Cracking and Orientation of Solution-Deposited Rutile TiO_2 Films

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In this study, *c*-axis oriented rutile phase TiO_2 films were deposited at 60 °C on silica glass substrates from acidic $TiCl_4$ aqueous solutions. X-ray diffraction and scanning electron microscopy showed that oriented film growth was the result of a combination of preferential growth of the primary crystallites and a geometrical constraint imposed on agglomerating crystallites. It was also observed that the film cracked during drying. The severity of cracking was reduced when the wash solvent was changed from water to methanol. As methanol has a lower surface tension, this indicated that film cracking was due to the high capillary stresses generated during drying and also meant that the film contained nanosized pores.

1. Introduction

TiO_2 exists in three main crystallographic forms, namely brookite, anatase, and rutile, with rutile being the thermodynamically stable form. Because of its higher index of refraction, the rutile form is preferred for optical applications. Rutile TiO_2 single crystals are used as polarizers in many optical communication devices such as isolators, modulators, switches, and interferometers not only because of their high refractive index, but also because of their large birefringence and chemical stability.[1] For use in integrated optical and optoelectronic devices, thin films rather than bulk crystals are essential for miniaturization. A simple and cost efficient method of film deposition is the use of low temperature (<200 °C) aqueous chemical reactions such as in hydrothermal synthesis[2] and liquid-phase deposition.[3] With these low-temperature solution methods the as-synthesized films are crystalline, unlike the sol−gel technique which requires a postdeposition calcination step to crystallize the film.

Presently, films of both the anatase[3−5] and rutile[6−8] phases of TiO_2 have been produced by low-temperature solution methods. In those studies, films were synthesized at temperatures ranging from room temperature to 140 °C. Many of these films were often cracked,[4,5,8] limiting their usefulness. A solution to the cracking of TiO_2 films is important because cracking limits the thickness, optical properties, mechanical integrity, and ultimately the usefulness of solution methods in producing technologically important TiO_2 films.

In this study, the growth of an oriented rutile film with the highest degree of *c*-axis orientation is reported for the first time. This orientation, as revealed by X-ray diffraction, is correlated with the film morphology. Because the ability to control the orientation of the optic axis (the *c*-axis for rutile) is particularly advantageous for optical applications,[9] understanding how film orientation develops is an important first step. In addition, it was determined that the films cracked during drying when high capillary stresses were generated in nanosized pores present in the as-synthesized rutile material.

2. Experimental Section

Films were synthesized by placing substrates previously cleaned with acetone and 2-propanol at the bottom of Teflon-lined acid digestion bombs (Parr, Moline, IL). The silica glass substrates were supplied with a 100-nm amorphous TiO_2 seed layer on one side (Nippon Sheet Glass, Japan). Aqueous precursor solutions consisting of 0.5 M $TiCl_4$ and 2 M HNO_3 were added, and the bomb was sealed and placed in the oven at 60 °C. After the required processing time, the bomb was taken out and allowed to cool to room temperature. Films were then rinsed with deionized water and dried at room temperature. In an attempt to eliminate film cracking, the deionized water rinse for some films was followed by boiling in methanol for 1 h or soaking in methanol for 72 h before drying at room temperature.

Film morphology was examined by field emission scanning electron microscopy (JEOL JSM 6700, Japan) and tapping mode atomic force microscopy (Digital Instruments DI3000, Santa Barbara, CA), whereas phase identification and rocking curves were determined by X-ray diffraction (Philips X'pert, NJ). Nitrogen adsorption and desorption isotherms were carried out at 77 K using a Quantachrome NOVA system after powder samples had been baked in a vacuum at 120 °C for 3 h to remove surface moisture. The pore size distribution was calculated from the nitrogen desorption isotherm using the Barrett−Joyner−Halenda (BJH) method. The transparency of the film in the wavelength range from 200 to 800 nm was measured with a UV−Vis spectrophotometer (UV 3103PC, Shimadzu, Japan).

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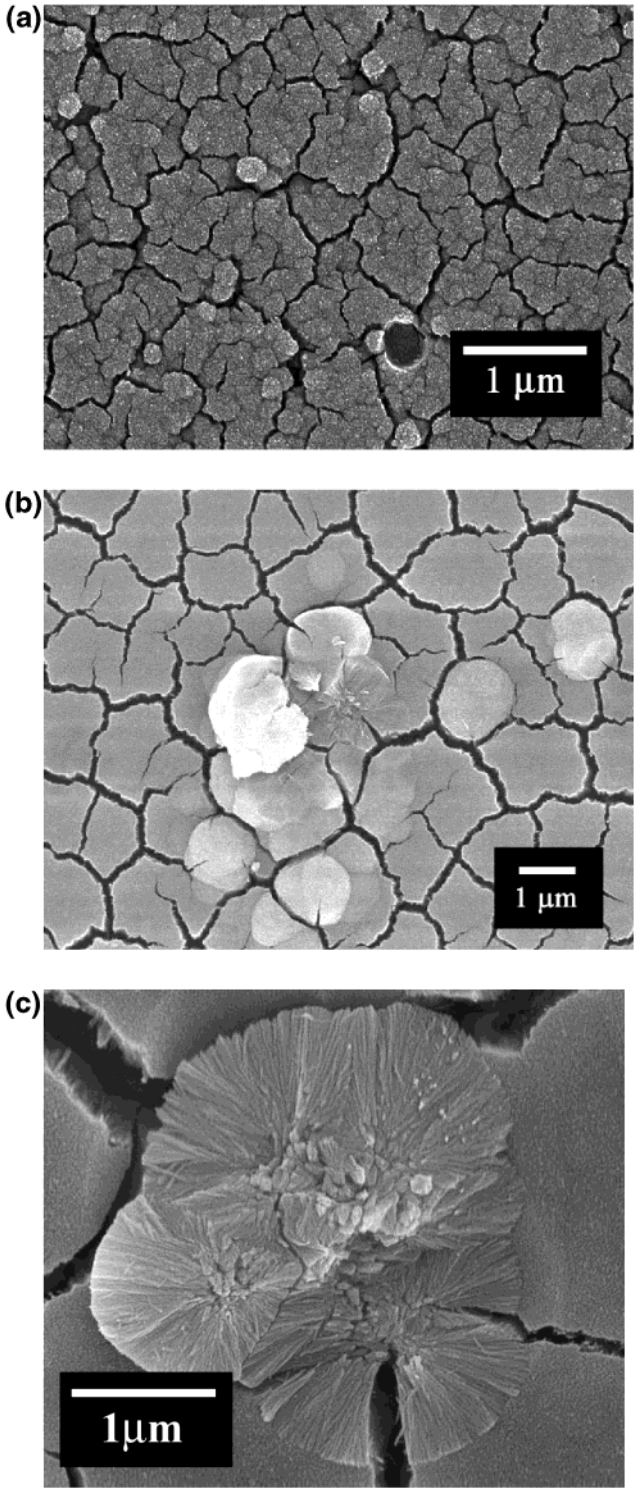

Figure 1. SEM of film synthesized after (a) 8 h and (b) 16 h, and (c) a fractured cluster of embedded particles in the film.

3. Results and Discussion

A scanning electron micrograph (SEM) of a film synthesized after 8 h is shown in Figure 1a. The film is cracked and the rough morphology is reminiscent of solution-synthesized rutile films reported by Yamabi and Imai[8] who deposited rutile films at 60 °C using $TiOSO_4$ as the titanium source. There are also circular pits which apparently are sites where particles were previously embedded. After 16 h (Figure 1b), the film is also cracked but it is smoother. In addition, significantly more powder particles were found embedded in the 16-h film than for the 8-h film. This coincides with the observation that white powder particles are present in solution after 16 h but have not precipitated in significant amounts after 8 h.

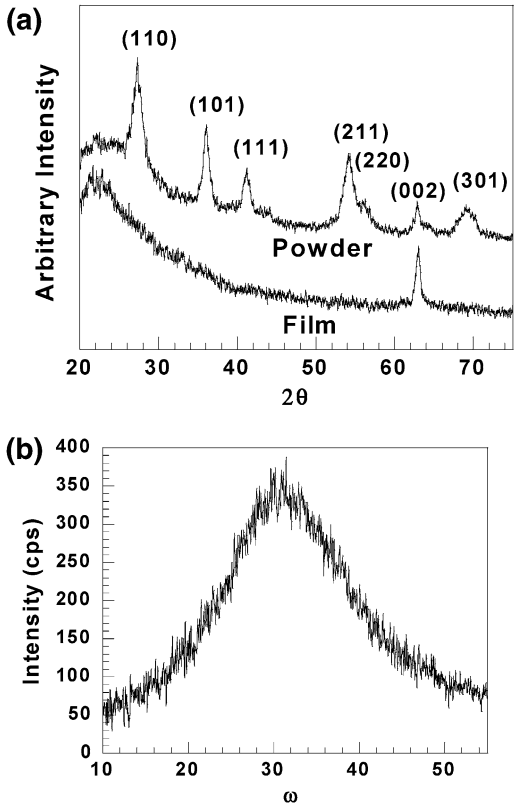

Figure 2. XRD of rutile (a) powder and film synthesized at 60 °C after 16 h with 0.5 M $TiCl_4$/2 M HNO_3 precursor solution, and (b) rocking curve of the (002) peak.

Closer examination of a fractured cluster of particles embedded in the 16-h film (Figure 1c), reveals that each spherical particle consists of whiskers emanating radially from the core. It is believed that the long axis of each whisker is parallel to the *c*-axis of the rutile structure as determined by electron diffraction by Li and co-workers[10] who synthesized individual rutile whiskers hydrothermally at 200 °C in 1 M $TiCl_4$ solutions. This is also supported in this study on the basis of observations of the film cross section and X-ray diffraction results, as presented in the following sections.

X-ray diffraction (XRD) of the synthesized TiO_2 powders confirmed that they had the rutile structure, while the rutile films synthesized along with the powders had a (002) preferred orientation. Figure 2a shows an example of this for the case of rutile material synthesized after 16 h. A rocking curve of the (002) plane (Figure 2b) reveals an extremely broad full width at half-maximum (fwhm) of 18.3°. In oriented film growth, the rocking curve of the out-of-plane peak gives an indication of how parallel that plane is with respect to the substrate surface. Typical values for the fwhm for solution-synthesized films are usually less than 1°.[2,11] Therefore, the extremely broad rocking curve for the oriented rutile film in this study indicates that some of the (002) planes in the films are quite far from being

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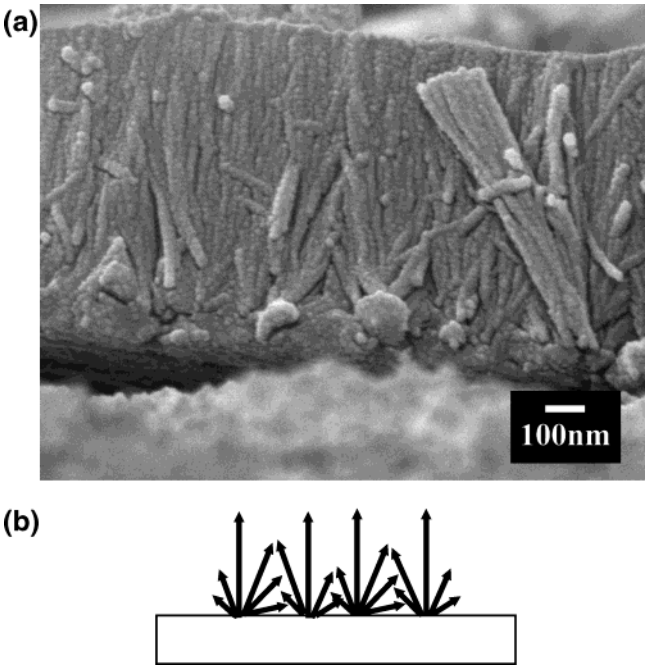

Figure 3. (a) SEM of the cross section of a film synthesized after 16 h, and (b) schematic illustrating development of film's *c*-axis orientation.

parallel to the surface of the substrate. This is because film growth is not truly columnar, as discussed next when the film cross section is examined by SEM.

SEM of the film cross section shown in Figure 3a revealed that the film consisted of whiskerlike crystallites (similar to those observed for the powder particles), most of which are oriented with their long axis normal to the substrate. This observation coupled with the fact that XRD shows a *c*-axis orientation in the film indicates that the long axis of each whisker is parallel to the *c*-axis of the rutile structure, consistent with the electron diffraction observations of Li and co-workers.[10] Closer examination of the interface region (Figure 3a) shows that the whiskers initially emanate almost radially from their nucleation sites, similar to the powder particles.

For the film, whiskers that grow inclined away from the substrate normal obstruct inclined whiskers growing from adjacent nucleation sites on the interface. Therefore, it is mainly the whiskers that are normal to the substrate that grow unobstructed, resulting in the film's *c*-axis orientation. This is illustrated schematically in Figure 3b where the arrows indicate the [002] direction and also the growth direction of each whisker. As the (002) planes of the off-normal whiskers are not parallel to the surface of the substrate, these planes lead to the extremely broad rocking curve observed in Figure 2b.

As for film cracking, the "mud-cracking" type pattern observed (Figure 4a) is an indication that cracking occurred under biaxial tensile stress. Observations by optical microscopy revealed that the film cracked during the drying stage when deionized water was used. When methanol instead of water was used as the drying solvent, the extent of cracking was significantly reduced, as shown by the AFM micrograph in Figure 4b. When the drying rate was decreased by lowering the temperature of methanol-infused film with liquid nitrogen and then letting the film warm slowly to room temperature in a cryostat, crack-free films (Figure 4c) were obtained. This indicated that film shrinkage was induced by high capillary stresses exerted by the meniscus of the drying solvent. This shrinkage was in turn opposed by the film's adherence to the substrate, leading to a state of biaxial tension that eventually caused the film to crack.

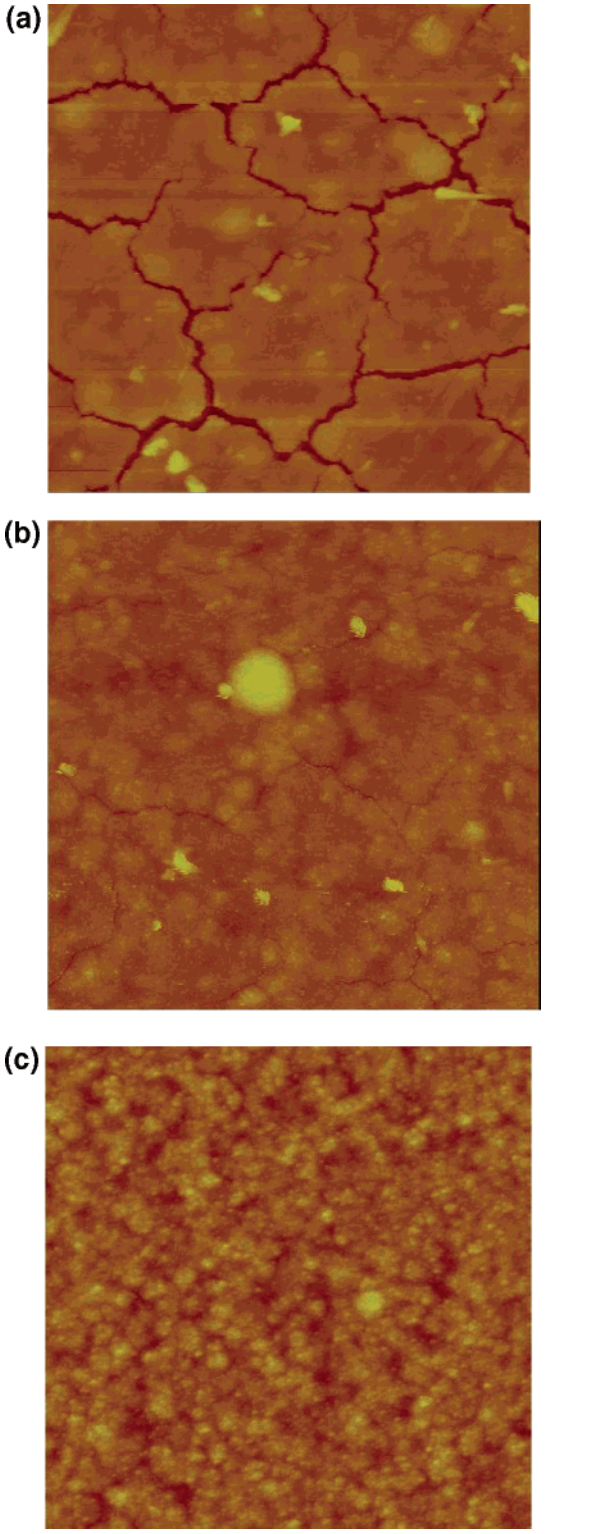

Figure 4. AFM micrographs of films after washing and drying with (a) deionized water and (b) methanol, and (c) after washing in methanol and dried from liquid nitrogen temperature in a cryostat (4×4 μm image size).

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This is often observed in the drying of high-porosity materials such as nanoporous silicon.[12]

The presence of porosity in the as-synthesized rutile material was confirmed by measuring the nitrogen adsorption and desorption isotherms for the rutile powder, as shown in Figure 5a. The pore size distribution calculated using the BJH formula from the desorption branch of the isotherm (Figure 5b) reveals that the pore diameters are mostly less than 10 nm. It is believed that the pores are located between the whiskerlike crystallites. To verify that this is a reasonable location, a close packing of cylindrical crystallites (each of radius R) is assumed, as shown in Figure 5c for 3 crystallites surrounding a pore of radius r. As the triangle connecting the centers of these 3 cylinders forms an equilateral triangle, simple geometry shows that

$$(R + r)\cos 30° = R \tag{1}$$

From Figure 3a, a reasonable estimate of 15 nm for the crystallite radius, R, gives a pore diameter, $2r$, of 4.6 nm. This agrees very well with the experimentally observed pore diameters and reinforces the proposal that the pores are located between the crystallites.

The capillary stress develops as the result of the pressure difference (ΔP) across the liquid−vapor interface of the solvent in a pore of radius, r, and is related to the surface tension (γ) of the meniscus by the Laplace equation

$$\Delta P = -2\gamma\cos\theta/r \tag{2}$$

where θ is the contact angle.[12] Therefore, replacing water, which has a surface tension, γ, of 72×10^{-3} J/m^2, with methanol ($\gamma = 22 \times 10^{-3}$ J/m^2) before drying can reduce the stress in each pore by more than three times during drying. Note that the critical stress required to cause cracking of a nanoporous film could be significantly lower than that for a dense film if the total film porosity is high. The use of an even lower surface tension solvent such as pentane (15.5×10^{-3} J/m^2) may be able to completely prevent film cracking without the need for very slow drying rates. Alternatively, drying techniques such as freeze-drying and supercritical drying in which the liquid−vapor interface is completely avoided could also be effective.[12]

The cracking of solution-deposited TiO_2 films due to their porous structure has serious consequences for their potential applications as films and coatings. Although it may not be too difficult to obtain an initially uncracked film through the use of a suitable drying technique, subsequent use in a wet or very humid environment (e.g., for self-cleaning coatings) would again fill the pores with water. Uncontrolled drying would then generate sufficiently high capillary stresses to crack the coating, possibly causing the coating to lose its porous structure or peel from the underlying support. As there may be a critical film thickness below which the porous film does not crack,[12] more thorough film growth experiments will be required to determine this limit. Even this may not be a suitable solution, as the critical thickness places a limit on film thicknesses allowed. Alternatively, one may increase the size of the pores in the films so that the capillary stress generated is lower (see eq 2) and tolerable for the film thickness required and yet fulfill internal surface area requirements.

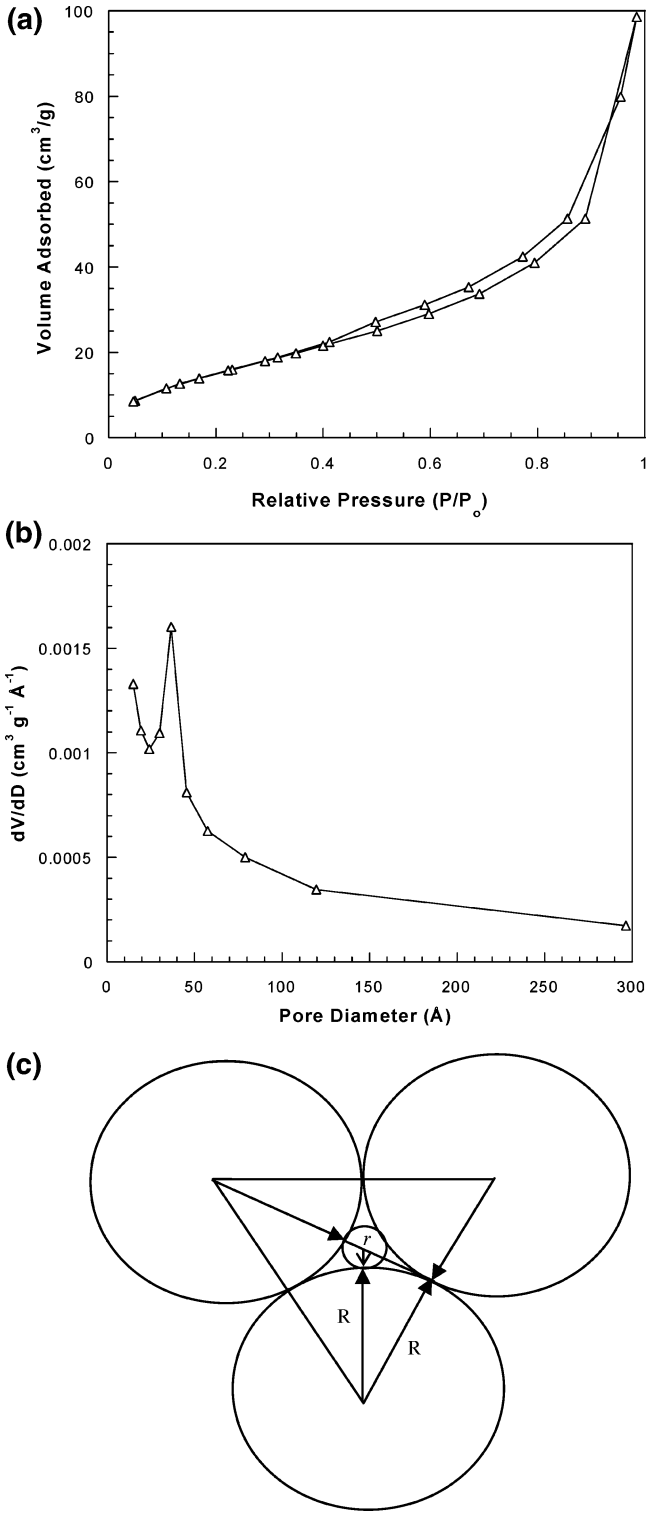

Figure 5. Nanosized porosity in rutile powders synthesized after 16 h at 60 °C as revealed by (a) nitrogen adsorption−desorption isotherms, (b) BJH pore size distribution plot, and (c) a plan-view schematic showing 3 cylindrical crystallites of radius R surrounding a pore of radius r.

Finally, films that had been boiled in methanol before drying so that only closed cracks were present were also tested for optical transparency, as shown in Figure 6 for films synthesized after 8 and 16 h. The fringes are the result of interference between radiation from the air−film and film−substrate interfaces. The presence

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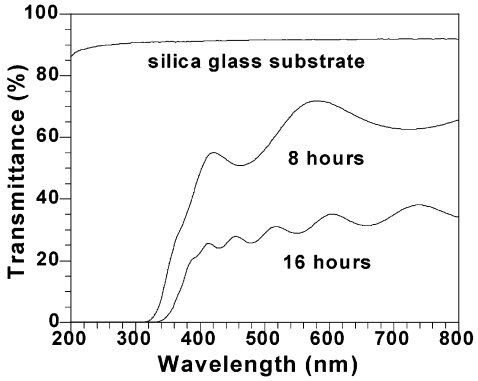

Figure 6. Optical transmittance as a function of wavelength for films synthesized after 8 and 16 h.

of these fringes indicates that the films are quite uniform in thickness, as nonuniform thickness would destroy all interference effects resulting in a smooth transmittance curve. The closer-spaced fringes (or greater number for a given range of wavelengths) for the 16-h film also indicate that the film is thicker than the 8-h film, as would be expected for the longer deposition time. It is believed that the lower transmittance value for the 16 h-film is a result of increased scattering caused by the greater number of embedded powder particles in this film (Figure 1a and b). Work is presently underway to reduce the number of particles embedded so as to improve the transmittance of the films.

4. Conclusions

It was observed that the *c*-axis orientation of rutile films grown in aqueous acidic solutions at 60 °C was not a result of truly columnar growth. Instead, the film grew by the coalescence of islands composed of whiskerlike crystallites emanating almost radially from its initial nucleation site, with the long axis of the these whiskers parallel to the rutile *c*-axis. Subsequently, coalescence of the islands prevented further growth of the lateral and off-normal whiskers, such that only whiskers oriented normal to the substrate could grow further, resulting in the *c*-axis orientation observed.

In addition, it was observed that the film cracked during drying as the result of high capillary stresses exerted by the meniscus of the drying solvent on the walls of nanosized pores as it moved through the film. The porous nature of the rutile material produced was confirmed by nitrogen physisorption, which indicated that most of the pores present had diameters of less than 10 nm. The extent of cracking was significantly reduced by displacing the water used for drying with methanol, a solvent with a surface energy more than three times less than that of water. Slowing the drying rate in addition to the use of methanol leads to a completely crack-free film.

Last, it was observed that particles precipitated in solution became embedded in the growing film. This seriously reduced the transparency of the film.

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