Optical properties and charge transport in nanocrystalline TiO$_2$–In$_2$O$_3$ composite films

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Abstract

This work involves a comparative study of nanocrystalline titanium and indium oxides as well as TiO$_2$–In$_2$O$_3$ composites prepared by a sol–gel method from concentrated hydrous titanium dioxide and indium hydroxide sols. Highly transparent uniform films were fabricated from the sols by a spin-coating technique. TiO$_2$–In$_2$O$_3$ nanocomposites possess pronounced extreme dependencies of both the apparent bandgap and the refractive index on the film composition. No chemical interaction between the oxides was observed during annealing to temperatures between 200 and 700°C. This behavior was attributed to the effect of surface states formed at the nanocrystallite interfaces. Other possible causes of the pronounced dependence of the optical and electronic properties on the TiO$_2$–to-In$_2$O$_3$ ratio are also discussed. Abrupt changes in resistivity, photoresistivity and photocurrent decay time of the composite films were observed for composites where the TiO$_2$ content ranged from 25 to 50 wt.% and are associated with the formation of a three-dimensional infinite cluster of interconnected In$_2$O$_3$ nanoparticles. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the past decade, there has been considerable interest in the structural, optical and transport properties of thin films consisting of nanometer sized semiconductor particles [1]. Sol–gel derived films are very attractive candidates for a variety of new applications in microelectronics, integrated optics, electro- and photoelectrochemistry, sensor devices, etc. Preparation of nanocrystalline heterogeneous composites also offers new possibilities to the development of novel materials. In this case, properties of the composite obtained often cannot be considered as a simple superposition of the properties of the pure components. This is due to strong surface interactions between closely packed nanoparticles in the composite [2,3]. Indeed, taking into account that for nanocrystals the surface-to-volume atomic ratio can be appreciable (e.g. in 5 nm CdSe particles, more than 25% of atoms comprise the surface), the contribution from interparticle boundaries will play an important role even if no new phases are formed. In other words, in a composite material prepared by sintering of two kinds of nanocrystals, a significant portion of atoms will belong to the third ‘component’, i.e. the interface between the nanocrystals.

Titanium dioxide and indium (III) oxide are commonly used materials in optical thin film filters [4], antireflection coatings [5], and sensors [6]. In addition, the optical and electrical properties of doped In$_2$O$_3$ films make them well suited in applications such as conducting window coatings [5,7]. In this work, the fabrication of highly transparent TiO$_2$–In$_2$O$_3$ composite films with various Ti/In ratios using concentrated TiO$_2$ and In(OH)$_3$ sols as well as characterization of their structural, optical and charge transport properties is presented.

2. Experimental

TiO$_2$–In$_2$O$_3$ nanocrystalline films were obtained from stabilized hydrous titanium dioxide and indium hydrox-
ide sols mixed in a definite proportion before their deposition onto a substrate. The titanium dioxide sol was prepared as described in detail in Poznyak et al. [8]. Briefly, the hydrous titanium dioxide precipitate was obtained by titration of TiCl₄ in aqueous HCl solution with NH₄OH solution at 0 °C. The precipitate was then thoroughly washed and ultrasonically treated after addition of HNO₃ to obtain an opalescent stable TiO₂ sol with a concentration of approximately 80 g/l. Variation of both the amount of HNO₃ added and the duration of the ultrasonic treatment enabled the mean size of the particles in the sol to be varied. The indium hydroxide sol was prepared in an analogous fashion using indium nitrate solution (0.25 M) as a starting material. Thin films were deposited onto quartz substrates by spin coating and subsequently heated at 200 °C for 20 min. This procedure was repeated several times to achieve the required film thickness. Finally, the samples were annealed at different temperatures ranging from 200 to 700 °C for 1 h in air. Film thicknesses were estimated, using transmission electron microscopy data, to be 0.12–0.15 μm after four deposition cycles.

Powder X-ray diffraction analysis of the films was performed on a Philips X’Pert diffractometer (Cu Kα radiation). High-resolution transmission electron microscopy (HRTEM), microelectron diffraction and energy-dispersive X-ray analysis (EDX) were carried out using a Philips CM 300 UT microscope operating at 300 kV. TEM samples were prepared from finely divided xerogels annealed at the required temperatures and dispersed in ethanol under sonification. The dispersion was dropped onto a 400-mesh carbon-coated copper grid and the solvent was evaporated immediately. Optical transmission and absorption spectra as well as the specular reflection of the films were measured using Cary 500 UV-Vis-NIR spectrometer (Varian). The refractive indexes were calculated from the specular reflection data for the p-component of monochromatic light incident on the film at variable angles [9]. Electrical and photoconductivity measurements were carried out using a pair of comb-shaped Au electrodes deposited on the quartz substrates (electrode spacing was 100 μm). All measurements were made by the DC method with a solid state electrometer 610C (Keithley Instruments). The polychromatic light from a 100-W xenon lamp equipped with an infrared filter was used for the photocurrent generation. It should be noted that the resistivity of the films studied is strongly influenced by some environmental factors such as humidity and exposure to the scattered visible light. Therefore, the dark resistance of the samples as well as the resistance under illumination were measured in a closed vessel equipped with an optical quartz window and containing P₂O₅ as a drying agent.

3. Results and discussion

3.1. Structural measurements

Fig. 1 shows a set of the X-ray diffraction (XRD) patterns obtained for TiO₂, In₂O₃ and TiO₂–In₂O₃ composite films annealed at 200, 400 and 700 °C. XRD analysis demonstrates that individual sol–gel derived In₂O₃ and TiO₂ films heated at temperatures from 200 to 450 °C consist of nanocrystallites of cubic phase In₂O₃ and anatase TiO₂, respectively. In the individual
TiO$_2$ films, anatase-to-rutile transformation starts to occur at 450–500 °C and is completed in the temperature interval from 700 to 750 °C. XRD patterns of TiO$_2$–In$_2$O$_3$ films heated at different temperatures up to 800 °C do not reveal any additional phases other than those observed for the individual oxide samples. This indicates that the chemical interaction of TiO$_2$ with In$_2$O$_3$ does not occur in the temperature range mentioned. The average sizes of the oxide nanocrystallites estimated from the X-ray line broadening according to Scherrer’s equation are collected in Table 1. These data show evidence that in the binary oxide films, there is a marked suppression of the anatase crystallite growth during the thermal treatment up to 700 °C in comparison with the individual oxide films. Therefore, for TiO$_2$ (50%)–In$_2$O$_3$ (50%) films, the anatase crystallites grow only from 4.3 to 11.1 nm in the temperature interval from 200 to 700 °C. This process, which inhibits crystal growth, was previously observed in a number of multiple oxide systems such as CuO–Fe$_2$O$_3$, Cr$_2$O$_3$–Fe$_2$O$_3$, NiO–Al$_2$O$_3$, Al$_2$O$_3$–ZrO$_2$ and others [10,11]. In these systems the addition of 10–30 mol% of foreign component tended either to retard or even prevent the crystallization of the major component. This effect may be explained by the fact that the particles of one component hinder the interaction between the particles of another component during the heat treatment. The fact that In$_2$O$_3$ nanoparticles in the binary TiO$_2$ (75%)–In$_2$O$_3$ (25%) system start to grow more rapidly at $T>500$ °C in comparison with the individual In$_2$O$_3$ samples, is rather unusual. The nature of this effect is not clear and further studies are needed.

In addition, the anatase-to-rutile transformation in the TiO$_2$–In$_2$O$_3$ samples occurs at markedly higher temperatures as compared with that in the individual oxide samples. It was previously reported that the rate of the anatase-to-rutile conversion is very strongly dependent on impurities and much work has dealt with the influence of additives on this process [12,13]. Thus, the addition of Li$^+$, Cu$^{2+}$, Co$^{2+}$, Mn$^{4+}$ and Cd$^{2+}$ as oxides or fluorides (approx. 1%) was found to promote the polymorphic transformation while Nb$_2$O$_5$, PO$_4^{3-}$ and SO$_4^{2-}$ inhibit this reaction [13,14]. It may be assumed that indium (III) ions as an impurity also inhibit the conversion of anatase to rutile in the TiO$_2$–In$_2$O$_3$ composites. However, we suppose that another reason is, probably, responsible for the effect observed. According to Zhang and Banfield [15], the thermodynamic stability of the TiO$_2$ phases is particle size-dependent, and at particle diameter below approximately 11 nm, anatase is more stable than rutile. Since the growth of anatase particles is retarded in the TiO$_2$–In$_2$O$_3$ systems, these particles reach a size of approximately 11 nm only at 700 °C for the TiO$_2$ (50%)–In$_2$O$_3$ (50%) composite and namely, at this temperature, traces of rutile appear in this composite.

Table 1
The average size (nm) of TiO$_2$ and In$_2$O$_3$ nanocrystallites estimated from the XRD analysis of TiO$_2$–In$_2$O$_3$ composites annealed at different temperatures

<table>
<thead>
<tr>
<th>Composition</th>
<th>Anatase phase</th>
<th>Cubic In$_2$O$_3$ phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$ (100%)</td>
<td>5.1 7.9 62*</td>
<td>200 °C</td>
</tr>
<tr>
<td>TiO$_2$ (75%)–In$_2$O$_3$ (25%)</td>
<td>4.6</td>
<td>4.6</td>
</tr>
<tr>
<td>TiO$_2$ (50%)–In$_2$O$_3$ (50%)</td>
<td>4.3</td>
<td>4.5</td>
</tr>
<tr>
<td>TiO$_2$ (25%)–In$_2$O$_3$ (75%)</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>In$_2$O$_3$ (100%)</td>
<td>18</td>
<td>19</td>
</tr>
</tbody>
</table>

* The average size of rutile crystallites.

3.2. Optical properties

Optical transmission spectra of the sol–gel derived nanocrystalline films reveal their high transparency (> 90%) in the visible region of the spectrum. The spectra of TiO$_2$–In$_2$O$_3$ composite films are characterized by an absorption edge shifted to shorter wavelengths in comparison with those of the individual oxide films (Fig. 3). To estimate the direct band gap values of different samples, we have plotted $(A\ h\omega)^2$ against $h\omega$ (where $A$ is the absorbance, which is proportional to the absorption coefficient $\alpha$, and $h\omega$ is the photon energy) in accordance with common practice [16]. We have not estimated the indirect transition energy from the optical spectra due to the possible influence of thin film...
interference on the low-energy part of the absorption edge. The direct band gap energy vs. film composition dependencies are presented in Fig. 4 for annealing temperatures of 200, 400 and 700 °C. In all cases, the \( E_g \) values are markedly higher in the binary oxide films than in the individual oxides. Maxima of the apparent \( E_g \) were obtained for the composite TiO\(_2\) (50\%)–In\(_2\)O\(_3\) (50\%) (Fig. 4). These extreme dependencies of the absorption edge shift as well as the direct band gap on the composition cannot be explained by the Burstein–Moss effect since the TiO\(_2\) (50\%)–In\(_2\)O\(_3\) (50\%) films show no decrease in the resistivity in comparison with the TiO\(_2\) films (Fig. 5b).

We suppose that the causes of the behavior observed can be rather different for the samples heated at 200, 400 and 700 °C. In a case of the films annealed at 200 °C, removal of the structural water from the films with different composition may substantially affect their optical properties. For films heated at 700 °C, the suppression of the anatase-to-rutile transformation discussed above should be taken into account for adequate analysis of the optical properties. Therefore, XRD analysis shows mainly the rutile phase in the pure TiO\(_2\) samples annealed at 700 °C, while the anatase phase is the predominant component in the TiO\(_2\) (50\%)–In\(_2\)O\(_3\) (50\%) composites. The band gap of rutile is known to be somewhat lower (by 0.15–0.20 eV) than that of anatase [17,18]. The most intriguing case is that of the films heated at 400 °C when the X-ray patterns show only anatase and cubic In\(_2\)O\(_3\) phases for all compositions and no anatase-to-rutile transformation occurs. A blue shift of the absorption edge for the TiO\(_2\)–In\(_2\)O\(_3\) composites in comparison with the single-component films could be explained by the quantum size effect in oxide nanoparticles. However, this explanation is partly con-

Fig. 4. Dependencies of the apparent direct band gap on the film composition for samples annealed at (–Δ–) 200, (–○–) 400 and (–■–) 700 °C.

Fig. 5. (a) Dependence of the refractive index at \( \lambda = 600 \) nm on the film composition for films heated at 400 °C. (b) Dark resistivity and resistivity under illumination as a function of the film composition for films heated at 400 °C. The dashed vertical line shows the calculated film composition corresponding to the formation of three-dimensional infinite cluster of In\(_2\)O\(_3\) nanoparticles.
troubling when compared to recent work of Serpone et al., where no evidence has been found for the band edge shift in anatase sols with the particles’ size ranging from 2.1 to 26.7 nm [17].

The blue-shifted band edge of the TiO$_2$–In$_2$O$_3$ composite films may be associated with an effect of various surface and interface species on the optical spectra. This assumption is based on the results of recent studies devoted to the spectroscopic and structural characterization of other binary oxide systems. The occurrence of Ti–O–Si or Ti–O–Al cross-linking bonds has been revealed for titanium dioxide supported on Vycor glass and silica or dispersed into SiO$_2$ and Al$_2$O$_3$ matrices [19–24]. These bonds modify strongly the electronic state of oxygen and titanium atoms at the particle interface and may be responsible for the band gap enhancement observed [20,22]. Another important consideration is related to the geometry of the oxygen coordination around Ti. Tetrahedrally coordinated titanium atoms have been shown to be present in TiO$_2$–SiO$_2$ and TiO$_2$–Al$_2$O$_3$ systems [20,22,23]. Moreover, five-coordinate Ti sites on anatase surfaces have been revealed by EXAFS and XANES methods in nanostructured TiO$_2$ xerogels [25]. As proposed in these various works, the occurrence of such species, as well as surface species with dangling bonds [e.g., HO–Ti–(OTi)$_3$ or H$_2$O–Ti–(OTi)$_4$] might induce a marked blue shift in the band edge. It should be noted that in the case of nanocrystalline samples, the effect of such species on the optical properties can be significantly more dramatic due to the very high surface-to-volume ratio.

For the TiO$_2$–In$_2$O$_3$ composites, an extreme dependence of the refractive index ($n$) on the film composition is also observed (Fig. 5a). The values of $n$ vary through a wide range from 1.67 for TiO$_2$ (25%)–In$_2$O$_3$ (75%) composite film to 2.30 for individual TiO$_2$ samples. Characteristically, the refractive index of the sol–gel derived TiO$_2$ films matches the range of values (2.2–2.4) reported for different anatase films, whereas the $n$ value of 1.74 obtained for nanocrystalline In$_2$O$_3$ samples is markedly lower than that (approx. 2.0) reported for compact In$_2$O$_3$ thin films [26–28]. The reduced index values for the individual oxides in comparison to their single crystal values seem to be due to the presence of nanoparticles in the nanostructured films. The nature of the anomalous decrease in refractive index of the composite films with decreasing the TiO$_2$ content is not yet completely clear, and additional investigations are needed. A composition-dependent pore volume may account for the observed anomaly. For example, an extreme dependence of the average pore size and pore volume on the silica content has been previously revealed for nanostructured TiO$_2$–SiO$_2$ composites [29].

### 3.3. Electrical measurements

Fig. 5b presents the specific electrical resistivity ($\rho$) measured in the dark and under UV illumination as a function of the composition of the nanocrystalline films heated at 400 °C. The dark resistivity of the binary oxide films rises abruptly from 34 to $3.4 \times 10^7$ Ω cm as the TiO$_2$ content changes from 25 to 50 wt.% (Fig. 5b). Values of the specific resistivity for the composites containing <25 wt.% and >50 wt.% of TiO$_2$ are close to the resistivity of the individual In$_2$O$_3$ (approx. 2 Ω cm) and TiO$_2$ (approx. $8 \times 10^7$ Ω cm) films, respectively. In a similar manner, the photoresistivity measured under UV illumination changes as a function of the TiO$_2$ content in the nanostructured films. According to the previously reported data [30,31], the electronic transport in nanostructured TiO$_2$ films is dispersive and mainly controlled by trapping and detrapping of electrons in nanoparticle surface intra-band-gap states. The conductivity of the TiO$_2$ films is rather low in contrast to the In$_2$O$_3$ films having significantly higher conductivity (Fig. 5b). In this case, the sharp decrease in the resistivity upon lowering of the TiO$_2$ content in the composites may be explained in terms of conduction by a percolation mechanism. The percolation threshold cannot be predicted theoretically in composite materials made of a mixture of conducting and insulating phases having particles with different sizes and shapes [32,33]. Therefore, to calculate the content of In$_2$O$_3$ ($C_{\text{crit}}$) in the composite films which should correspond to the formation of three-dimensional infinite clusters of interconnected In$_2$O$_3$ nanoparticles, we used a value of the critical volume fraction of the conducting phase ($x_c$) which was determined experimentally by Abeles et al. [34]. They studied nanoparticulate W–Al$_2$O$_3$ films with the particle sizes being close to those in the TiO$_2$–In$_2$O$_3$ composites and revealed that the resistivity of the films increased abruptly in the vicinity of $x_c$ equal to 0.47. A value of the $C_{\text{crit}}$ (~62 wt.%) calculated for the TiO$_2$–In$_2$O$_3$ composites using $x_c$ = 0.47, coincides with the concentration range within which the film resistivity changes abruptly (Fig. 5b).

Fig. 6 shows the photocurrent transients after applying UV illumination and also upon switching off the illumination. The ordinate presents the photocurrent divided by the dark current for each sample. The photoconductive sensitivity of the composite films is markedly lower than that of the single-component TiO$_2$ films. The decrease in the photosensitivity may be related to the recombination losses at centres which exist predominantly at the interfaces between TiO$_2$ and In$_2$O$_3$ nanoparticles. The rise and, especially, decay of photocurrents are rather slow, indicating that it is not a pure electronic process. The time for the photocurrent to decay by a factor of 10 and 50 is shown in Fig. 6 (inset) for different film compositions. This time increases sharply...
by several orders of magnitude with decreasing the TiO\textsubscript{2} content from 50 to 25 wt.%. This effect may be associated with reaching the percolation threshold above which the electronic transport occurs predominantly through the network of TiO\textsubscript{2} nanoparticles and below which — through three-dimensional infinite cluster of interconnected In\textsubscript{2}O\textsubscript{3} nanoparticles. It has been previously reported [35,36] that the photoconductivity in In\textsubscript{2}O\textsubscript{3} results from the combined effect of photoexcitation of electrons from the valence band and/or defect levels and photodesorption of oxygen which leaves free electrons in In\textsubscript{2}O\textsubscript{3}. The latter mechanism is considered to predominate in nanoparticle films due to their extremely large specific surface area. Significantly longer photocurrent decay times for the In\textsubscript{2}O\textsubscript{3}-enriched nanoparticle films in comparison to those for the TiO\textsubscript{2}-enriched films may be due to a greater contribution from oxygen involved in photodesorption/adsorption processes in the overall photoconductivity generation process in the former case.

4. Conclusions

In the present work, highly transparent TiO\textsubscript{2}–In\textsubscript{2}O\textsubscript{3} composite films with various Ti/In ratio were fabricated using concentrated TiO\textsubscript{2} and In(OH)\textsubscript{3} sols prepared without organic precursors. Structural transformations in the binary oxide samples studied by the X-ray diffraction method during the thermal treatment (up to 700 °C) of the films show no chemical interaction between indium and titanium oxides. However, a strong mutual influence of the components was observed as the suppression of the anatase crystallite growth during the thermal treatment. Moreover, the optical properties of the composite films exhibit strongly extreme dependencies of the apparent optical band gap and the refractive index on the film composition which could be attributed to an effect of surface states at semiconductor nanoparticle boundaries. The electrical charge transport in the composite films occurs mainly through the network of interconnected In\textsubscript{2}O\textsubscript{3} particles and drastically changes when a three-dimensional infinite cluster of these particles is formed. The photoconductivity decay is very slow for the In\textsubscript{2}O\textsubscript{3}-enriched composite films, which suggests a considerable contribution of oxygen desorption and adsorption to the photoconductivity generation process in these nanoparticulate films.

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