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Size Effects in the CO Sensing Properties of Nanostructured TiO_2 Thin Films Fabricated by Colloidal Templating

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This study investigates the CO sensing properties of nanostructured TiO_2 thin film gas sensors fabricated with colloidal templates using different sizes of polymer spheres. Compared to plain films, the nanostructured films show enhanced gas sensing in the form of greater sensitivity and a faster response. More interestingly, the use of colloidal templates with smaller spheres (300 nm in diameter) leads to close-packed nanostructured TiO_2 thin films with very large-scale uniformity and a more pronounced improvement in CO sensing compared to the use of larger spheres (1 μm in diameter). This result suggests that an understanding of the sphere size effects on the gas sensing properties of nanostructured TiO_2 thin films created by colloidal templating is important in the development of these films for actual applications.

Keywords: TiO_2 thin film gas sensors, colloidal templating, nanostructured, size effects, large-scale uniformity

1. INTRODUCTION

Due to their high surface-to-volume ratio and compatibility with well-established semiconductor processes, nanostructured metal oxide thin films have attracted a considerable amount of interest for application to highly sensitive gas sensors with a fast response time and a small size. Various nanostructured metal oxide materials such as SnO_2,[1] WO_3,[2] TiO_2,[3] In_2O_3,[4] and ZnO[5] have been reported to be good candidates for novel semiconductor thin film gas sensors. Among them, TiO_2 is considered to be a key material for reliable and durable gas sensors owing to its superior chemical stability at elevated temperatures.[6] Various synthesis methods, including wet chemical solution processes,[6,7] sol-gel processes,[3,8] photolithographic processes,[9] glancing angle deposition,[10] and anodized aluminum oxide templating [11] have been demonstrated as feasible for the fabrication of nanostructured TiO_2 thin films.

Recently, Kim *et al.*[12] showed enhanced NO_2 gas sensitivity of macroporous TiO_2 thin film gas sensors obtained using colloidal templating, which is an effective method to fabricate quasi-ordered sub-micron structures of various materials.[13] However, it is challenging to exploit this method for wafer-scale uniformity and throughput because the wetting of sub-micron polymer spheres from a colloidal solution onto a substrate is highly sensitive to the chemical homogeneity of the surface of the substrate.[14] The maximum area of close-packed monolayer colloidal templates without voids and sphere-free regions is about 1 cm^2.[15] In practice, the formation of voids in colloidal templates can be affected by the size of the polymer spheres. Furthermore, the gas sensitivity and response time of TiO_2 thin film gas sensors fabricated using colloidal templates can changes with the sphere size. This suggests that investigating the influence of the sphere size on the sensing properties of nanostructured TiO_2 thin films fabricated using colloidal templating is a critical step toward the development of nanostructured thin film gas sensors for real applications. The present study demonstrates that the use of smaller polymer spheres in colloidal templating leads to more uniform and close-packed nanostructured TiO_2 thin films as well as a faster CO gas sensing response.

2. EXPERIMENTAL DETAILS

Aqueous suspensions of 300 nm carboxylated poly (methyl methacrylate) spheres (2.7 wt. %) and 1 μm carboxylated polystyrene spheres (2.6 wt. %) were used in this work. The suspensions were ultrasonicated for 30 minutes to disperse the spheres uniformly without agglomeration. A drop of suspensions was dripped by a pipette onto a SiO_2/Si substrate with Pt interdigitated electrodes (IDE) in which the gap between each electrode was 20 μm. To obtain monolayer templates, overflowing suspensions were suctioned using filter papers. The samples were then dried overnight in a dry box at room temperature. 100-nm-thick TiO_2 films were deposited onto the microsphere templated substrates at room temperature by RF sputtering using a polycrystalline

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TiO_2 target. The base pressure, working pressure, RF power, gas flow rate, and growth rate were 2×10^{-6} m Torr, 10mTorr, 150 W, 30 sccm (Ar:O_2 =1:1), and 6.3 nm/min, respectively. After the deposition of the film, the samples were calcined in air at 550°C for 60 min to burn out the organic materials and simultaneously improve the crystallinity of the TiO_2 films. The microstructures of the films were characterized by an x-ray diffractometer (XRD) (TTK 450 model) using a monochromatised Cu K_α (λ = 1.54 Å) radiation source. The surface morphology of the films was investigated using a scanning electron microscope (SEM) (XL-30 FEG-ESEM) operating at 15 kV.

The response of the nanostructured TiO_2 films fabricated by colloidal templating to CO gas was tested at 300°C and compared to that of a plain TiO_2 film deposited onto an untemplated substrate. The change in the resistance values of the films was monitored while changing the flow gas from dry air to the test gas (50 ppm and 500 ppm CO mixed in dry air). To eliminate interfering effects, a constant flow rate of 100 sccm was used for both the dry air and the test gases. The film resistance was measured under a dc bias voltage of 1 V using a source measurement unit (Keithley 236).

3. RESULTS AND DISCUSSION

Figure 1 shows SEM images of nanostructured TiO_2 films obtained by colloidal templating. For the 1-ìm-sphere templated film, sphere-free regions can be observed. The coverage by the spheres is estimated to be approximately 90% on average. In contrast, the 300-nm-sphere templated film exhibits very uniform surface morphology that exceeds 500 μm × 500 μm. This represents the first time such a perfectly spherical templated film has been produced in this manner.[12–16] No irregularities were observed in the sample under an optical microscope. In cross-sectional views of the films, openings were found in the walls of the hollow spheres near the interfaces between the films and the substrates. These were formed during the calcination process at 550°C. It was also noted that the 300-nm-sphere templated film has relatively large openings to the sphere walls compared to the 1-μm-sphere templated film.

X-ray diffraction patterns of plain and nanostructured TiO_2 films are plotted in Fig. 2. All of the films consist of anatase TiO_2 phases and essentially identical diffraction patterns. This result indicates that the calcination temperature is sufficient to crystallize TiO_2 films deposited at room temperature and, more importantly, that the crystallinity of TiO_2 films is not affected by the colloidal templating.

Figure 3 shows the response of plain and nanostructured TiO_2 films to 50 ppm and 500 ppm CO gases at 300°C. The decrease of the film resistance upon exposure to the CO gases indicates that the TiO_2 films are n-type semiconductors, which is consistent with previous reports.[6–11] With colloidal templating and a decrease in the sphere size, the resistance of the film increases due to the increase in the number of notched boundaries with high resistance values. It

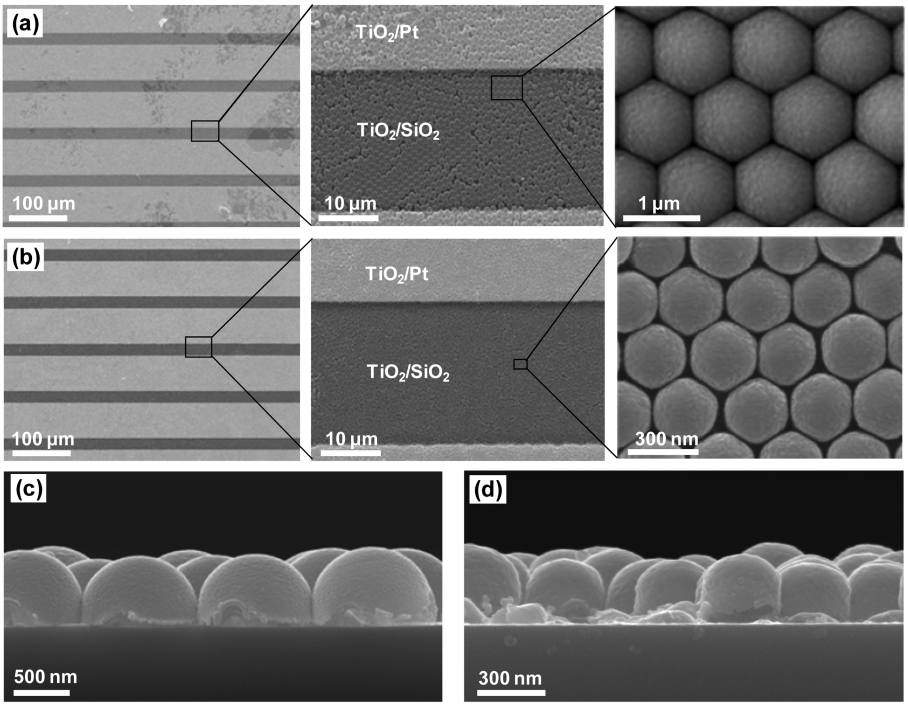

Fig. 1. (a, b) Top-view and (c, d) cross-sectional SEM images of nanostructured TiO_2 (100 nm thick) thin films with (a, c) 1 μm hollow spheres and (b, d) 300 nm hollow spheres on Pt IDE/SiO_2/Si substrates.

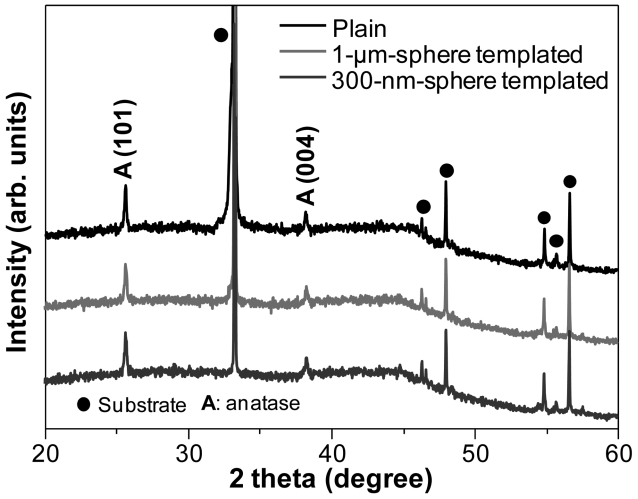

Fig. 2. X-ray diffraction patterns of plain and nanostructured TiO_2 thin films.

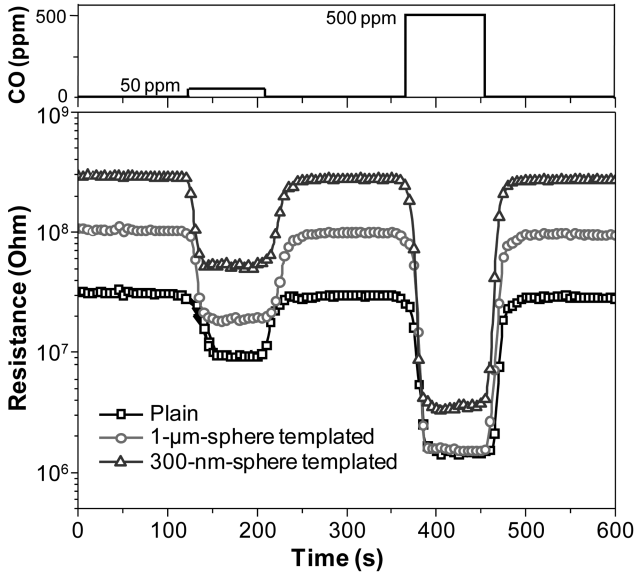

Fig. 3. Typical response curves of plain and nanostructured TiO_2 thin film gas sensors to 50 ppm and 500 ppm CO gases at 300°C. The resistance was measured at a dc bias of 1 V.

is evident that the nanostructured films shows enhanced sensing properties with higher sensitivity and faster response times compared to the plain film.

In order to clarify the enhancement, the sensitivity and 90% response and recovery times of the three films are plotted in Fig. 4. Compared with the plain film, the higher sensitivity of the nanostructured films is attributed to the approximately four-fold larger surface-to-volume ratio. In principle, the 1-ìm-sphere and 300-nm-sphere template films should have the same surface-to-volume ratio. Thus, both films might show the same sensitivity. However, the 1-um-shpere templated film displays slightly lower sensitivity due

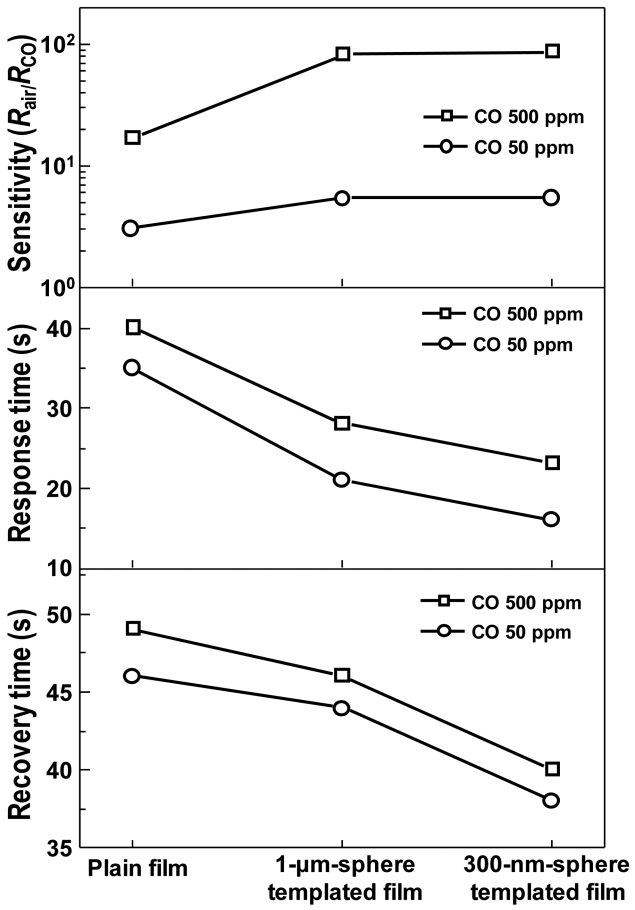

Fig. 4. Plots of sensitivity (R_{air}/R_{CO}), response time, and recovery time for plain and nanostructured TiO_2 thin film gas sensors. For the response and recovery times, the time to reach the 90% of $|R_{air} - R_{CO}|$ was evaluated.

to the sphere-free regions shown in Fig. 1(a). In addition to the higher sensitivity, the nanostructured films show shorter response and recovery times. The faster response also originates from the larger surface-to-volume ratio.[12] Hence, the differences in the response and recovery time between the 1-ìm-sphere and 300-nm-sphere templated films can be explained in terms of the geometrical aspects of the spheres. As shown in Figs. 1(c) and 1(d), the 300-nm-sphere templated film has relatively large openings in the sphere walls. These larger openings allow CO gas to move faster into and out of the insides of the spheres, leading to the shorter response and recovery times. These results suggest that control of the geometrical shapes of the hollow spheres is important for optimization of the gas sensing properties of nanostructured TiO_2 thin film gas sensors fabricated using colloidal templating.

4. CONCLUSION

The enhanced CO gas sensing properties of nanostruc-

tured TiO_2 thin film gas sensors fabricated by colloidal templating were investigated. A direct comparison between 1-ìm-sphere template films and 300-nm-sphere template films demonstrated that the use of smaller polymer spheres during the colloidal templating process leads to uniform and close-packed TiO_2 nanostructured thin films in a very large scale as well as a simultaneously shorter response and recovery time for CO gas sensing. This finding therefore expedites the realization of nanostructured metal oxide thin films by colloidal templating as novel gas sensors that are feasible for use in various applications.

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