Characteristics of Low-Temperature Annealed TiO_2 Films Deposited by Precipitation from Hydrolyzed $TiCl_4$ Solutions

Kang-Jin Kim,*,† Kurt D. Benkstein,‡ Jao van de Lagemaat,‡ and Arthur J. Frank*,‡

Division of Chemistry and Molecular Engineering, Korea University, 136-701, Korea, and National Renewable Energy Laboratory, Golden, Colorado 80401

Received June 26, 2001. Revised Manuscript Received October 10, 2001

The effect of annealing temperature on the properties of TiO_2 films prepared from hydrolyzed $TiCl_4$ solutions was characterized by X-ray diffraction (XRD) and photoelectrochemical measurements. It is found that the amount of rutile in the TiO_2 films increases from room temperature to 250 °C. Above 250 °C, the amount of crystalline rutile material did not change. Analysis of XRD data suggests that a noncrystalline phase is converted to the rutile phase of TiO_2 by heat treatment of the films. Furthermore, the analysis indicates that the size of the rutile crystallites increases with temperature from about 100 to 400 °C. The photocurrent and conversion efficiency of the cells improved substantially with annealing temperature. The higher photocurrent appears to correlate with the increased crystallinity of the film. The TiO_2 material displayed a photochromic effect.

Introduction

Anatase TiO_2 has been widely regarded as the material of choice for the nanocrystalline metal oxide film used in a novel type of solar cell for the past decade,[1] although a few studies have explored other semiconducting metal oxides such as SnO_2,[2] ZnO,[3] Nb_2O_5,[4] CeO_2,[5] and $SrTiO_3$.[6] The novel solar cell is based on the dye sensitization of nanocrystalline titanium dioxide to visible and near-IR light. Interest in the study of dye-sensitized solar cells stems from their high solar conversion efficiency and their potential amenability to low-cost processing techniques.

Less attention has been paid to the rutile form of TiO_2 possibly because of the expectation that it would yield a lower photovoltage than that of the anatase form because of rutile having a more positive conduction band potential. Surprisingly, however, the photovoltages of anatase and rutile TiO_2 based dye-sensitized solar cells are comparable at one-sunlight intensity.[7] Furthermore, compared to anatase, rutile TiO_2 has superior light-scattering properties because of its higher refractive index, which is beneficial from the perspective of effective light harvesting. Rutile TiO_2 is also chemically more stable and potentially cheaper to produce than anatase. These findings suggest that additional research on rutile TiO_2 from the perspective of solar energy conversion may be fundamentally interesting.

The hydrolysis of $TiCl_4$ is currently the method of choice for depositing highly porous rutile TiO_2 films for dye-sensitized solar cells,[7] although other methods (e.g., chemical vapor deposition and sputtering) for preparing rutile films[8] are available. The hydrolysis of $TiCl_4$ can yield either anatase[9−11] or rutile[7,12] TiO_2 depending on the synthetic conditions used. Rutile is formed when $TiCl_4$ is added to pure water resulting in a low pH solution,[7,12] whereas anatase can be formed in the presence of other components in the reaction mixture (e.g., poly(alkylene oxide) block copolymer[9,10] or sulfate ions[11]).

---

* To whom correspondence should be addressed.

† Korea University.

‡ National Renewable Energy Laboratory.

(1) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737.

(2) (a) Bedja, I.; Hotchandani, S.; Kamat, P. V. *J. Phys. Chem.* **1994**, *98*, 4133. (b) Ferrere, S.; Zaban, A.; Gregg, B. *J. Phys. Chem. B* **1997**, *101*, 4490.

(3) (a) Redmond, G.; Fitzmaurice, D.; Grätzel, M. *Chem. Mater.* **1994**, *6*, 686. (b) Rensmo, H.; Keis, K.; Lindström, H.; Sodergren, S.; Solbrand, A.; Hagfelt, A.; Lindquist, S.-E.; Wang, L. N.; Muhammed, M. *J. Phys. Chem. B* **1997**, *101*, 2598. (c) Rao, T. N.; Bahadur, L. J. *J. Electrochem. Soc.* **1997**, *144*, 179. (d) Keis, K.; Vayssieres, L.; Lindquist, S.-E.; Hagfelt, A. *Nanostruct. Mater.* **1999**, *12*, 487.

(4) (a) Sayama, K.; Sugihara, H.; Arakawa, H. *Chem. Mater.* **1998**, *10*, 3825. (b) Guo, P.; Aegerter, M. A. *Thin Solid Films* **1999**, *351*, 290.

(5) Turkovic, A.; Crnjak, Z. *Sol. Energy Mater. Sol. Cells* **1997**, *45*, 275.

(6) El Zayat, M. Y.; Saed, A. O.; El-Dessouki, M. S. *Int. J. Hydrogen Energy* **1998**, *23*, 259.

(7) (a) Park, N.-G.; Schlichthörl, G.; van de Lagemaat, J.; Cheong, H. M.; Mascarenhas, A.; Frank, A. J. *J. Phys. Chem. B* **1999**, *103*, 3308. (b) Park, N.-G.; van de Lagemaat, J.; Frank, A. J. *J. Phys. Chem. B* **2000**, *104*, 8989.

(8) See, for example: (a) Hitchman, M. L.; Alexandrov, S. E. *Interface* **2001**, *10*, 40. (b) Rodríguez, J.; Gómez, M.; Lindquist, S.-E.; Granqvist, C. G. *Thin Solid Films* **2000**, *360*, 250. (c) Gómez, M.; Lu, J.; Olsson, E.; Hagfeldt, A.; Granqvist, C. G. *Sol. Energy Mater. Sol. Cells* **2000**, *64*, 385.

(9) Kavan, L.; Rathousky, J.; Grätzel, M.; Shklover, V.; Zukal, A. *Microporous Mesoporous Mater.* **2001**, *44*, 653.

(10) Kavan, L.; Rathousky, J.; Gratzel, M.; Shklover, V.; Zukal, A. *J. Phys. Chem. B* **2000**, *104*, 12012.

(11) Zheng, Y.; Shi, E.; Chen, Z.; Li, W.; Hu, X. *J. Mater. Chem.* **2001**, *11*, 1547.

(12) (a) Matijević, E.; Budnik, M.; Meites, L. *J. Colloid Interface Sci.* **1976**, *61*, 302. (b) Harada, H.; Ueda, T. *Chem. Phys. Lett.* **1984**, *106*, 229. (c) Cheng, H.; Ma, J.; Zhao, Z.; Qi, L. *Chem. Mater.* **1995**, *7*, 663.

10.1021/cm0106421 CCC: $22.00

Analyses by intensity-modulated photocurrent spectroscopy along with SEM data suggest that electron transport is slower in the rutile layer than in the anatase layer due to differences in the extent of interparticle connectivity associated with the particle-packing density.[7b] Therefore, producing more densely packed films of smaller nanoparticles is expected to improve the photocurrent. One possible way of achieving this goal is to decrease the annealing temperature of the TiO_2 film. Lowering the annealing temperatures is expected to produce a smaller crystallite size.[13−15] The effect of temperature on the crystallinity of TiO_2 and the overall cell efficiency of cells fabricated with such material is unexplored.

In this paper, we characterize the effect of annealing temperature on the crystallinity of TiO_2 prepared from the hydrolysis of $TiCl_4$ solutions and on the overall conversion efficiency of dye-sensitized solar cells made with the material. The relations of crystallite size, morphology, and surface properties of the films to the current−voltage characteristics were also studied.

Experimental Section

The synthesis and deposition of the TiO_2 films were adapted from the literature.[7] Conducting glass plates (Libbey-Owens-Ford Co., TEC 8 (8 ohm/sq), 75% transmittance in the visible) were used as substrates for depositing nanocrystalline TiO_2 films. The films were grown by precipitation of TiO_2 formed in solutions of hydrolyzed $TiCl_4$ at room temperature. The transparent tin oxide conducting glass plates (1.5 × 1.5 cm) were first cleaned with ethanol and then immersed into hydrolyzed $TiCl_4$ solutions containing a concentration equivalent to 0.2 M TiO_2 for 3 days. The resulting white, nontransparent films deposited onto the plates were rinsed with distilled water and dried for 30 min in an oven at 100 °C. Subsequently, the films were annealed for 1 h at 450 °C or for 12 h at a lower temperature (100−400 °C). The vacuum heating was carried out with a base pressure of 3×10^{-8} Torr.

X-ray diffraction (XRD) patterns of the TiO_2 films were obtained with Cu Kα radiation ($\lambda = 1.5406$ Å) using a SCINTAG DMS-2000. The area under the peak at $2\theta = 36.1°$ corresponding to the rutile (101) plane was analyzed by fitting to a Gaussian or Voigt line shape. It was assumed that films annealed at 450 °C were completely crystalline for determining the relative amount of crystalline material at lower annealing temperature. When measurements were conducted over several days, a specimen from the previous day's sample set was always re-examined for possible variance in the area under the rutile (101) peak. In all cases, the difference between the two measurements was less than the fitting error (i.e., less than ∼1.5% of the total value). The morphology of the film was investigated with a JEOL model 6320F scanning electron microscope. The thickness of the films was measured with a Nikon Labophot2-Pol optical microscope. Thermogravimetric analysis was conducted with a TA Instruments TGA 51 thermogravimetric analyzer; the temperature was increased at a rate of 10 °C/min, and samples were exposed to a continuous stream of N_2.

For photosensitization studies, the TiO_2 electrodes were immersed in acetonitrile/*tert*-butyl alcohol (50:50 v/v) containing 3×10^{-4} M $Ru(LL')(NCS)_2$ (where L = 2,2′-bipyryridyl-4,4′-dicarboxylic acid and L′ = 2,2′-bipyridyl-4,4′-ditetrabutylammoniumcarboxylate) for 72 h at room temperature. The dye-covered electrodes were then rinsed with ethanol and dried under a N_2 stream. Pt counter electrodes with a mirror finish were prepared on a glass plate.[7] The Pt electrode was placed over the dye-coated TiO_2 electrode, and the edges of the cell were sealed with 0.5 mm wide stripes of 50 μm thick Surlyn (Dupont, grade 1601). Sealing was accomplished by pressing the two electrodes together at a pressure of 100 psi and a temperature of about 120 °C. The redox electrolyte was introduced into the cell through one of the two small holes drilled in the counter electrode. The electrolyte consisted of 0.8 M 1,2-dimethyl-3-hexyl imidazolium iodide and 50 mM I_2 in methoxyacetonitrile. A typical cell had an active area of about 0.3 cm^2.

Photocurrent−voltage measurements were performed using an EG&G PAR 173 potentiostat at room temperature. A 1000 W sulfur lamp (Fusion Lighting Inc.) was used as a light source, and its light intensity was adjusted with a Si solar cell equipped with KG-5 filter (Schott) to approximate one-sunlight intensity (100 mW/cm^2). The amount of dye adsorbed to TiO_2 films was determined by absorption measurements of the desorbed dye using an HP 8450A diode array spectrometer. The dye was desorbed from the TiO_2 surface by immersing the electrode in 1 mM KOH aqueous solution.[16]

Photochromic studies were conducted on TiO_2 samples placed in a glass vacuum chamber that was heated using a heating mantle. The light source was a 150 W Xe lamp equipped with a 10 cm long water filter to eliminate unintentional heating of the sample.

Results and Discussion

Figure 1 compares plain-view SEM images of a TiO_2 film dried at ambient temperature (Figure 1a) and a film annealed at 450 °C (Figure 1b). Both films display highly porous structures, consisting of ellipsoidal clusters that were on average about 1.2 μm in length and 0.7 μm in diameter. The ellipsoidal clusters are randomly connected but not close-packed, creating large void volumes inside the film. The size of the clusters in the two films appeared to be essentially the same. Films annealed between 100 and 350 °C exhibited the same morphology as films annealed at room temperature and at 450 °C. At all annealing temperatures, the ellipsoidal clusters appear to consist of large numbers of minute filaments (needles), having an average dimension of 20 × 80 nm and pointing outward from the centers of the clusters (Figure 1c), resembling sea urchins.[17]

A cross-sectional view of TiO_2 films annealed at 100 and 450 °C is shown in Figure 2. Both films show a similar morphology and are composed of two distinct layers: a randomly packed, loosely interconnected layer of needle clusters and a compact base layer directly on top of the tin oxide. The size and shape of the clusters are almost independent of annealing temperature and their location in the film. Furthermore, the clusters had essentially the same morphology as those in Figure 1. These results indicate that the clusters of needles formed in solution precipitate only when a critical mass is reached. The proposed mechanism for film formation is supported by the finding that all films had about the same thickness (ca. 30 μm) regardless of annealing temperature. The invariance of film thickness with annealing temperature is not surprising because, except for water, no volatile materials, such as organic poly-

---

[13] Nam, H.-D.; Lee B.-H., Kim, S.-S., Jung, C.-H., Lee, J.-H., Park, S. *Jpn. J. Appl. Phys.* **1998**, *37*, 4603.

[14] Cheng, H.; Ma, J.; Zhao, Z.; Qi, L. *Chem. Mater.* **1995**, *7*, 663.

[15] Huang, W.; Tang, X.; Wang, Y.; Koltypin, Y.; Gedanken, A. *Chem. Commun.* **2000**, 1415.

[16] Lindström, H.; Rensmo, H.; Södergren, S.; Solbrand, A.; Lindquist, S.-E. *J. Phys. Chem.* **1996**, *100*, 3084.

[17] Park, N.-G.; Chang, S.-H.; van de Lagemaat, J.; Kim, K.-J.; Frank, A. J. *Bull. Korean Chem. Soc.* **2000**, *21*, 985.

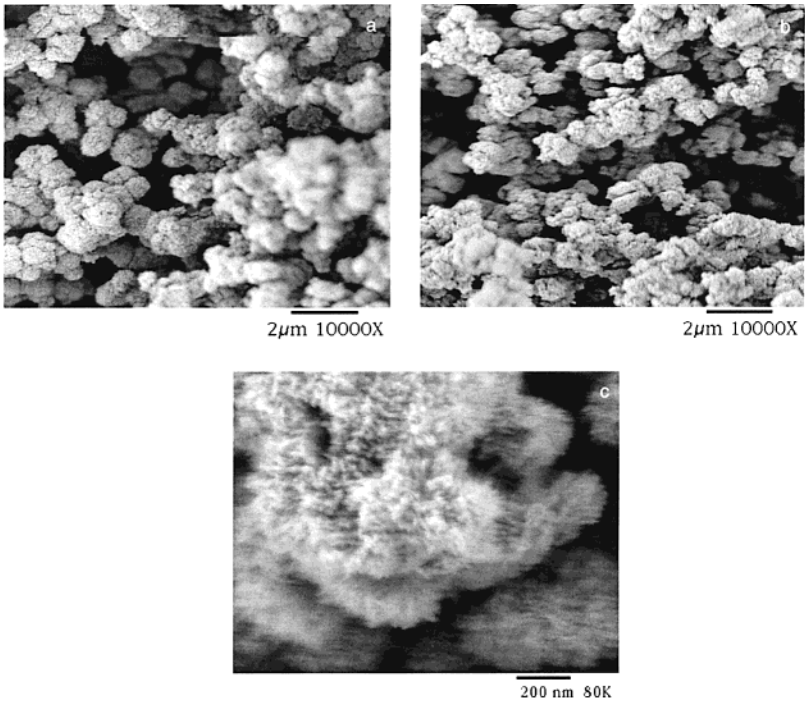

Figure 1. Plain-view SEM images of TiO_2 films annealed at (a) room temperature (10 000× magnification), (b) 450 °C (10 000× magnification), and (c) 450 °C (80 000× magnification).

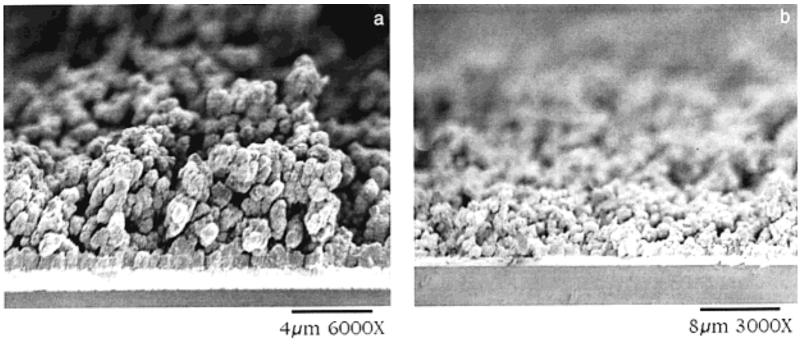

Figure 2. Cross-sectional view of the SEM image of TiO_2 films annealed at (a) 100 °C and (b) 450 °C.

mers, are used for film preparation. The presence of such materials could cause film shrinkage during annealing.

The unique morphology of the base layer on the conducting glass surface indicates that it grows differently than the rest of the film. The base layer is more uniform and more compact than the cluster layer deposited afterward. The contact between the base TiO_2 layer and tin oxide substrate is relatively robust, inasmuch as the films do not flake off while being rinsed. It is noteworthy that the vertical length of the base layer is comparable to the length of a cluster, about 1.2 μm. The base layer grows in a manner that is epitaxial like on the tin oxide surface, while the clusters are formed in solution. The TiO_2 films were deposited on LOF TEC 8 conducting glass. Ordinary slide glass and several other types of conducting glass proved ineffective for this purpose, although conducting glass from Asahi Glass[7] and Nippon Glass Corporations were also suitable substrates for film deposition. The common feature that distinguished the substrates that were effective, from those that were not, was their relatively high haze level (ca. 5%), suggesting that surface roughness may play a role in film deposition.

Figure 3 shows that the TiO_2 films crystallize as rutile regardless of their annealing temperature (T_a). With increasing T_a, the relative area of the (101) diffraction peak (Figure 4, curve a) increases up to an annealing temperature of about 250 °C while the peak width declines, reaching a constant value at temperatures above 250 °C. The analysis of the XRD data suggests that films annealed below 250 °C consist of both crystalline and noncrystalline materials and that the noncrystalline material is progressively converted to rutile with increasing temperature. Contrary to the observation of others,[13,14,18] we find a relatively large amount of rutile TiO_2 is present in films that were simply dried at room temperature. The area under the peak at $2\theta = 36.1°$ for nonannealed films is about half of that for films annealed at 450 °C, indicating that half of the material is already crystalline at room temperature. Using the Scherrer equation [$L = 0.9\lambda/B(2\theta)\cos\theta$, where L is the crystallite size and $B(2\theta)$ is the line width], it is estimated that the crystallite size grows monotonically by a factor of 1.6 from room temperature to 450 °C (Figure 4, curve b). The peak area and peak

---

(18) Xia, B.; Huang, H.; Xie, Y. *Mater. Sci. Eng.* **1999**, *B57*, 150.

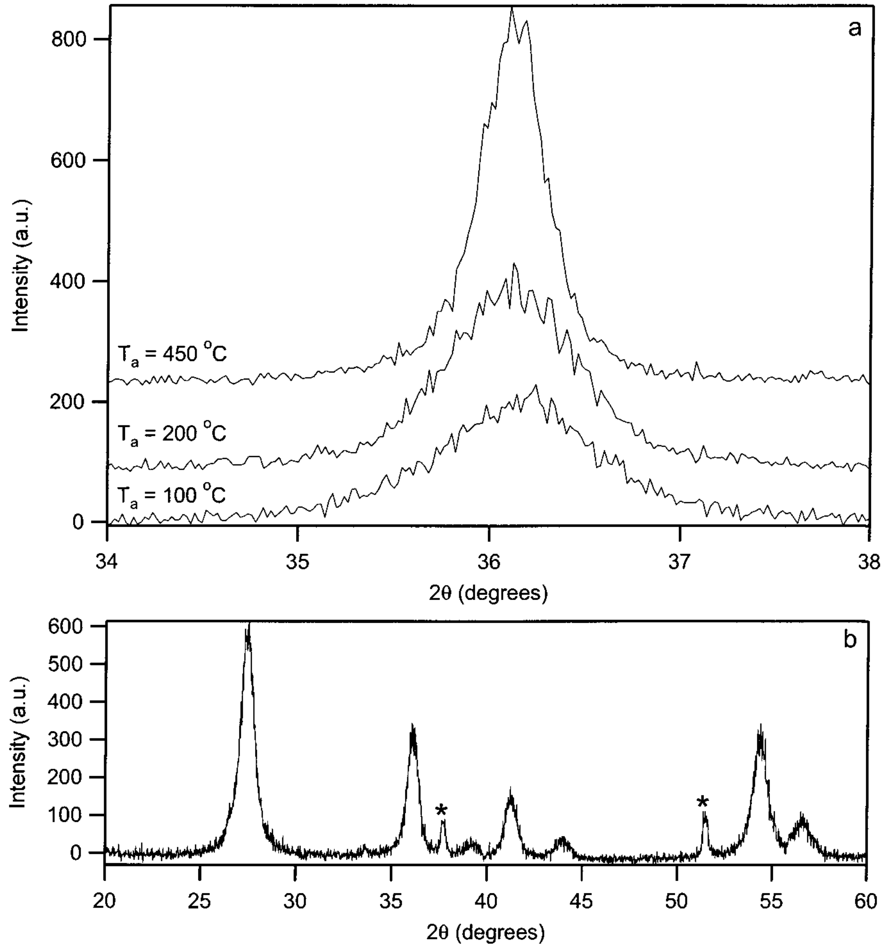

Figure 3. Temperature dependence of the XRD pattern of TiO_2 films for the rutile 101 diffraction peak at $2\theta = 36.1°$ (a) and the full XRD scan of a film annealed at 450 °C (b). The asterisks denote peaks attributed to the SnO_2 substrate.

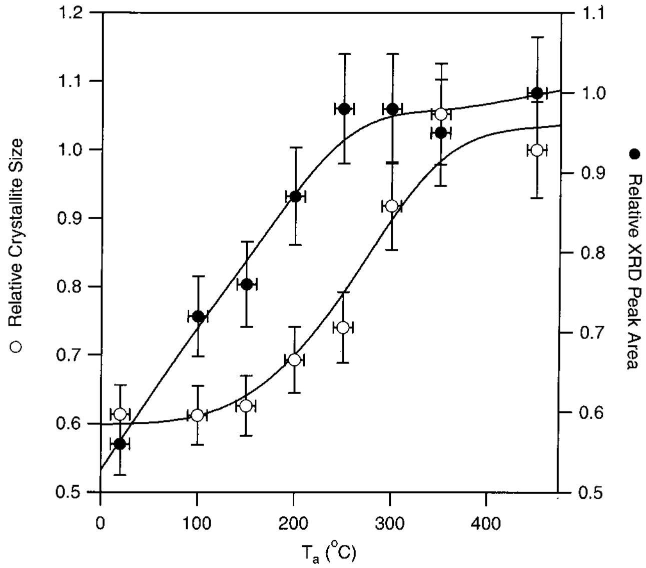

Figure 4. Dependence of the relative peak area and relative crystallite size associated with $2\theta = 36.1°$ (rutile 101) diffraction peak of TiO_2 films annealed at various temperatures.

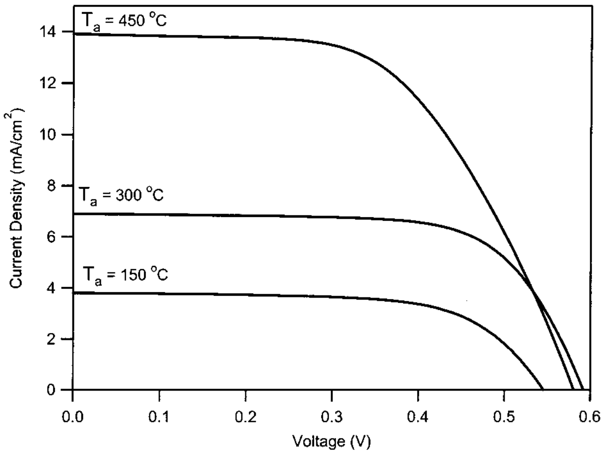

Figure 5. $J-V$ curves for dye-sensitized solar cells prepared with TiO_2 films annealed at several temperatures.

width of other rutile diffraction peaks (e.g., $2\theta = 27.4°$) showed similar trends. These results suggest that the increase of crystallite size with T_a correlates with the conversion of noncrystalline material to the rutile phase of TiO_2. It can be envisioned that before annealing, a filament consists of a crystalline nucleus surrounded by noncrystalline material. During heating, the conversion of noncrystalline to crystalline material probably involves the crystalline nucleus growing outwardly. This mechanism would account for the absence of morphological change with temperature discussed above.

Figures 5 and 6 show the $J-V$ characteristics as a function of annealing temperature for dye-sensitized solar cells prepared with rutile films. It can be seen in Figure 5 and Figure 6a that when T_a increases from 100 to 450 °C, the short-circuit photocurrent density (J_{sc}) increases from 2 to 13.5 mAcm^{-2}, almost a 7-fold

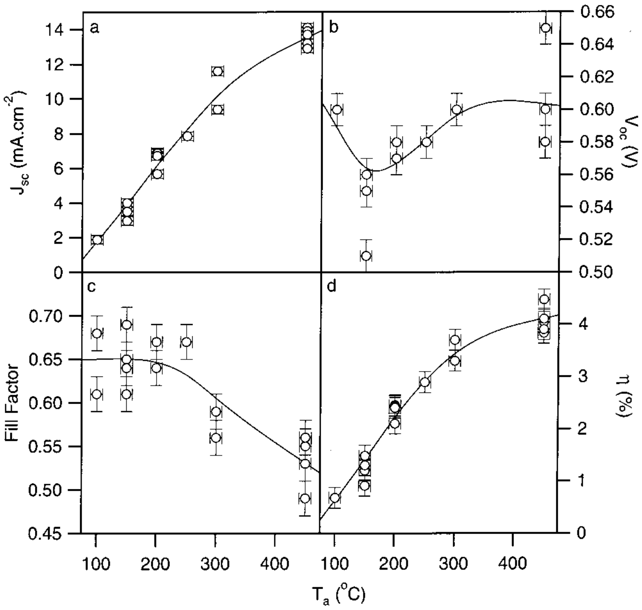

Figure 6. Dependence of the short-circuit photocurrent density (a), open-circuit voltage (b), fill factor (c), and overall energy conversion efficiency (d) on the annealing temperature of films used in the fabrication of dye-sensitized solar cells.

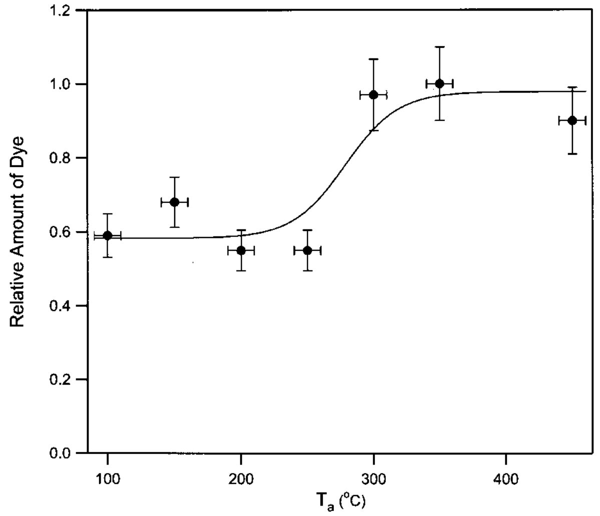

Figure 7. Relative concentration of adsorbed dye on TiO_2 films as a function of the annealing temperature of the films.

increase. Over the same temperature range, the open-circuit photovoltage (V_{oc}) fluctuates between 0.55 and 0.65 V, and the fill factor decreases from 0.65 to 0.55 (Figure 6). As a result of these variations, the overall energy conversion efficiency (η) of the cell increases from 0.7 to about 4%, indicating that the increase of η is almost entirely due to an increase of J_{sc}. A similar observation is reported for TiO_2 films by DC magnetron sputtering.[19]

One explanation for the J_{sc} behavior (Figure 6a) may be related to the amount of dye adsorbed to the film. Figure 7 shows that the amount of dye that desorbs from the surface of films increases with the annealing temperature of the films, indicating that the increase of J_{sc} with annealing temperature is related, in part, to increased amounts of adsorbed dye, i.e., to an improved light-harvesting efficiency. This trend also follows the increase in crystallinity with annealing temperature, suggesting that the dye may adsorb more strongly to the crystalline component of the film than the noncrystalline one. The relative amount of dye is, however, substantially less than the increase of the photocurrent (ca. a 7-fold increase), implying that the dye adsorbs to both noncrystalline and crystalline TiO_2. These results further suggest that the charge-injection efficiency and/or the efficiency of collecting injected electrons increases with the crystallinity of the film. A higher electron-collection efficiency could result from improved interparticle electrical contact associated with the conversion of noncrystalline to crystalline material. Also, as the size of particles increases with T_a, light scattering and, therefore, the light-harvesting efficiency are expected to increase.

Contrary to the strong dependence of J_{sc} on T_a, the open-circuit voltage shows only a slight increase with T_a (Figure 6b). With increasing T_a, the crystallinity of the TiO_2 film increases considerably (Figure 4) along with its surface area. The larger crystalline surface area is expected to increase the number of surface recombination centers, leading to a decrease of V_{oc}.[20] However, the effect of recombination on the photovoltage is probably more than offset by an increase in photocurrent. The combination of both effects likely results in only a small increase of V_{oc} with T_a.

The fill factor (FF) of the cells shows a marked decline with increasing T_a (Figure 6c). Information about the cause of the decrease can be obtained from Figure 5, which shows that the slope of the $J-V$ curves around V_{oc} does not depend strongly on annealing temperature, i.e., the series resistance of the cell does not depend strongly on T_a. This implies that the decrease of the fill factor can be ascribed to an increase of the ohmic drop over the series resistances in the cell owing to the higher photocurrents. The cell resistance is the sum of the sheet resistances of the conducting glass and the counter electrode, the resistance of the substrate/TiO_2 interface, the resistance associated with ion transport in the electrolyte, and the resistance connected with charge transfer at the counter electrode.

Low-temperature heating (100−200 °C) combined with moderately high vacuum did not affect the $J-V$ characteristics and XRD patterns of the films. Also, UV irradiation of the films while heating them under vacuum had no effect on their $J-V$ characteristics and the XRD patterns. In the case of both vacuum and UV irradiation, each of the $J-V$ parameters (J_{sc}, V_{oc}, and FF) was within 5% of each other, and the area under the rutile (101) peak in the XRD data was within the fitting error (1.5%). TGA analysis showed, however, that UV illumination of TiO_2 powder annealed at 100 °C under vacuum did cause a 3 wt % water loss. The amount of water loss from the powder was about half of the water loss observed from TiO_2 powders annealed at 100 °C in the dark at atmospheric pressure. These experiments suggest that water loss at the 3−6 wt % level had no significant effect on the overall photoelectrochemical characteristics of solar cells prepared with films annealed at low temperatures.

---

(19) Gömez, M. M.; Lu, J.; Solis, J. L.; Olsson, E.; Hagfelt, A.; Granqvist, C. G. *J. Phys. Chem. B* **2000**, *104*, 8712.

(20) Schlichthörl, G.; Huang, S. Y.; Sprague, J.; Frank, A. J. *J. Phys. Chem. B* **1997**, *101*, 8141.

The photochromic effect in anatase (Degussa P25) and rutile (Bayer) TiO_2 has been investigated,[21,22] although no correlation of it has been made with combined UV irradiation and heating. In the present study, the influence of both UV irradiation and heat treatment are probed. UV irradiation of the films under vacuum caused them to turn from white to blue, which is indicative of photochromism. The blue color appeared darker for films annealed at 200 °C than for those annealed at 100 °C. Furthermore, the color was much paler when the TiO_2 films had been dehydrated at 200 °C under vacuum for 12 h before UV irradiation. The absorption spectrum of (thin) films, which had been irradiated with UV light under vacuum, showed a broad band, which displayed a continuous rise beginning at 550 nm and extending into the near-IR. The dark blue color was stable under the vacuum but rapidly disappeared upon exposure to air. This behavior contrasts with that of WO_3. The color of WO_3 films is stable at room temperature but disappears when the films are heated at 300 °C in air.[23] When UV irradiation of the films was momentarily blocked, the pressure in the vacuum chamber decreased by 10−20%, suggesting that the photolysis produced gaseous materials. A likely candidate is O_2 from either the photo-oxidation of adsorbed water or the creation of oxygen vacancies. In the first case, O_2 may be produced by the reaction of photogenerated holes with water (in Kröger-Vink notation).[24]

$$h^{\bullet} + H_2O \leftrightarrow 2H_i^{\bullet} + 1/2O_2 \qquad (1)$$

This reaction could lead to the stabilization of photoinjected electrons and possible intercalation of protons into the TiO_2 film. Another possibility that is consistent with O_2 evolution and the photochromic effect is the formation of oxygen vacancies in the TiO_2. As in the case of eq 1, this would generate electrons in the conduction band.[25,26]

$$TiO_2 \leftrightarrow V_O^{\bullet\bullet} + 2e' + 1/2O_2 \qquad (2)$$

Irradiating the TiO_2 films under vacuum is expected to accelerate the creation of the oxygen vacancies. Whether electrons are introduced into the TiO_2 films by the oxidation of water or the creation of oxygen vacancies, one expects, as is observed, that exposing the films to oxygen quickly results in the films turning from blue to white, suppressing the photochromism.

Conclusion

The properties of low-temperature annealed TiO_2 films deposited by precipitation from hydrolyzed $TiCl_4$ solutions were investigated by XRD and photoelectrochemical measurements. Regardless of the annealing temperature (T_a), which ranged from 25 to 450 °C, the films crystallized as rutile TiO_2. The crystallinity gradually increased as T_a increased from room temperature to about 250 °C and then leveled off. However, the size of the rutile crystallites increased from a temperature of about 100−400 °C. The film consisted of randomly interconnected but loosely packed clusters that were about 1.2 μm in length and 0.7 μm in diameter. Each cluster was composed of fine filaments with a dimensions of about 20 × 80 nm. The photocurrent and conversion efficiency of the cells improved substantially with annealing temperature. The higher photocurrent was correlated with the increased crystallinity of the film and several related factors. The decrease of the fill factor can be ascribed to an increase of the ohmic drop over the series resistances in the cell due to increased current. The TiO_2 films under vacuum displayed a photochromic effect, which had no influence on the $J-V$ characteristics of the cells.

Acknowledgment. This work was supported by the Center for Electro- and Photo-Responsive Molecules and by the Office of Science, Division of Chemical Sciences and the Office of Utility Technologies, Division of Photovoltaics, U.S. Department of Energy, under contract DE-AC36-99GO10337.

CM0106421

---

(21) Highfield, J. G.; Grätzel, M. *J. Phys. Chem*. **1988**, *92*, 464.

(22) Su, L.; Lu, Z. *Spectrochim. Acta, Part A* **1997**, *53A*, 1719.

(23) Colton, R. J.; Guzman, A. M.; Rabalais, J. W. *Acc. Chem. Res.* **1978,** *11*, 170.

(24) Szczepankiewicz, S. H.; Colussi, A. J.; Hoffmann, M. R. *J Phys. Chem. B* **2000**, *104*, 9842.

(25) Zhong, Q.; Vohs, J. M.; Bonnell, D. A. *J. Am. Ceram. Soc.* **1993** *76*, 1137.

(26) Zerfoss, S.; Stokes, R. G.; Moore, C. H., Jr. *J. Phys. Chem*. **1948**, *16*, 1166.