Materials Science-Poland, Vol. 23, No. 1, 2005

The effect of poly(ethylene glycol) on the crystallisation and phase transitions of nanocrystalline TiO_2 thin films

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Titanium dioxide (TiO_2) films, composed mainly of anatase nanocrystallites, have been obtained from a low temperature poly(ethylene glycol) (PEG) modified sol-gel method. The maximum process temperature in this method is around 90 °C. An addition of PEG in the films accelerates the formation of anatase nanocrystallites. In order to better understand the nature of the influence of PEG on film crystallization, sol-gel solutions were prepared with PEG of different molecular weights (200, 400 and 600). The reference solution without PEG was also prepared. In addition, the influence of different PEG chain lengths on the films' phase transition from anatase to rutile was studied by means of Raman spectroscopy and XRD. Anatase was found to be stable up to 900–1000 °C, depending on the molecular weight of the PEG used in the films.

Key words: *nanocrystalline titania films; sol-gel, poly(ethylene glycol) (PEG); phase transition; Raman; XRD*

1. Introduction

Titanium dioxide films are used in technological applications such as optical filters, optical wave-guides, chemical sensors, solar cells, thin film capacitors, and electrochromic materials [1–10]. Especially, the nanostructured (NS) form of these films has attracted the attention of researchers, because their porous nature and large internal surface enhances their performance compared to traditional coarse-grained (CG) films [11]. Thin films of titania (TiO_2) composed of nanosized particles in the anatase form show a very high photocatalytic activity due to their large internal surface [12].

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Both the optical properties and the photocatalytic activity of TiO_2 coatings depend on the crystallite size, the phase, and porosity of the coatings. Hence, the micro- or nanostructure of the TiO_2 films and their strict control through the preparation methodology is of paramount importance. Recently, significant effort has been directed towards the low-temperature transformation of TiO_2 by using the sol-gel process. In a previous work, we have found that nanostructured anatase phase TiO_2 thin films can be fabricated by a sol-gel method at temperatures as low as 100 °C [7]. These films, with nanometric (5 nm) grain size, were obtained by using a structure-directing agent such as poly(ethylene glycol) (PEG).

We report on the synthesis of TiO_2 nanocrystalline thin films with a low-temperature method by treating the sol-gel deposited TiO_2 films in hot water. Nanoscale anatase films have been obtained by using PEG as a templating agent. In order to better understand the nature of the influence of PEG on film crystallization, sol-gel solutions were prepared in the presence of PEG of different molecular weights (200, 400 and 600). In addition, the influence of the PEG chain lengths on the film's phase transition from anatase to rutile was studied using Raman and XRD.

2. Experimental

In the preparation of PEG-containing TiO_2 films, titanium tetra-*n*-butoxide (TTB) obtained from Aldrich Chem Co. was used as the starting material. The concentration of TTB in the solution was 0.5 mol/L. TTB was first mixed with a small amount of ethanol in a container and stirred for 30 min. A mixture of water containing 3 wt. % HCl and ethanol was poured under stirring into the transparent solution to promote hydrolysis; the molar ratio of H_2O to TTB was 1:1. Finally, an organic polymer (PEG) was added slowly to this solution and stirred for one hour. The resulting solution was used for the TiO_2 film coating. The sol-gel solutions were prepared in the presence of PEG of various molecular weights (200, 400 and 600). The molar ratio of PEG to TTB was 1. A reference solution without PEG was prepared as well.

Films annealed at 400 °C and below were coated on corning glass substrates, whereas films annealed at temperatures from 500 to 1000 °C were deposited on vitreous silica. A dip-coating apparatus constructed in our laboratory was used for the depositions. The substrate was lowered into the coating solution and then withdrawn at a regulated speed of 4 mm/s. After each coating, the films were first dried at 60 °C for 2 minutes and then heat-treated at 90 °C for 1 hour in air inside an oven. These samples were then treated in hot water at 90 °C for 1 hour. Thereafter, the films were heated at a rate of 0.5 °C to annealing temperatures ranging between 100 to 1000 °C in order to study their evolution. The samples were held at the peak temperature for one hour and then cooled to room temperature.

Raman spectra were collected at room temperature with a Jobin-Yvon Labram HR combined Raman-IR microanalytical spectrometer equipped with a motorized *xy* stage and autofocus. The spectra were generated with excitation at 632.8 nm and were dispersed with an 1800 gr/mm grating across the 0.8 m length of the spectrograph. The laser power was kept low in order to avoid undesired heating effects on the samples. The spectral resolution of this apparatus is approximately 0.5 cm^{-1}.

X-ray diffraction measurements were carried out with a custom-built diffractometer equipped with a graphite monochromator and analyser crystals. The data were taken in reflection mode with $Cu_{K\alpha}$ radiation (λ = 0.1542 nm). The signal measured from the glass and quartz substrates was subtracted from the data. The data are shown in Figs. 7–10 as a function of the length of the scattering vector, $q = 4\pi\lambda^{-1}\sin\theta$, where 2θ is the scattering angle. The crystalline phases were identified using the ICDD/JCPDS database [13]. Crystal sizes were determined based on the anatase (101) and (200) peaks using the Scherrer formula [14].

3. Results and discussion

3.1. FTIR and Raman microspectroscopy

Figure 1 shows the Raman (1a – IR) and FTIR (1a – IR) spectra of the as-deposited TiO_2 film containing PEG on a glass substrate (the molecular weight of PEG was 600 in this film). Raman and IR spectra were recorded at the same point of the sample, by using the SameSpot technology. The a-IR infrared absorption spectrum shows a ν_{OH} at 3457 cm^{-1}, assigned by us to PEG hydrogen bonded to TiO_2 [15]. It is known that PEG molecules adsorb exothermically onto TiO_2 oligomers by forming hydrogen bonds between oxygen atoms in the PEG and hydroxyl groups on the TiO_2 oligomers [16]. The bands at 2862, 1462, and 1347 cm^{-1} correspond to C–H vibrations, while the bands centred at 1093 and 1246 cm^{-1} originate in the C–O–C bonds of PEG. The Raman spectrum (1a – IR), measured at the same spot, shows only the PEG bands. The O–H stretching band seen in the FTIR spectra at 3457 cm^{-1} is not observed in Raman spectrum.

Figure 2 shows spectral changes occurring in the film when heated to 90 °C in hot water for an hour. Once again, the Raman (a-R) and FTIR (a-IR) spectra were recorded at the same point. The most significant Raman bands appear at 150, 399, 522, and 646 cm^{-1}. They correspond to TiO_2 modes in the anatase phase [17]. The main anatase band is shifted to a higher frequency (150 cm^{-1}) compared to that of the bulk (144 cm^{-1}). The FTIR spectrum changes entirely (Fig. 2a-IR) when the film is immersed in boiling water for one hour. The bands corresponding to PEG disappear almost entirely with hot water treatment, indicating that the PEG molecules leach out of the film. Matsuda [18] showed that during heat treatment in air PEG starts to decompose only around 250 °C and that the temperature of at least 300 °C is necessary to completely remove PEG from the film.

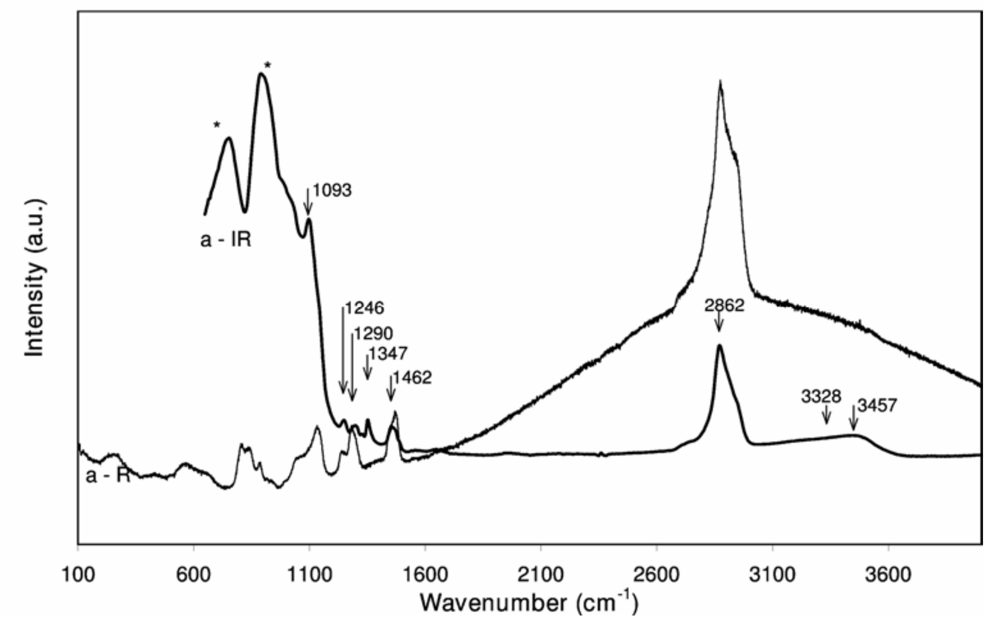

Fig. 1. Raman and FTIR spectra recorded at the same point of the as-deposited TiO_2-PEG 600 (TiO_2:PEG molar ratio of 1:1) composite film on a glass substrate. The peaks of the glass substrate are marked by asterisks

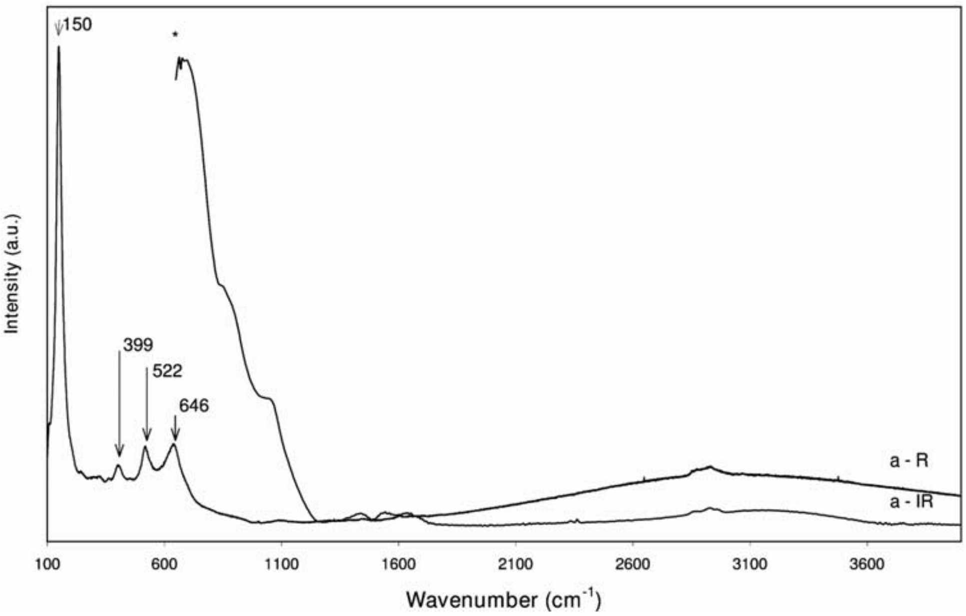

Fig. 2. Raman and FTIR spectra recorded at a single point of a TiO_2-PEG 600 composite film on a glass substrate, treated at 90 °C in hot water for 1 hour. The peaks of the glass substrate are marked by an asterisk

3.2. Raman spectroscopy

Figure 3 shows the Raman spectra of samples prepared from PEG-free dipping solution and treated at 90 °C in hot water. After that, the films were annealed at the temperature ranging from 100 to 1000 °C. The Raman spectra of the films annealed up to 300 °C showed they were quasi-amorphous. The TiO_2 started to be transformed to anatase at 400 °C, and the transition was completed at 500 °C. Only typical features of anatase are present in the spectra until the temperature of the film reaches 1000 °C. At this temperature, a mixed anatase-rutile phase is seen. The formation of anatase nanocrystals was not observed in PEG-free TiO_2 even when the films were treated in hot water for more than 5 hours. Thus, it is evident that the formation of anatase nanocrystals with hot water treatment is initiated and accelerated by the addition of PEG to the dipping solution.

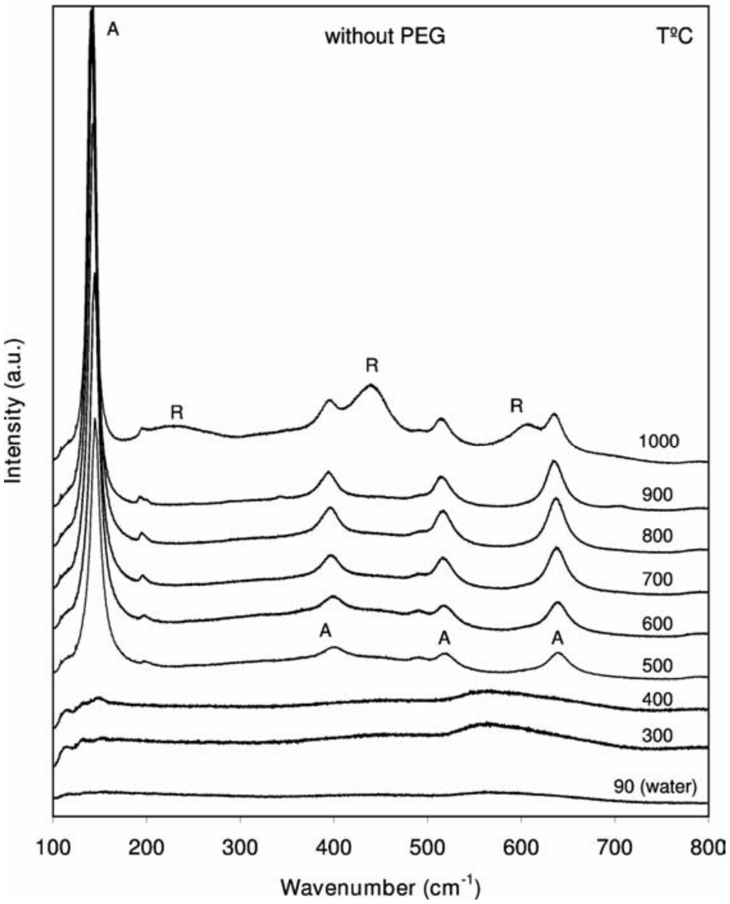

Fig. 3. Raman spectra of TiO_2 films prepared without PEG as a function of temperature; A and R indicate anatase and rutile, respectively

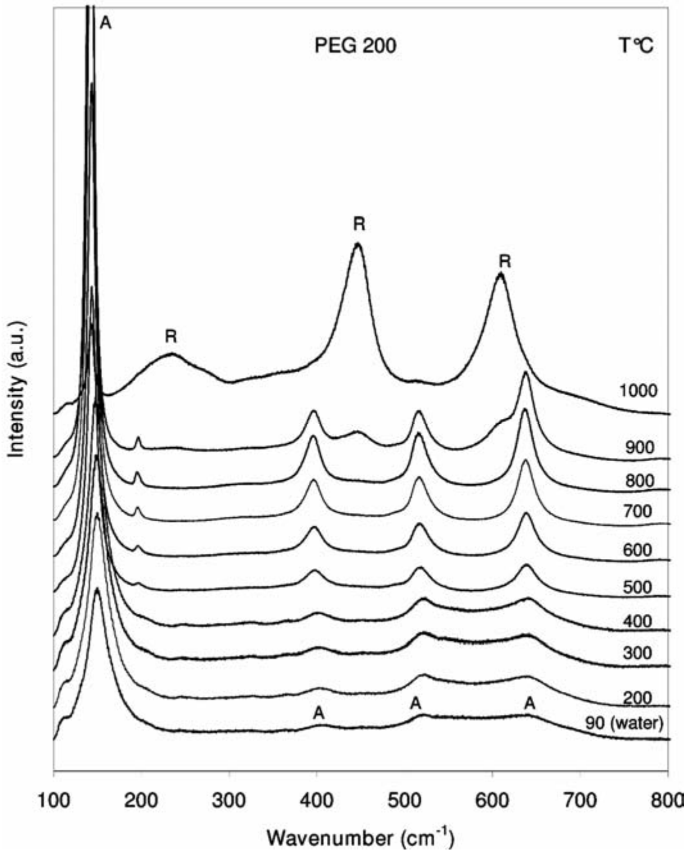

Fig. 4. Raman spectra of TiO_2 films prepared with PEG 200 as a function of temperature; A and R indicate anatase and rutile, respectively

Figures 4–6 show the Raman spectra of samples prepared in the presence of PEG of various molecular weights (200, 400 and 600) and treated at 90 °C in hot water. Subsequently, films were annealed at the temperatures ranging from 100 °C to 1000 °C. The crystallization to anatase was complete when the film was treated in hot water at 90 °C for 1 hour (Figs. 4–6). Only small differences are observed between the spectra. This indicates that there is no systematic effect of PEG molecular weight on the TiO_2 film. In films prepared with PEG 200 and 600, the anatase phase is stable up to 800 °C, followed by a partial transformation to rutile at 900 °C. This transformation is almost complete after annealing at 1000 °C (Figs. 4 and 6). Figure 5 shows that only a partial anatase-to-rutile transformation occurs at 1000 °C for samples prepared with PEG 400.

For samples containing PEG and annealed at low temperatures, the anatase Raman bands are blue-shifted and broadened with respect to the single-crystal spectrum. With increasing temperature, the frequency and width of the peaks tend towards single -crystal values. Using a phonon confinement model [19], it is possible to obtain a rough estimate of the crystal size from the width and position of the main anatase Raman peak. In the sample prepared with PEG 200 and treated in hot water for 1 h, the anatase main Raman peak is centred at 151.5 cm^{-1} (the bulk value being 144 cm^{-1}), with a full width at half maximum (FWHM) of 23 cm^{-1} (7 cm^{-1} being the bulk value). This corresponds to the crystal size of 6.2 nm. For the films prepared with PEG 400 and PEG 600 and treated in the same way, the peak frequency is centred at 151 and 150.5 cm^{-1} with the FWHM of 21.5 and 22 cm^{-1}, corresponding to the crystal size of 8 and 7.4 nm, respectively. We can attribute such large shifts and broadening of the main Raman bands of the anatase phase mainly to the particle size effect [17, 20–23].

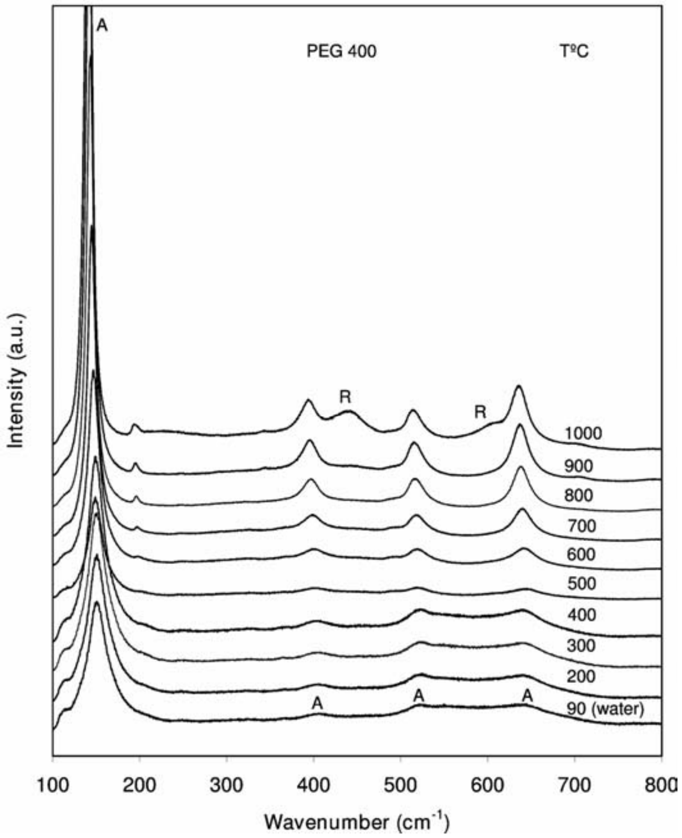

Fig. 5. Raman spectra of TiO_2 films prepared with PEG 400 as a function of temperature; A and R indicate anatase and rutile, respectively

However, the non-stoichiometry of anatase, which is likely to contain defects such as hydroxyl groups or oxygen vacancies as a result of the low temperature of synthesis (90 °C in hot water), is known to produce significant broadening and frequency shifts of the main anatase band [17]. Again, the evolution of the crystallite size is largely independent of the molecular weight of the PEG used in sample preparation.

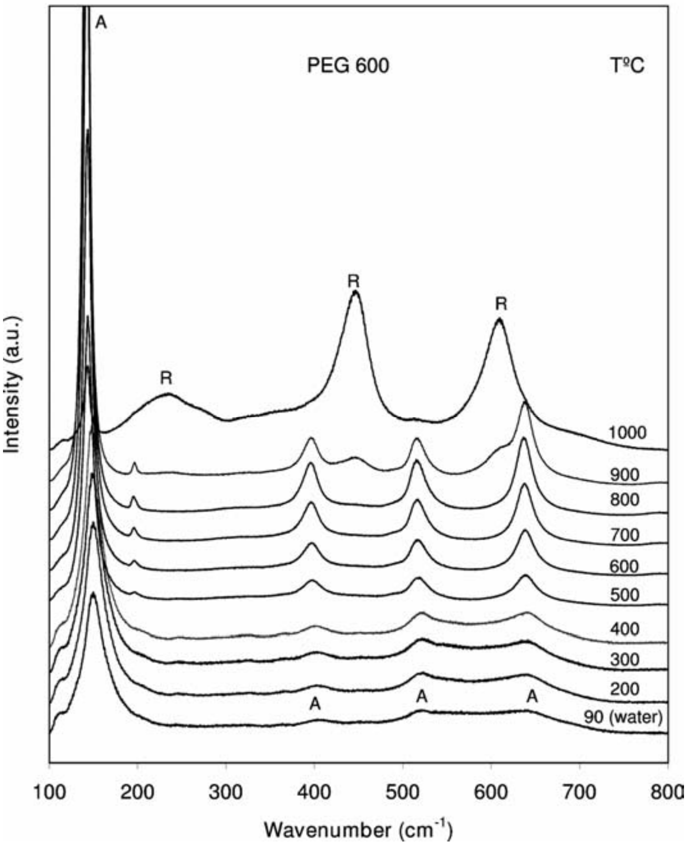

Fig. 6. Raman spectra of TiO_2 films prepared with PEG 600 as a function of temperature; A and R indicate anatase and rutile, respectively

3.3. X-Ray Diffraction

Samples without PEG, prepared on glass slides at annealing temperatures not higher than 400 °C, show no signs of crystallization (Fig. 7). Samples without PEG prepared on vitreous silica substrates show anatase crystals. After annealing at 1000 °C, anatase crystals coexist with rutile. Enhancement of the (110), (220), and (330) peaks, at 19.35, 38.70 and 58.03 nm, indicates the preferred orientation of the rutile crystallites. A rocking centre measurement shows that these crystallites are aligned to within 6.5° FWHM with the substrate surface.

Samples prepared with PEG 200, PEG 400, and PEG 600 evolve in nearly identical ways upon heating (Figs. 8–10). The as-deposited films scatter X-rays below 5 nm^{-1}, as well as between 11 and 18 nm^{-1}. Treatment in water at 90°C eliminates most of this diffuse scattering, and leads to nanoscale anatase crystals. Annealing after treatment in hot water leads to a sharper anatase (101) peak at 17.85 nm^{-1}. The anatase (200) peak at 33.21 nm^{-1} is the second prominent peak of this phase. The absence of the brookite (121) peak at 21.67 nm^{-1} indicates that brookite does not form. The XRD data are in good agreement with the Raman results discussed above. For the film prepared from PEG-free dipping solution, however, no anatase phase can be seen in the XRD pattern (Fig. 7) corresponding to 400 °C. Generally, Raman scattering is more sensitive than X-ray diffraction to small quantities of anatase [24].

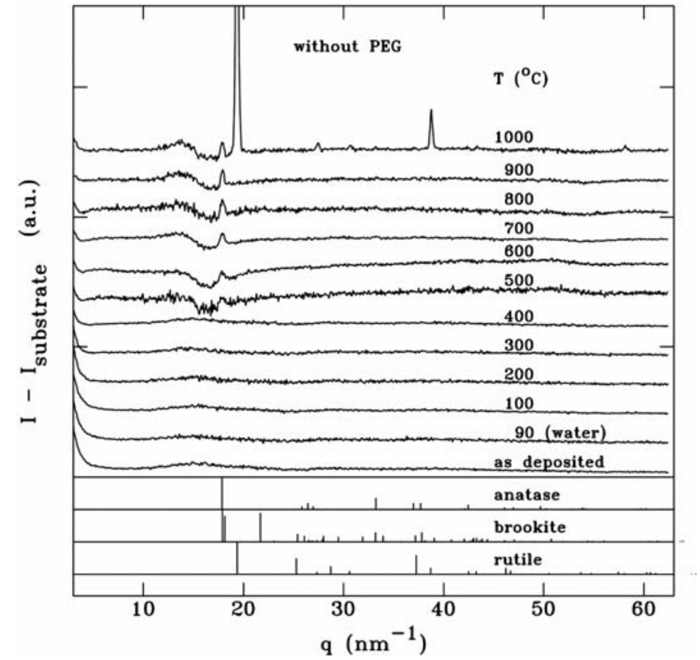

Fig. 7. X-ray scattering intensities of films without PEG as a function of the scattering vector. The scattering originating from an empty substrate was subtracted. The films were annealed at the indicated temperatures (100 °C and above). The powder scattering intensities for anatase, brookite, and rutile are shown at the bottom of the diagram

The evolution of crystal size is shown in Fig. 11. After treatment in hot water, the crystallite size is about 5 nm. Upon annealing at temperatures not higher than 400 °C, crystallite size remains unchanged, increasing continuously to about 19 nm as the annealing temperature is raised to 900 °C, followed by a (partial) transformation to rutile at 1000 °C. The width of the anatase (101) peaks are, within experimental error, equal to the width of the anatase (200) peaks. This indicates that the peak width is indeed caused by small crystal size rather than strain. Considering the additional broadening effects in the Raman spectra, the crystallite sizes calculated from XRD and Raman are consistent. Furthermore, the evolution of the crystallite sizes is largely independent of the molecular weight of the PEG used in sample preparation.

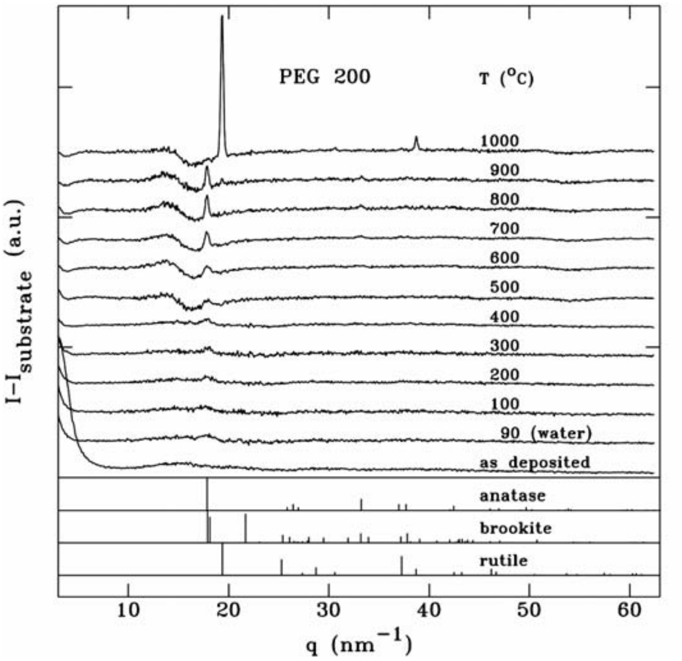

Fig. 8. X-ray scattering intensities of films with PEG 200 as a function of the the scattering vector

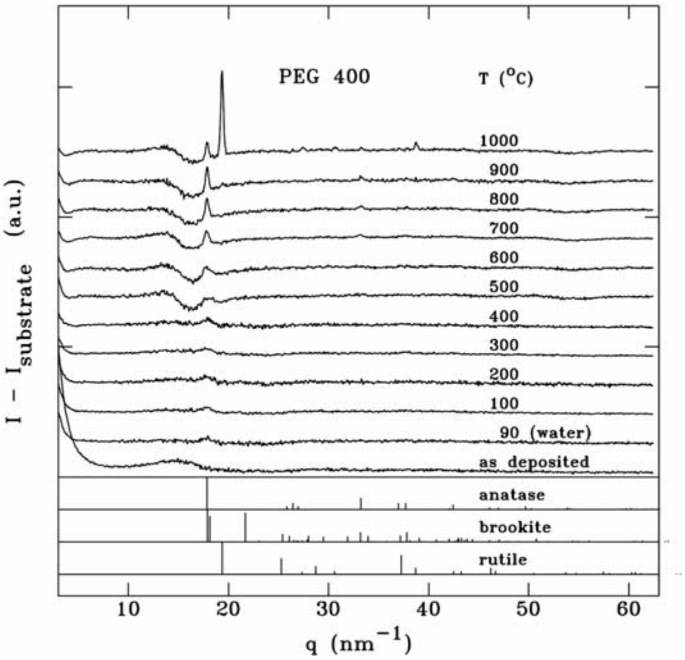

Fig. 9. X-ray scattering intensities of films with PEG 400 as a function of the scattering the vector

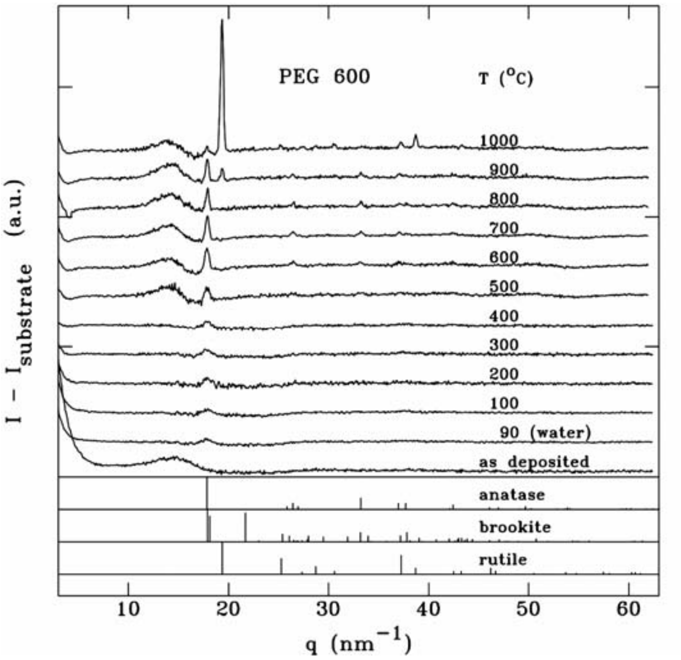

Fig. 10. X-ray scattering intensities of films with PEG 600 as a function of the scattering vector

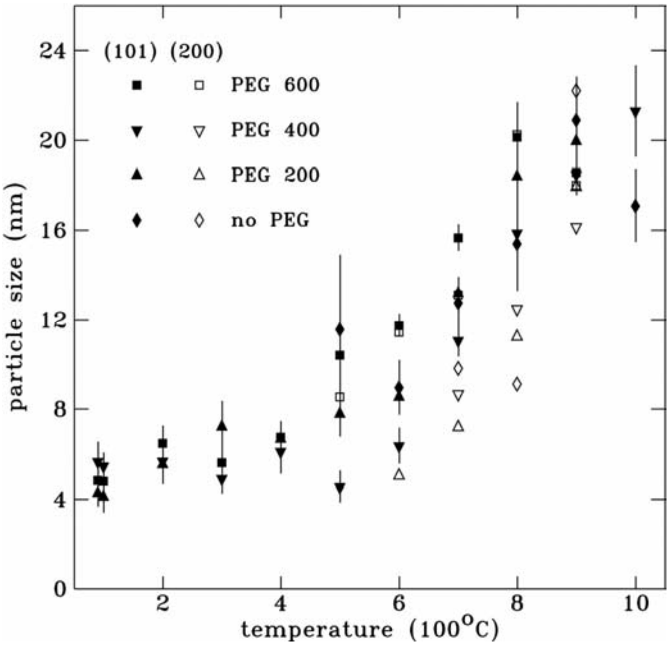

Fig. 11. The size of the anatase particles as a function of annealing temperature. For clarity, error bars are only shown for anatase (101) peaks

4. Conclusion

Transparent nanocrystalline anatase films have been synthesised by treating sol-gel TiO_2 samples containing PEG of different molecular weights in hot water. The maximum process temperature in this method was around 90 °C. The effect of PEG of different molecular weights on the crystallization of TiO_2 films and the anatase-to -rutile phase transition has been studied by Raman spectroscopy and XRD. The results indicate that crystallization was complete when PEG-containing films were treated in hot water at 90 °C for 1 hour. The films are composed of anatase crystallites with dimensions of about 5 nm. Upon annealing at temperatures not higher than 400 °C, the crystallite size remains unchanged. The anatase-to-rutile phase transition and crystallite sizes are independent of the molecular weight of the PEG used in sample preparation. The anatase phase was found to be stable up to 900–1000 °C, beyond which it transforms to highly oriented rutile crystallites. A film of nanometric anatase particles on a transparent substrate, stable against crystal growth at temperatures up to 400 °C, is a promising candidate for use in photocatalytic or photovoltaic devices at high temperatures.

Acknowledgements

The financial support of New-Brunswick Innovation Foundation – Research Innovation Fund Innovation Capacity Development and Atlantic Innovation Fund (FIA) – in carrying out this work is gratefully acknowledged.

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Received 6 June 2004
Revised 11 June 2004