SURFACE RECONSTRUCTION OF POLYCRYSTALLINE TiO$_2$ IN OXYGEN ATMOSPHERE

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Abstract—Polycrystalline TiO$_2$ surface reconstruction in oxygen atmosphere has been investigated by atomic force microscopy (AFM) and cathodoluminescence in the scanning electron microscopy (SEM-CL). The reactivity to oxygen is related to the presence of defects as interstitial Ti ions, that induce growth of protrusions, large terraces and polygonal shaped structures.

1. INTRODUCTION

The evolution of the surface structure of TiO$_2$, in oxygen atmosphere and particularly the reconstruction of the (110) surface of rutile phase, has attracted the attention in the last years. The interest is related to applications of TiO$_2$ as catalyst, photocatalyst, in monitoring the ambient atmosphere and for oxygen and gas-sensors fabrication [1]-[3]. Several types of structures have been reported to form on the TiO$_2$ (110) surface, including longer periodic structures, step-terraces and regular (1x1) structures [4]-[7]. The reactivity of the surface to oxygen is related to the bulk nonstoichiometry. Structural defects such as oxygen vacancies and Ti^{n+} intersitial atoms are formed when crystalline TiO$_2$ is annealed in high vacuum. If the concentration of vacancies is high, crystallographic shear planes result and act at the surface as preferential sites with increased reactivity to oxygen. Scanning tunneling microscopy (STM) has been used to analyze the surface topography and reconstruction at the atomic level. It was observed that, the reaction of TiO$_2$ (110) with oxygen at elevated temperatures results in bridging oxygen atoms, and formation of Ti$_2$O$_3$ nonstoichiometric phase which subsequently change to the stoichiometric (1x1) structure [8]-[11].

In the present study we report on the growing of elongated structures with size of about 1μm, and large stepped terraces on the surface of polycrystalline rutile and anatase polymorphs of TiO$_2$, after treatment in oxygen atmosphere. Heat treatment for prolonged periods of time determines the formation of that polygonal structures form upon the large terraces as the final stage of the surface modification. The preferential sites for surface reconstruction are related to grain boundaries regions and to the presence of interstitial Ti atoms.

2. EXPERIMENTAL

Polycrystalline samples of the two phases of TiO$_2$ anatase and rutile have been prepared from powders under a compresive load of 12 MPa, to form disk shaped samples of about 7 mm diameter and 2 mm thickness. The samples were treated in argon and in air. Some of the samples were treated in a furnace in oxygen flow of 2 l/min, at 800 °C for intervals from 30 minutes up to 2 hours. For comparison another set of samples has been treated in an atmosphere containing hydrogen and nitrogen (10% H$_2$+90% N$_2$).

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used to investigate the structure of the samples surface. Cathodoluminescence in the scanning electron microscope (CL-SEM) has been used to analyze the evolution of the ligth emitting centers in relationship with the structural changes of the sample surface.

CL emission spectra and images in visible and infrared spectral regions were obtained using an accelerating voltage of the SEM electron beam of 20 kV. Visible light has been detected using a Hamamatsu R-928 photomultiplier, and a cooled ADC germanium detector has been used for the near infrared spectral region. CL spectra were recorded using an Oriel 78215 computer controlled monochromator and a CCD camera with a built-in spectrograph (Hamamatsu PMA-11) for both visible and infrared spectral regions.

3. RESULTS AND DSCUSSION

Figure 1a) shows the AFM image of a rutile TiO_2 film after treatment in oxygen for 30 min. Protrusions have grown on the grains surface with sizes in the range from 0.5 to 1μm. The higher protrusions appear to form near the grain boundaries region. The three dimensional image shown in Fig.1b) evidences that large terraces and small protrusions are formed on the grain surface, while the high elongated structures grow at the grain boundaries.

Fig. 1. AFM image of protrusions formed on the surface of rutile sample following the treatment in oxygen for 30 min (a). 3D image corresponding to the aria from (a): protrusions and terraces structures (b).

After two hours of treatment in oxygen, the surface shows interconnected terraces terminated by polygonal structures. The AFM image of the interconnected terraces on the rutile sample surface is presented in Fig. 2a). The step height, shown in Fig. 2b) increases from 20 to 80 nm and the polygonal shaped structure side is 26 nm. Considering the dimension of the substrate cell along the [1 1 0] direction to be 6.5Å [12], it results that the top structure reproduces the stochiometric (1x1) bulk structure.
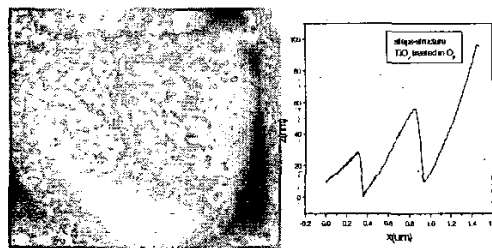

Fig. 2. Interconnected terraces formed after annealing in oxygen for 2 hours (a), and line profile of the structure presented in detail, (b).

Previous studies of the (110) surface of a TiO_2 crystal treated in oxygen have shown the occurrence of changes in the surface

morphology from flat and large terraces to small (1x1) structures, at the atomic level [12], [13]. The mechanisms proposed in order to explain the formation of the structures involves the diffusion of the intersitial Ti^{n+} ions, which exist in the volume of the TiO_2 crystal, and their reaction with the oxygen from atmosphere of the thermal treatments [7], [14]. These mechanisms could also explain the reconstruction of the polycrytals surface in our experiment, assuming that the growth of TiO_2 overlayers and varrious types of microstructures are due to the presence of a large concentration of interstitial Ti^{n+} ions able to react with oxygen from the atmosphere.

Whereas in the case of TiO_2 single crystals the interstitial Ti concentration is rather uniform, in the polycrystalline material one can expect that its distribution is different within the grain as compared with that at the grain boundaries. Moreover, the increased diffusivity in the defective region at the grain boundaries favors the terrace formation in such sites. In our experiment, the presence of intersitial Ti^{n+} ions, with n=3, was clearly evidenced in the cathodoluminescence emission spectra of both rutile and anatase TiO_2 polycrystals.

Figures 3a) and 3b) show the CL emission spectra of the anatase and rutile powders of TiO_2 which were used in the sintering process of the polycrystalline samples. The main emission band exhibits a peak at 580 nm.
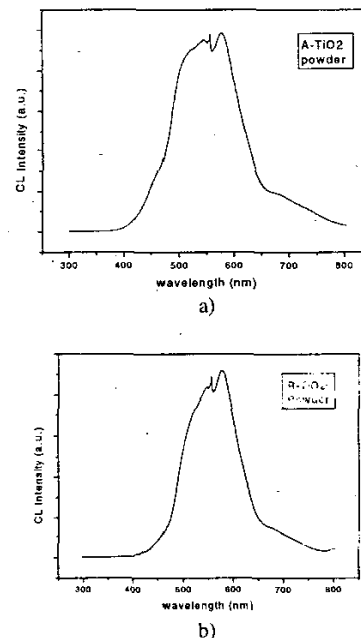

Fig. 3. CL spectra of initial powders a) anatase and b) rutile TiO_2.

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After the sintering process, the spectra show intense emission bands peaked at 800 nm in rutile and at 820 nm the in anatase phase. We have observed that structural defects, Ti^{3+}-oxygen vacancy, appear during sintering at temperatures above 1100 °C [14]. The formation of Ti^{3+}-O vacancy defect centers takes place by loosing oxygen atoms in the basic cell, as it has been observed in single crystalline as well as polycrystalline anatase TiO_2 thin films [15]. It can be observed in the spectra shown in Figure 4, that the treatment in oxygen for 2 hours at 800 °C does not influence the infrared emission. It was previously reported that the defect levels associated with the Ti^{3+} ions give rise to radiative transitions with the wavelength of 820 nm and 850 nm [16].
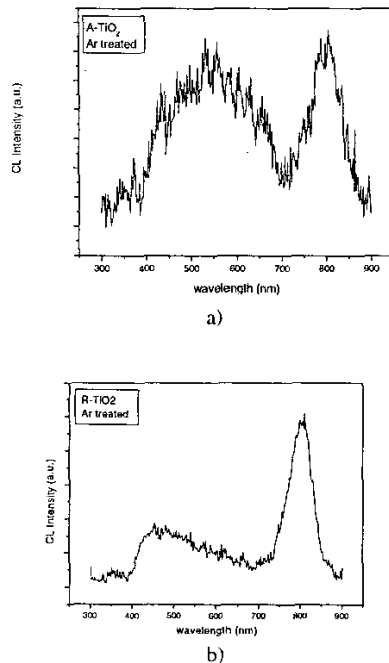

Fig. 4. CL spectra from anatase and rutile TiO_2 polycrystals formed by treatment of the powders at 1100°C in argon.

The defect levels corresponding to the O vacancies are situated near the bottom of the conduction band and the light emission appears in the near ultraviolet domain [16].

The spectrum of anatase (see Fig.4a) shows weak bands situated at 380, 450 and 520 nm. One may observe that the intensity of the 450 nm band increases after the heat treatment

in oxygen, in the rutile polycrystal (see Fig.4b). It is likely that the treatment in oxygen removes the nonradiative traps and determines an increase of the intensity band at 450 nm. In order to identify the origin of the radiative centers, a set of samples has been treated in 10%H_2+ 90%N_2 atmosphere for 30 minutes at 800 °C. Their CL spectra are shown in Figures 5a) and 5b). The infrared emission associated with Ti^{3+} is still observed and emission bands at 350 nm and 480 nm are present. The band at 480 nm appears more intense in anatase (Fig.5a), while the band at 350 nm shows higher intensity in rutile polycrystal (Fig.5b).
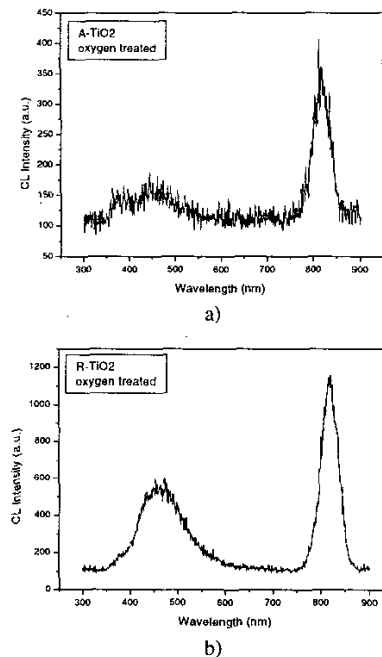

Fig. 5. CL spectra of anatase (a) and rutile (b) polycrystals treated in oxygen for 2 hours at 800 °C.

Several features are observed in these spectra. Firstly, the presence of the IR emission associated with the Ti^{3+} ions, which do not passivate during the hydrogen treatment. Two new bands, not observed in the samples treated only in O_2, appear at 480 nm and 350 nm, respectively. The 350 nm transition has theoretically been predicted and assigned to a center located in the conduction band, at 0.3 eV above the bottom of the band. The center is related to a surface vacancy defect [17]. We attribute the 480 nm transition to the appearance

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of a shallow donor center in the band gap, just bellow the bottom of the conduction band. Various defect levels are associated with the formation of bulk vacancy defect centers [16], [18], [19].

3. CONCLUSIONS

CL spectra of rutile and anatase polymorphs of TiO_2 show the presence of defect centers associated to interstitial atoms of Ti^{3+} and to bulk and surface oxygen vacancies. The concentration of defect centers is different in the two TiO_2 phases, and results in variations of the intensity of emission bands. Ti^{3+} ions appear to be involved in the formation of protrusions during treatment in oxygen. Rutile polycrystals exhibit a higher concentration of vacancies at the surface region, which determines an increased reactivity to oxygen in the atmosphere. The reactivity is increased at the grain boundaries region.

References

[1] V. Guidi, M.C. Carotta, M. Ferroni, G. Martinelli, L. Paglialonga, E. Comini, S. Sberveglieri, *Sensors and Actuators*, **B 57**, p. 197, 1999.

[2] M. Ferroni, M.C. Carotta, V. Guidi, G. Martinelli, F. Ronconi, M. Sacerdoti, E. Traversa, *Sensors and Actuators*, **B 77**, p. 163, 2001.

[3] F. Edelman, H. Hahn, S. Seifried, C. Alof, H. Hoche, A. Balogh, P. Werner, K. Zakrzewska, M. Radecka, P. Pasierb, A. Chack, V. Milhelashvili, G. Eisenstein, *Mat. Sci. Eng.*, **B 69**, p. 386, 2000.

[4] R.A. Bennett, S. Poulston, P. Stone, M. Bowker, *Phys. Rev.*, **B 59**, p. 10341, 1999.

[5] S. Gan, Y. Liang, D.R. Baer, *Surf. Sci.*, **459**, p. L498, 2000.

[6] U. Diebold, J.F. Anderson, K.-On Ng, D. Vanderbilt, *Phys. Rev. Lett.*, **77**, 1996.

[7] W. S. Epling, C. H. F. Peden, M. A. Henderson, U. Diebold, *Surf. Sci.*, **412/413**, p. 333, 1998.

[8] H. Nörenberg, R.E. Tanner, K.D. Schierbaum, S. Fischer, G.A.D. Briggs, *Surf. Sci.*, **396**, p. 52 1998.

[9] R.A. Bennett, P. Stone, N.J. Price, M. Bowker, *Phys. Rev. Lett.*, **82**, p. 3831, 1999.

[10] S. Gan, Y. Liang, D.R. Baer, *Surf. Sci.*, **459**, p. L498, 2000.

[11] E. Asari, R. Souda, *Vacuum*, **68**, p. 123, 2003.

[12] M. Li, W. Hebenstreit, U. Diebold, *Surf. Sci.*, **414**, p. L951, 1998.

[13] M. Li, W. Hebenstreit, L. Gross, U. Diebold, M.A. Henderson, D.R. Jenninson, P.A. Schultz, M.P. Sears, *Surf. Sci.*, **437**, p. 173, 1999.

[14] H. Onishi, Y. Iwasawa, *Phys. Rev. Lett.*, **76**, 791, 1996.

[15] R. Plugaru, A. Cremades, J. Piqueras, accepted for presentation at BIAMS 2003 Conference, France, May 26-29, 2003.

[16] A.K. Ghosh, F.G. Wakim, R.R. Addis Jr., *Phys. Rev.*, **184**, p. 979, 1969.

[17] M. Ramamoorthy, R.D. King-Smith, D. Vanderbilt, *Phys. Rev.*, **B 49**, p. 7709, 1994.

[18] R. Sanjines, H. Tang, H. Berger, F. Gozzo, G. Margaritondo, F. Levy, *J. Appl. Phys.*, **75**, p. 2945, 1994.

[19] A. Rothschild, A. Levakov, Y. Shapira, N. Ashkenasy, Y. Komem, *Surf. Sci.*, 2003, in press.