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Nitridation and crystallization of titanium oxynitride by thermal treatment of TiO_2-anatase films in NH_3

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Nitrogen is often used for doping TiO_2 films to improve their photocatalytic properties in visible light. Multilayer TiO_2 anatase films were deposited by sol–gel method on quartz substrate and thermally treated in O_2 and NH_3 flow in 500-800 °C range. The effect of the annealing treatment (temperature and atmosphere) on the structural properties of TiO_2 films was studied by X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and selected area electron diffraction (SAED). Nitridation causes the amorphization of the anatase tetragonal phase at 600 °C. The film re-crystallization into the cubic oxynitride phase is observed at 800 °C. EDX results confirms that the incorporation of nitrogen into the amorphous films takes place before thermally activated growth of the oxynitride phase and demonstrates that the relative O:N composition in the crystalline phase is dependent on the temperature of the thermal treatment.

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1. Introduction

Sol–gel and dip-coating methods [1-6] have been used for preparation of nanostructured TiO_2 films [7-10]. A subsequent thermal treatment of the deposited films in air enhances the crystallization of the TiO_2, while annealing in reductive atmosphere (H_2 plasma, N_2, NH_3) leads to the creation of oxygen vacancies, which is considered a band gap-narrowing pathway [11,12]. The thermal treatment in ammonium atmosphere above 550 °C results in the incorporation of nitrogen and the formation of titanium oxynitride in the TiO_2 films [13]. Titanium oxynitride has been extensively investigated due to its physico-chemical properties (such as hardness, durability, corrosion resistance photocatalytic activity, etc) depending on the N/O ratio which makes it suitable for a large variety of applications including thin film technology, optical coatings as solar selective absorbers, transparent IR window electrodes, photocatalytic applications in the visible range and wear-resistant coatings [14,15]. In those studies, the structural and chemical changes owing to the nitrogen percentage variation have been investigated. Most of the studied TiO_xN_y films have been obtained using different physical methods, such as ion implantation, CVD, reactive magnetron sputtering [16-18], or laser irradiation in reactive atmosphere [19,20]. In this work, we employed the sol–gel method to prepare TiO_2 films in order to achieve a higher level of nitridation during the thermal treatment of the films in ammonium atmosphere. We used the XRD, Raman, SEM, TEM, EDX, and SAED measurements of the films treated in reductive (NH_3) atmosphere in the range of temperatures from 500 to 800 °C to study the amorphisation and re-crystallization processes associated to the nitridation of the film as well as the compositional changes in the film.

2. Experimental details

2.1 Sample preparation

TiO_2 films were prepared by the sol-gel and dip coating technique on quartz substrates. Two groups of films, with three and five layers, were obtained by repeating the dip-coating procedure. Tetrabutylorthotitanate (TBOTi, Aldrich) was used as titanium precursor and mixed with ethanol (Panreac) in a molar ratio TBOTi/ethanol = 2/57. Polyethyleneglycol with average molecular weight 2000 (PEG_{2000}) was added and the solution was stirred until PEG dissolution. Acidic conditions (pH = 1.5) were created by addition of 65% nitric acid (Riedel-de Haen AG). Deionized water was added dropwise to the solution which remained under stirring at room temperature for 20 h until the completion of the hydrolysis process. TiO_2 gel films were deposited on quartz substrates by dip-coating. The films were thermally treated in air at 450 °C for 30 min (heating rate of 5 °C/min) in a "Carbolite" muffle furnace and named "as- prepared TiO_2". Using a "Thermawatt" tube furnace, the films were additionally treated for 2 h under O_2 or NH_3 flow at 500, 600 and 800 °C [21, 22].

2.2 Characterization methods

The crystallinity of the as-prepared and thermally treated TiO_2 films was studied by XRD, SEM, TEM and SAED. A Siemens D500 diffractometer with secondary graphite monochromator and CuKα radiation was used to obtain diffraction patterns of the samples in Bragg–Brentano geometry. The measured 2θ range, between 20 and 60 deg, was scanned with the velocity of 0.03 deg /10 s. The Raman spectra were recorded at room temperature, in the range from 30 to 1900 cm^{-1}, by using a triple Jobin Yvon/ Atago-Bussan T-6400 spectrometer, equipped with Ar^+ laser (λ= 514.5 nm), liquid N_2 cooled CCD detector. SEM characterization was carried out with a Jeol JSM-840 microscope equipped with an INCA Energy 250 (Oxford Instruments) EDX system. TEM and SAED images were recorded using a Jeol 200CX electron microscope, on specimens prepared by mechanical extraction of film fragments from the sample [23].

3. Results and discussion

The SEM measurements (Fig. 1) on the surface of the TiO_2 films demonstrated the homogeneity of the films. XRD features of the TiO_2 films untreated or treated in O_2 atmosphere showed the typical pattern of anatase [24] in agreement with the JCPDS card number 21-1272. In the sample treated at 500 °C in NH_3 anatase phase is also detected, while the sample treated at 600 °C in NH_3 atmosphere (Fig. 2) exhibits an amorphous structure.

The increase of the thermal treatment temperature from 500 °C to 600 °C decreases the crystallinity of the film as the result of the reaction between the film and NH_3. The weak peak at around 43° observed after treatment at 600 °C, shown in Fig. 2, appears in the diffraction patterns of TiO (JCPDS card: No. 77-2170), osbornite (JCPDS card No. 6-0642), $TiN_{0.9}$ (JCPDS card No. 31-1403) or titanium nitride, with cubic structure. The process of re-crystallization at the above mentioned conditions (over 600 °C, NH_3 atmosphere) is of great interest and has been the subject of detailed investigations. We carried out a thermal treatment in NH_3 at higher temperature (800 °C), in order to study the disordering and re-crystallization process in NH_3 atmosphere by XRD, Raman, EDX, TEM and SAED.

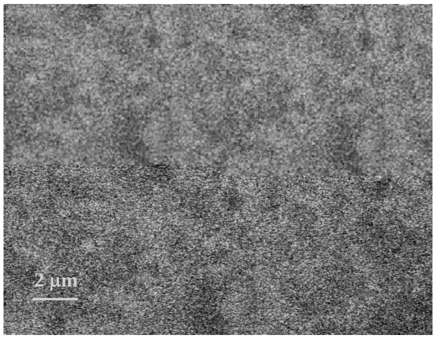

Fig. 1. SEM micrograph of the TiO_2 thermally treated film at 500 °C in NH_3.

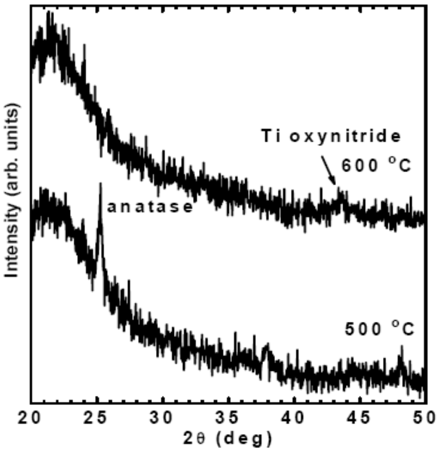

Fig. 2. XRD pattern of thermally treated films at 500 °C and 600 °C in NH_3.

The typical XRD patterns of the film after treatment at 800 °C in NH_3 is presented in Fig. 3A, showing the characteristic (200) main peak of titanium nitride at ~ 42-44°. We have carried out detailed XRD analysis in the (200) peak region (Fig. 3b) to determine the composition of the cubic phase.

The XRD spectra at 800 °C (Fig. 3B) shows that the peak width at half maximum is reduced, and the intensity of the peak clearly enhanced, indicating a thermally activated crystalline growth of crystallites embedded in amorphous phase. The peak at ~ 43° appears significantly shifted toward lower angles after treatment at 800 °C in NH_3. The displacement of the peak with treating temperature reflects the variation of the lattice parameter *a,* of the cubic phase. Such a change indicates the substitution of O by N in an oxynitride phase, TiN_xO_{1-x} (x between 0 and 1).

The extents of the compositional change can be calculated from the lattice parameters of pure TiO and TiN values with a pure NaCl-type structure [S.G. F*m3m* (225)], according to the Vegard´s Law, with lattice parameters a = 4.186 Å and a = 4.204 Å for the samples treated at 600 °C and 800 °C, respectively. These parameters are between the reported values of a = 4.185 Å for TiO (JCPDS card: No. 77-2170) and a = 4.241 Å for TiN (JCPDS card: No. 38-1420), which implies the existence of titanium oxynitride TiN_xO_{1-x}. For TiN_xO_{1-x} solid solution, the lattice parameter c is a linear function of the nitrogen content (x), according to the Vegard’s law $c = a + (b-a)x$, where a and b are the lattice parameters of stoichiometric TiO and TiN, respectively. After calculation, the values of x are 0.04 and 0.36 for the samples treated at 600 °C and 800 °C, respectively. This result indicates that the crystallites detected in the XRD spectra can be considered as titanium oxynitride $TiN_{0.04}O_{0.96}$ and $TiN_{0.36}O_{0.64}$, respectively (Fig. 4). According to the Debye–Scherrer equation, the average crystallite sizes are about 5 and 7 nm.

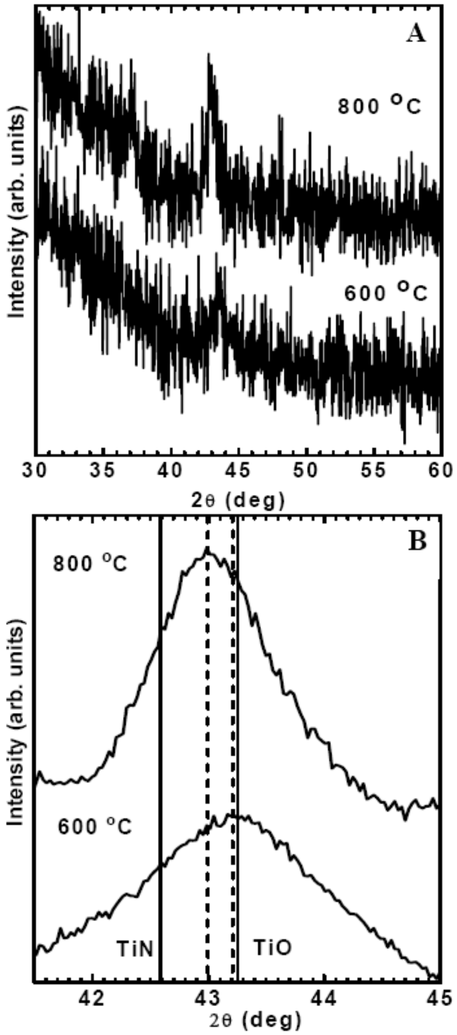

Fig. 3. (A) XRD pattern of films after thermal treatment at 600 °C and 800 °C in NH_3 and (B) detail of the XRD spectra showing the shift of the (200) oxynitride peak.

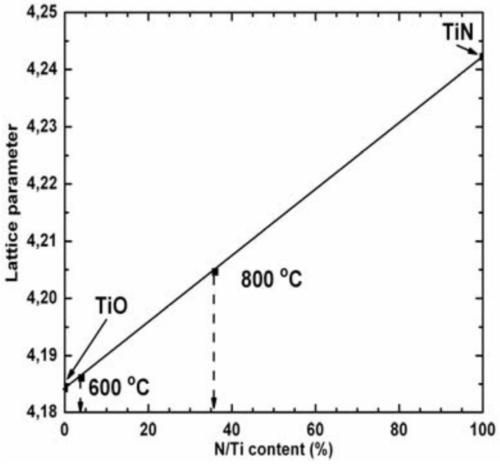

Fig. 4. N content of the oxynitride phase, determined using Vegard´s Law from the lattice parameter of the cubic oxynitride phase obtained from the (200) XRD peak position.

The characteristic peaks of anatase phase can be clearly observed in the Raman spectrum (Fig. 5) of the films treated at 500 °C in NH_3. Raman measurements clearly demonstrate the structural disordering of the anatase films after treatment at 600 °C in NH_3. In the spectral range of the main anatase peak, only a weak and wide bump remains, the intensities being one order of magnitude lower, with a full width at half maximum one order of magnitude wider (90 cm^{-1} and 10 cm^{-1}, respectively). Therefore, the local order of Ti-O bonding in the anatase phase has been lost during the thermal treatment in reductive atmosphere, and it remains only a disordered structure.

The Raman spectra do not change significantly after treatment at 800 °C in NH_3 (Fig. 6), demonstrating that there is no re-crystallization of TiO_2 anatase or rutile phases, caused by thermal treatment. The weak band at around 150 cm^{-1} confirms the presence of local disordered amorphous Ti-O bonding in the film. Since both TiO and TiN phases have cubic symmetry and are not Raman active, their presence cannot be determined using Raman spectroscopy.

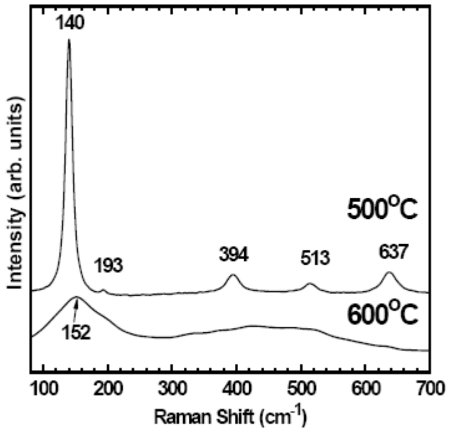

Fig. 5. Raman spectra of the films treated at 500 °C and 600 °C in NH_3.

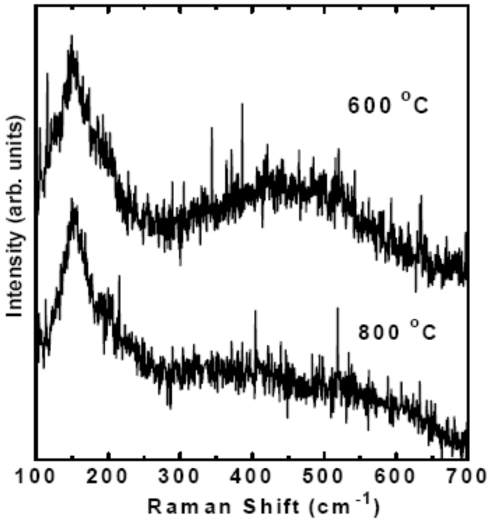

Fig .6. Raman spectra of the films treated at 600 °C and 800 °C in NH_3.

SEM observations of the film treated at 800 °C in NH_3 revealed the presence of elongated features, oriented in parallel, which are most likely associated to surface porosity or cracks appeared after thermal treatment (Fig. 7).

The presence of N in the film was clearly determined by EDX measurements. No nitrogen was detected in the untreated sample or in the sample treated at 500 °C, while the N peak was clearly observed of the sample treated at 600 °C, accompanied by a pronounced reduction of the intensity of the O peak, relative to the intensity of the Ti peaks, demonstrating the significative substitution of O by N in the film. (Fig. 8). Quantitative analysis showed an O:N elemental ratio of almost 1:1 after treatment at 600 °C.

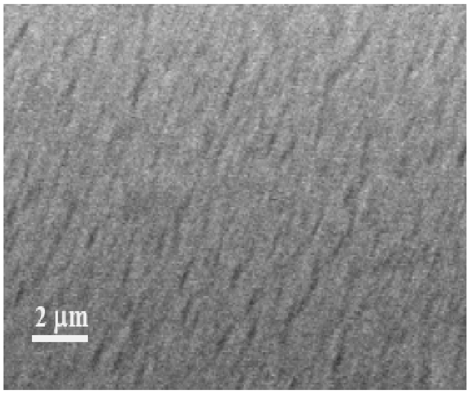

Fig .7. SEM micrograph of the film after thermal treatment at 800 °C in NH_3.

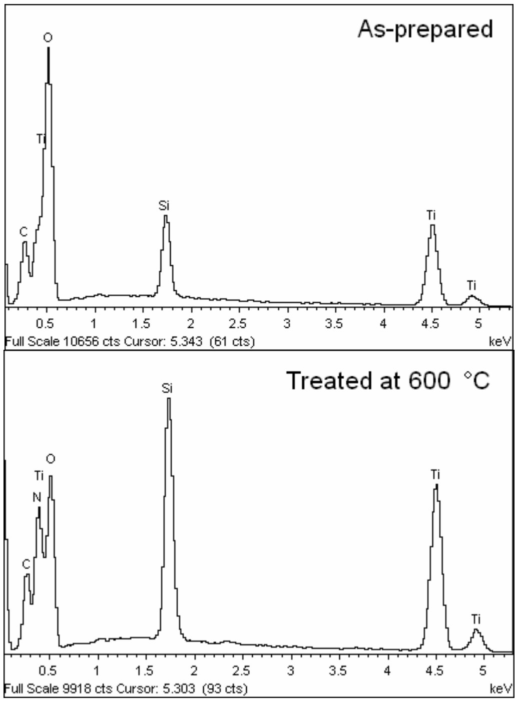

Fig. 8. EDX of the films as-prepared and treated at 600 °C in NH_3

The EDX results point out that nitridation occurs at 600 °C and is associated to the disordering of the anatase lattice, previous to the crystallization of cubic oxynitride. Comparing to the much higher nitrogen content of the whole film determined by EDX, the low nitrogen content calculated from the XRD lattice parameter for the oxynitride nanocrystallites present at 600 °C, indicates that the crystalline nuclei which remained embedded in the disordered film after nitridation have higher oxygen content than the amorphous part. The oxide-rich nuclei left in the amorphous film during nitridation process can act as the nucleation site for the growth of nitrogen-rich oxynitride crystallites through reaction with the amorphous part at higher temperature.

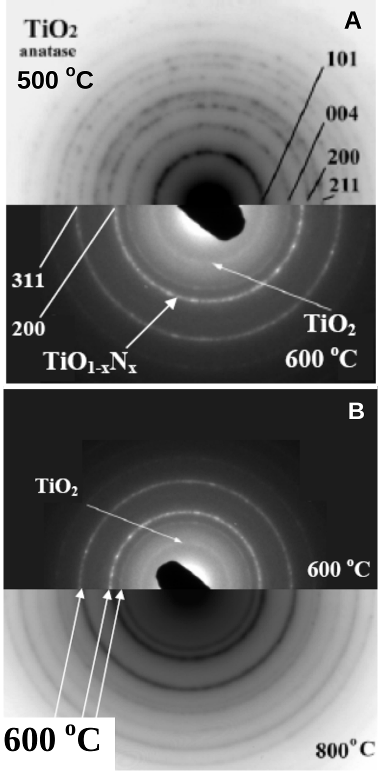

Fig. 9. (A) SAED images of the films treated at 500 °C and 600 °C and (B) SAED images of the films treated at 600 °C and 800 °C, showing the changes in the crystalline structure of the films.

The treated films were further characterized by TEM and SAED. Fig. 9A compares SAED images of the films treated at 500 °C and 600 °C.

At 500°C only the rings of crystalline anatase can be observed, while at 600 °C the amorphization of the anatase phase and the presence of new rings of the oxynitride are obvious. The well defined rings in the SAED spectra confirm the re-crystallization of the film as the oxynitride phase at 800 °C (Fig.9B).

The plan view TEM images of the films after annealing at 500 °C, 600 °C and 800 °C are exposed in Fig. 10. The Bragg contrast of the TEM images reveals the dimensions of the crystallites or grains in the film. The grains have 10 to 20 nm in the case of the anatase film (500 °C), become less than 5 nm in the quasi-amorphous structure resulted after annealing at 600 °C and have about 20 to 30 nm in size after film treatment at 800 °C. However, the real size of the crystalline blokes inside the film grains is smaller as is revealed by XRD.

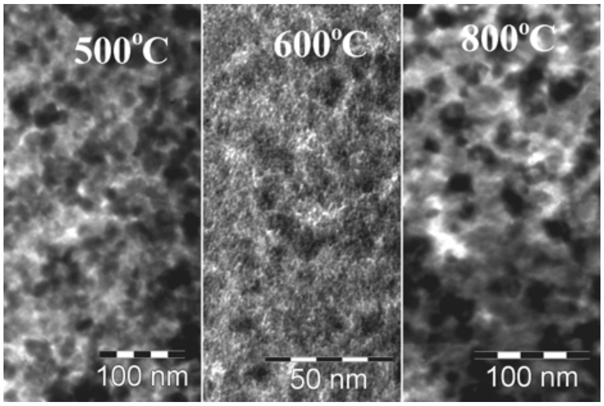

Fig. 10. Plan view TEM images of the thin films after annealing at different temperatures.

4. Conclusions

Anatase TiO_2 films on quartz substrate were thermally treated in O_2 and NH_3 flow atmospheres. Thermal treatment in NH_3 at 600 °C leads to amorphization of the film: due to the formation of oxygen vacancies and nitridation, the local order of Ti-O bonding in the anatase phase is destroyed. At this temperature the film structure and composition changes to a nitrogen-rich amorphous film, containing crystalline clusters of nitrogen doped titanium oxide with cubic TiN_xO_{1-x} structure, sized less than 5 nm. Thermal treatment in NH_3 at 800 °C leads to the growth of nitrogen-rich oxynitride crystallites at the expense of the nitrided amorphous phase which enhance the crystallinity of the film. Vegard´s Law was used to determine the stoichiometries of oxynitride nanocrystallites and it was found that the content of nitrogen, x, in the oxynitride phase increases with temperature.

Acknowledgements

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