure environments, and if so, how the competition or interplay affects the sensing performances, is still unclear.

On the other hand, in order to achieve high sensitivity and effective cost, various nanostructured SnO_2 with high surface-to-volume ratio, large number of surface reactive sites, and reduced bulk size were fabricated. Considerable research efforts have been devoted in this direction, synthesizing successfully various zero-dimensional (0D) to three-dimensional (3D) nanostructures with e.g., particle-like [14], wire-like [15], tubular-like [16,17], hierarchical or porous architectures [18–26]. Among these nanostructure morphologies, hierarchical or porous structures are one of the most attractive gas sensing families due to their high surface area, large number of surface reactive sites, low density, and surface permeability for gas transportation [19]. Various methods are developed to achieve porous structures. For examples, the porous SnO_2 microspheres or microcubes are synthesized via the chemical additives [20,21]. Via the hydrothermal method at low temperature, hierarchically mesoporous SnO_2 nanosheets were synthesized, showing highly sensitive response on ethanol [22]. By using colloidal crystals as templates, ordered porous structures with different morphologies, such as opal or inverse opal [23], and controllable necking [24], are experimentally demonstrated, resulting in good sensitivity on CO gas. With anodic aluminum oxide (AAO) membranes as a template, disordered SnO_2 porous structures were prepared [17]. In the past few years, even nature templates, e.g., the butterfly wings [25,26], the diatoms [27,28], the

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eggshell membrane [29], and the wood [30] are used in porous hierarchical architectures synthesis. However, those porous structures in which the air pores do not connect with each other may still make it an obstacle for rapidly adequate diffusion of gas molecule and large-area surface activation for molecule absorption [31].

In this work, we fabricated the bicontinuous nanoporous gold structures (NPG) via the phase-separation method of spinodal decomposition. Depositing the SnO_2 thin film by atomic layer deposition (ALD) with the structured gold film as skeletons, followed by the procedures of sintering and acid washing, we synthesized successfully the ultrathin SnO_2 polycrystalline film inheriting the bicontinuous morphologies. We found that the sensitivity of the resultant SnO_2 films shows strong dependences on the working temperatures and exposure environments. On 300 °C, the detection limit on NO_2 gas is as low as 170 ppb in dry N_2 flow. Strikingly, the gas response is dramatically enhanced, e.g., about 36 fold larger for 10 ppm NO_2 concentration, in dry clean air flow. The reaction competition generating NO_2^- and NO_3^-, as well as the dynamic balance of O_2, O_2^-, O^- density on the bicontinuous structure surface are responsible for such results.

2. Experimental

Bicontinuous SnO_2 thin films were fabricated as follows: The NPG film was fabricated at first by dealloying the Au–Ag alloy leaves (13.25 karat, TCP Global Corp, US) in 70% aqueous HNO_3 for 10 h at room temperature. The fabricated NPG film was then rinsed by deionized water (~18 MΩ) in order to get rid of residue acid and intermediate porous structures, followed by a dry process in an air oven. The obtained NPG film consisting of interconnected gold filaments and air channels, which originates from a phase-separation process known as spinodal decomposition, is actually bicontinuous. After the NPG film was transferred to quartz substrate, bicontinuous SnO_2 film was fabricated by templating NPG structures via ALD techniques. In the ALD deposition, the tetrakis (dimethylamino) tin (TDMASn) and ozone (O_3) were used as precursors which is carried by pure nitrogen (N_2) gas. One typical ALD cycle includes four alternative steps: TDMASn feed/N_2 purge/O_3 feed/N_2 purge with the exposure time of 1 s/15 s/15 ms/15 s, respectively. With the precursor of TDMASn keeping on 60 °C and the reaction temperature of the chamber maintaining on 100 °C, the growth rate of SnO_2 is ~1.2 Å, which is consistent with the previous reported values [32]. As a result, the SnO_2 filled up the air channels of NPG after the deposition of 300 cycles. The resultant SnO_2 thin films, together with the NPG template, were annealed at 800 °C for 1 h in air ambient for crystallization. Finally, the NPG skeleton was removed by nitrohydrochloric acid, leaving the porous SnO_2 thin films on quartz substrate.

The morphology of the prepared porous SnO_2 thin films was characterized by scanning electron microscope (SEM, Hitachi S-4000, Japan) and high-resolution transmission electron microscope (HRTEM, Jeol JEM-2100F, Japan). The crystalline phases of the films was examined by X-ray diffractometer (XRD, Bruker D8, German) in θ–2θ mode with Cu Kα radiation (λ = 0.15418 nm). The transmission spectra of the samples were measured by a spectrophotometer (spectral range of 200–800 nm, Shimadzu UV-3150, Japan) at room temperature. In addition, the chemical states of Sn and O ions on surface of the films were investigated by X-ray photoelectron spectroscopy (XPS, PH1500C Versa Probe spectrometer, Japan) with monochromatic Al Kα radiation ($h\upsilon$ = 1486 eV). All binding energies were calibrated with respect to C1s spectral line at 284.8 eV.

Gas sensing characteristics of the bicontinuous SnO_2 thin films were performed in a gas sensing test equipment (Gimix, USB/RS485 1.5, German). The contacting electrodes connecting to the equipment were directly pressed on the Ag paste coated on the edges of the SnO_2 thin films. The films were put, in a room-made transparent container, on the quartz substrate equipped with a ceramic heater underneath. By controlling the power output of the heater, the chamber temperature can be varied from 200 °C to 400 °C. Unless otherwise specified, the sensor was exposed to dry N_2 flow (500 sccm) for 1 h to achieve stable initial resistance (R_{N2}). Then different concentration of NO_2, obtained by the mixing of dry N_2 with NO_2, was introduced into the test chamber with the constant flow rate of 500 sccm. To fulfill the sensors recovery, the compressed dry N_2 was injected. In the sensor resistance measurements, the data was recorded every second automatically by a digital multimeter (Keithley 2700, US) interfaced with a computer. The sensor relative responses for NO_2 gas are defined as: $S_{N2} = (R_{NO2} - R_{N2})/R_{N2} \times 100\%$, where R_{NO2} is the film resistance in the presence of NO_2. The response/recovery time of the sensor is defined as the time during which the sensor resistance changes 90% compared to the maximum resistance.

3. Results and discussion

To manifest the structural evolutions of the bicontinuous SnO_2 thin film, top-view morphologies of the sample at each fabrication step were characterized by SEM. Fig. 1(a) shows the SEM image of the typical NPG template, from which the bicontinuous structure of NPG with continuous air pores and successional gold filaments interweaving in a 3D way can be evidenced. With the naked eyes, golden coloration can be observed for NPG [the inset of Fig. 1(a)]. From our previous study, the NPG is an amorphous nanostructure with the characteristic length scale of ~100 nm. The average size of the air nanovoids is ~30 nm. After depositing SnO_2 by ALD, this 3D bicontinuous structure of NPG template was almost filled with SnO_2 nanoparticles, as shown in Fig. 1(b). At the calcination temperature of 800 °C, the SnO_2 nanoparticles on surfaces of NPG were assembled together, forming much larger SnO_2 grains [Fig. 1(c)]. Fig. 1(d) shows the SnO_2 nanostructures after the removal of NPG template by acid washing. It is observable that the obtained thin film consists of filament-like air channels, which is faithfully inherited from the skeleton of gold filaments, forming the SnO_2 bicontinuous structure. Such interconnected air channels are beneficial to high surface-to-volume ratio and rapid gas diffusion, which is particularly favorable for the gas sensing.

To obtain more information on the bicontinuous SnO_2 thin film, TEM and HRTEM was carried to examine the fine microstructures. Fig. 2(a) displays the TEM image of the SnO_2 thin film annealed at 800 °C after the removal of the NPG skeleton. Similar with the SEMs, the picture reveals that the bicontinuous architecture is actually assembled by the nanocrystallites. Statistical size of the nanocrystallite is evaluated to be an average value of 14.9 nm in a close-up image [Fig. 2(b)]. Fig. 2(c) shows several typical SnO_2 nanocrystallites with higher resolution, from which the lattice fringes with different lattice constants, e.g., ~2.52 Å and ~3.33 Å, are clearly discerned. Such values are consistent with the spacing of the (101) and (110) planes of rutile SnO_2 structure. The selected area electron diffraction (SAED) pattern shown in the inset of Fig. 2(c) further indicates that the as-prepared SnO_2 is polycrystalline in nature. The (211), (101) and (110) planes of rutile SnO_2 structure are distinguished from the rings of SEAD patterns, which is in correspondence with the previous TEM data. Furthermore, XRD patterns of nanoporous SnO_2 thin film on quartz substrates were performed [Fig. 2(d)]. Although the background signals induced by the quartz substrate are strong [red line], the imposed small peaks observed at 2θ = 26.5°, 34.1°, 51.5° corresponding to (110), (101) and (211) (JCPDS File no.41-1445) plane of rutile SnO_2 structure are still