JOURNAL OF MATERIALS SCIENCE (2005) LETTERS

Electrical properties of titania films by hydrolysis of alkoxide titanium in micelles

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A well-known example of *the applications of oxygen sensors* is the feedback control of *Air/Fuel ratio* of automobile engine exhaust gases in order to improve the fuel economy efficiency and to reduce the harmful emission of gases. This property of semiconducting oxides has been exploited for gas sensing applications. An efficient gas sensor must have high sensitivity and reasonably good selectivity at low operating temperatures. Compared to the other oxygen sensors, titania is preferred as a oxygen sensor material. In reactions involving titania, oxygen vacancies are one of the major advantages of such material [1, 2]. Therefore, in this letter, we focus our attentions on the titania oxygen sensors.

In recent years, a variety of synthesis techniques for nanosized TiO_2 have been used, including homogeneous precipitation, sol-gel, spray-drying, freeze-drying, chemical vapor deposition etc. The sol-gel process is an inorganic polymerization procedure based on the hydrolysis and condensation reactions of metal alkoxides. Conventional sol-gel precursor solutions often contain metal alkoxides diluted in ethanol, water and acid. Therefore, the solution composition and preparation procedures play a key role in the sol-gel manufacturing of titania thin films [3–6]. Among sol-gel methods, water-in-oil microemulsions have been successfully utilized for the synthesis of titania films. Water-in-oil microemulsions offer a unique environment in which to form titania films by the hydrolysis of titanium alkoxide in the micelles of water [7–9]. This study investigates the formation of stable, nanosized TiO_2 films via hydrolysis of tetrabutyl titanate in the microemulsion containing Span-Tween 80, and elucidates the process parameters that control colloid stability and nanosized film properties [10]. Dip- and spin-coating methods have been commonly used for the deposition of this kind of films [11, 12]. These coating methods are based on the linear or centrifugal spreading of the sol on the substrate, respectively. The film thickness is essentially controlled by the solution viscosity and by the linear or rotational speed of the substrate.

The titania sols were prepared from tetrabutyl titanate diluted in a proper accessory solvent, which not only is able to cut down on the surface tension of the solution but also can enhance the solubility of the sols so that the emulsion can easily turn into microemulsion. Thus, *iso*-pentanol should be selected for an accessory solvent. W/O microemulsions were prepared by mixing precalculated quantities of Span-Tween 80, water, and finally adding toluene under stirring until uniform solutions were obtained. The amount of *iso*-pentanol needed for the emulsion of different [Span-Tween 80] changing into homogeneous microemulsion was determined. Titania reversed micelle microemulsion was formed by adding certain amount of tetrabutyl titanate into the above microemulsion. We tried to check the influence of each parameter separately by modifying the concentration of a single reagent while keeping all other parameters at a constant value. It appears that, at a room temperature, a critica1 parameter characterizing the microemulsion is the molar ratio of Span-Tween 80 to $Ti(OC_4H_9)_4$. A cleaned glass substrate was dipped into the above coating solution and withdrawn at a constant rate of 1 cm/min. The gel films were heat-treated in air at 200 ° for 10 min and then ultrasonicated in acetone solution for 1–2 min. This coating procedure was repeated 3 times. The surface roughness and porosity were measured with an atomic force microscope (DI Multimode Nanoscope III). The crystalline phase was determined by the X-ray diffraction method (XRD) (Model D/MAX-C, Rigaku. Tokyo, Japan). The thicknesses of the films deposited on glass substrates were measured with a Dektak 6 M stylus profilometer. Electrical connections were made to the disk through a pair of Pt wires and heated for two hours. The gas pressures have been regulated by mass flow controllers (MFC).

Titania films made through the reverse micellar route by using Span-Tween 80 and tetrabutyl titanate consist of uniformly sized, quasi spherical nanoparticles of a diameter of a few tens of nanometers. The RMS surface roughness of TiO_2 films and the surface morphology measured by AFM are shown in Fig. 1. The distance between the highest and the lowest point of the surface were 32.739 nm for $[\text{Span-Tween 80}]/[Ti(OC_4H_9)_4] = 1$ and 8.012 nm for $[\text{Span-Tween 80}]/[Ti(OC_4H_9)_4] = 2$. The corresponding surface roughness values calculated were 2.969 and 1.593 nm, respectively. The process allows the nanostructure of the film to be controlled through several parameters. The choice of the surfactant is the most important of these parameters. Surfactants containing a polyethylene oxide polar head

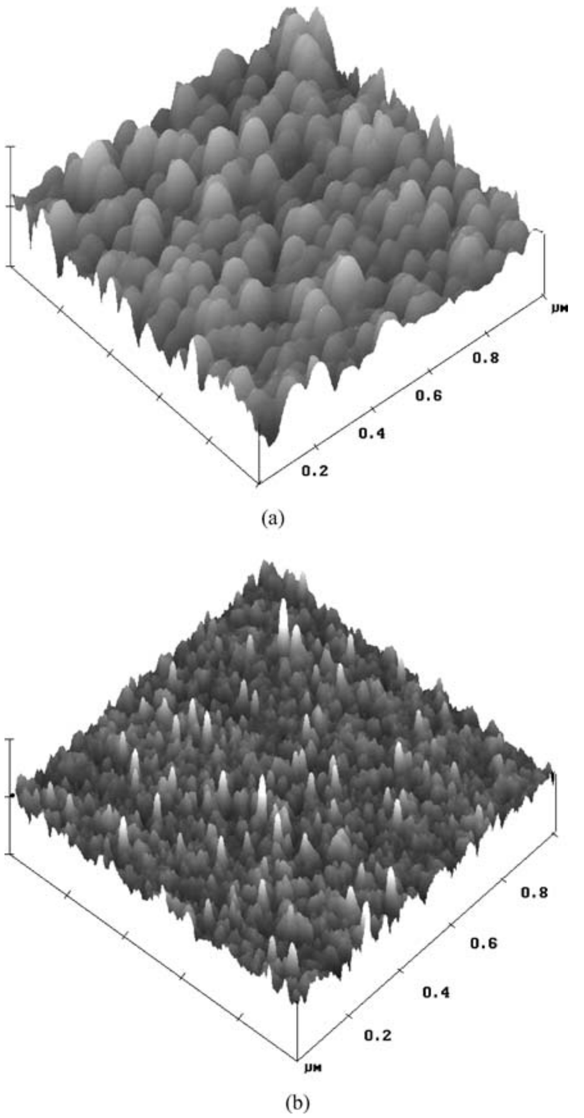

Figure 1 AFM-image of titania films: (a) [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 1, (b) [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 2.

are preferred, since they are strongly hydrated, thus strongly competing with alkoxide hydrolysis. Thus, the original sol is slowly transformed into a gel (sol-gel process). Among all surfactants tried, Span-Tween 80 gives the slowest hydration and gelation rates, apparently due to its large polyethylene oxide group. Once the type of surfactant making the reverse micellar phase is decided, film nanostructure can be varied by changing the surfactant or $Ti(OC_4H_9)_4$ content. As expected, the quantity of water by itself is not the decisive factor for the evolution of film but the molar ratio of surfactant to $Ti(OC_4H_9)_4$. The more amount of Span-Tween 80 increased, the smaller the size of nanoparticles constituting the film became. The finding from our studies that the initial crystallite sites of the nanoparticals are comparable to the dimensions of the micelle suggests that the growth of the primary particles is limited by the size of the interior micelles.

Typical X-ray diffractometer traces from TiO_2 samples in the as-deposited state at 500 °C are shown in Fig. 2. In the as-deposited state, the titania film formed at [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 0.5 was almost amorphous or consisted of anatase with very low degree of crystallinity. The as-deposited amorphous films were stable up to [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 1, and transformed to the anatase phase. This can be seen from the evolution of the anatase 110 peak intensities depicted in Fig. 2. The structure of the TiO_2 film at [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 2 was polycrystalline anatase with some negligible traces of rutile. It has been observed that the half width of all the peaks increases with increase in surfactant concentration in TiO_2. It indicates that grain growth of TiO_2 crystallites is hindered by the increase of surfactant. These peaks are broad and weak in intensity, suggesting that the grain sizes of the crystalline titania fall into the range of nanometers.

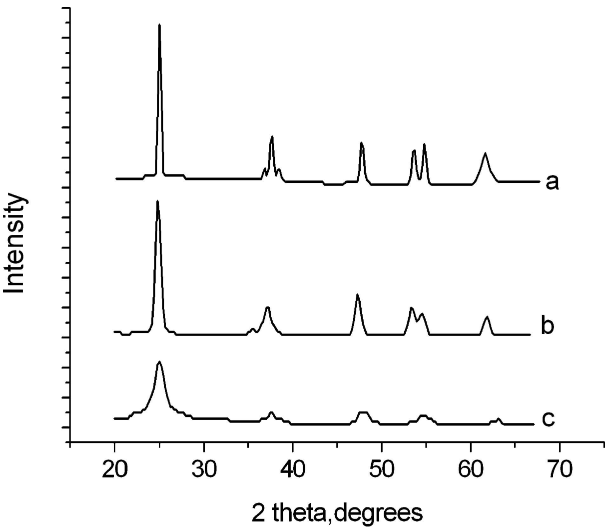

Figure 2 XRD patterns of TiO_2 films: (a) [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 2, (b) [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 1, (c) [Span-Tween 80]/[$Ti(OC_4H_9)_4$] = 0.5.

Fig. 3 shows FTIR spectra for the TiO_2 films prepared at various molar ratio of Span-Tween 80 to $Ti(OC_4H_9)_4$ ranging from 0.5 to 2. A broad band around 3400–3450 cm^{-1} which is attributed to free or bonded O-H groups was observed in each case. Pronounced changes upon surfactant concentrations were observed in the absorption bands related to Ti-O-Ti bonds, which

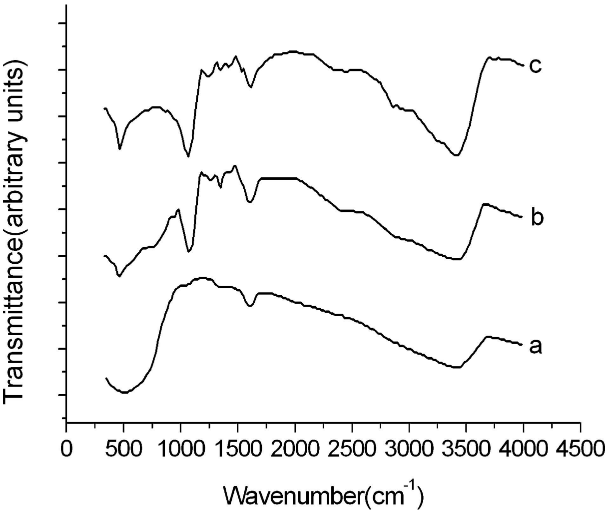

Figure 3 IR spectra of TiO_2 films in the case of [surfactant]/[$Ti(OC_4H_9)_4$] being (a) 0.5, (b) 1, and (c) 2.

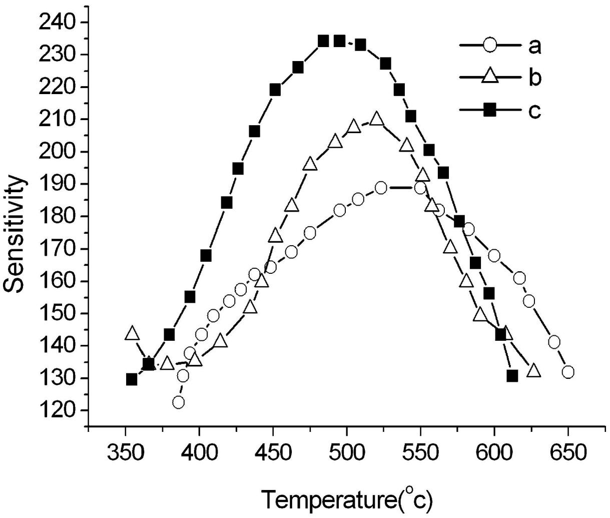

Figure 4 Sensitivity of the sensor as a function of operating temperature at the ratios [Span-Tween 80]/[Ti(OC_4H_9)$_4$] (a) 0.5,(b) 1, and (c) 2.

appeared in the range of 400–600 cm^{-1} as the result of condensation reactions. We can therefore conclude that the presence of a broad band in this region corresponds to the formation of Ti-O-Ti bonds and to the development of the titania network in the films. The peaks between 2800–2900 cm^{-1} is associated with the symmetric and antisymmetric stretching vibration modes of the $-CH_3$ and $-CH_2-$ groups of alkoxy groups. As the molar ratio of Span-Tween 80 to Ti(OC_4H_9)$_4$ was decreased, the intensities of absorption peaks due to near 1616 cm^{-1} not only reduced, which was ascribed to the bending vibration of H—O–H group in structure water, but also the absorption peak due to organics near 900–1300 cm^{-1} was weakened. It is considered that under high surfactant molar ratios, hydrolysis and condensation are relatively fast. The broad band between 450–550 cm^{-1} sharpened and increased in intensity with increasing surfactant concentration, which leads to the appearance of a sharp peak at 515 cm^{-1}, which is attributed to the presence of anatase in the TiO_2 films.

The sensitivity of the sensor has been defined as the ratio of the resistivity of the material in present and the resistivity in the absence of oxygen. Fig. 4 shows the variation of sensitivity with operating temperature of the range 350–650 °C while [Span-Tween 80]/[Ti(OC_4H_9)$_4$] was 0.5,1 and 2 at 1000 ppm oxygen partial pressure. The results show that in the case of [Span-Tween 80]/[Ti(OC_4H_9)$_4$] = 0.5, the sensitivity of sensor is very low even at 550 °C, while in the case of [Span-Tween 80]/[Ti(OC_4H_9)$_4$] = 2 sensor exhibits higher sensitivity at low operating temperature of 495 °C. The reduction in operating temperature of [Span-Tween 80]/[Ti(OC_4H_9)$_4$] = 2 sample is very significant. As the operating temperature increases further, the sensitivity of the sensor reduces. As [Span-Tween 80]/[Ti(OC_4H_9)$_4$] increases further up to 2, the sensor shows the maximum sensitivity of the order of ≈234, whereas in the case of [Span-Tween 80]/[Ti(OC_4H_9)$_4$] = 1 sensors exhibit a maximum sensitivity of the order of ≈209 at 520 °C. All the samples show maximum value of sensitivity at a particular operating temperature only above and below this temperature. The maximum sensitivity of the sensor indicates the maximum adsorption of the oxygen taking place at this operating temperature, as operating temperature increases or decreases the adsorption of the oxygen decreases. At the highest sensitivity, the equilibrium of the adsorption rate and desorption rate was achieved.

We have described a microemulsion-mediated reaction using a functionalized surfactant which can be utilized for the synthesis of nanosized films produced by the controlled hydrolysis of tetrabutyl titanate in sorbitol monooleate and polysorbate 80 micelles. The electronic properties of the TiO_2 films obtained were strongly dependent on [Span-Tween 80]/[Ti(OC_4H_9)$_4$]. This work has demonstrated the capability of titania nanostructured films for gas-sensing. In conclusion, we have observed that the film TiO_2 sensor exhibits best sensor characteristics in terms of sensitivity to oxygen partial pressure, which is attributed to the high activation energy and high concentration of defects due to high specific surface area of nano-scale TiO_2.

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Received 28 June 2004
and accepted 16 February 2005