

The effect of annealing in different atmospheres on the luminescence of polycrystalline TiO₂

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S261

(<http://iopscience.iop.org/0953-8984/16/2/031>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 07:45

Please note that [terms and conditions apply](#).

The effect of annealing in different atmospheres on the luminescence of polycrystalline TiO₂

R Plugaru¹, A Cremades and J Piqueras

Departamento de Física de Materiales, Facultad de Ciencias Físicas,
Universidad Complutense de Madrid, 28040 Madrid, Spain

Received 31 July 2003

Published 22 December 2003

Online at stacks.iop.org/JPhysCM/16/S261 (DOI: 10.1088/0953-8984/16/2/031)

Abstract

Polycrystalline samples of titanium oxide were prepared by thermal sintering, in argon and air atmospheres at temperatures ranging from 1100 to 1500 °C, from powders of anatase and rutile phases. The samples sintered in argon were further treated in oxygen at the temperature of 800 °C for intervals of time up to 8 h. The luminescence emission of the initial powders was situated in the green region, with the peak at 580 nm. The sintering treatment in argon leads to a decrease of the luminescence intensity that appears as a broad band peaked at 550 nm in the case of anatase and as a band peaked at 450 nm in the case of the rutile phase. The sintering treatment in air causes the quenching of the emission in the visible region. In both cases, a sharp and intense emission appears in the infrared region at 800 nm for rutile and 820 nm for the anatase phase.

The blue emission is sensitive to the treatment in oxygen atmosphere which causes mainly an intensity increase of the band at 450 nm. The treatment in oxygen results in the reconstruction of the polycrystalline sample surface as hexagonal shape protrusions and large terraces.

1. Introduction

Applications of titanium oxide over a wide area, ranging from use as a sensor to use as a catalyst, are related to its surface properties. A detailed study pointing out the influence of the surface structure of TiO₂ on the physical and chemical properties is presented in [1]. In recent studies [2, 3] on surface reconstruction of TiO₂ during treatments under various atmospheres it has been reported that defects of the surface and especially the oxygen deficiencies are sites with increased reactivity. It was found that some processes such as reducing treatments in vacuum favour the formation of defect centres in the volume, with influence on the surface structure [4–6]. In the present study the evolution of defect centres formed during the sintering of polycrystalline TiO₂ samples has been investigated in relation with their influence on the luminescence emission. The effect of thermal treatment in oxygen atmosphere on the

¹ Permanent address: National Institute for R&D in Microtechnologies, IMT-Bucharest, R-72996, Romania.

reconstruction of the sample surface has been investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), considering the presence of defect centres at the grain boundaries and in the grain regions.

2. Experimental details

Two titanium oxide phases, anatase and rutile as powder precursors, were used for the preparation of the polycrystalline samples. The powders were compacted under a compressive load of 2 ton to form disc shaped samples of about 7 mm diameter and 2 mm thickness. The process of annealing was performed at temperatures of 1100, 1300 and 1500 °C, in argon and air atmospheres. Some of the samples were then treated in oxygen at 800 °C, for various times from 30 min up to 8 h.

The structure of the films has been analysed by means of x-ray diffraction (XRD) measurements and Cu K α radiation in the volume and at grazing incidence, using a Philips X'PERT MPD diffractometer.

The luminescence emission spectra have been analysed by means of cathodoluminescence (CL) in scanning electron microscopy, using Hitachi S 2500 SEM and Leica 440 SEM equipment. The measurements were carried out at temperatures between 90 and 300 K.

CL emission spectra and images in the visible and infrared spectral regions were obtained at an accelerating voltage of 20 kV. Visible light has been detected with 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 the visible and infrared spectral regions.

The surface structure has been studied in the secondary electron mode of SEM and by AFM.

3. Results and discussion

The thermal treatment of the titanium oxide powders was carried out in an inert atmosphere of argon (Ar) and in air, in order to obtain polycrystalline samples. The XRD patterns of the TiO₂ powders fit the rutile and anatase structures with (110) and (101) texture respectively. In the temperature range of 1100–1500 °C the texture changes from the initial (110) to (211) in the case of the rutile phase and from (101) to (211) for anatase. In fact, XRD shows that the final structure obtained from anatase powder is a mix of rutile and anatase with an enhanced (211) rutile texture. Hereinafter we refer to these mixed phase samples obtained from anatase powder as anatase. Further treatment in oxygen atmosphere favours the growth of the (110) texture.

The emission spectrum of the anatase phase powder shows an emission peak at 580 nm and a relatively broad shoulder situated at 520–550 nm (figure 1(a)). The emission spectrum of rutile phase presented in figure 1(b) shows the same intense emission band situated at 580 nm, with a less pronounced shoulder at 550 nm. Annealing in the temperature range 1100–1500 °C quenches the green emission and leads to an intense emission in the infrared region situated at 800 nm for rutile and at 820 nm for anatase. The infrared band appears normally as the dominant emission in the spectra of the two phases after the sintering treatment in argon and in air.

The evolution of the green emission band is related to the annealing atmosphere. The emission spectrum of a polycrystalline anatase sample formed at 1100 °C in argon is shown in figure 2(a). It can be observed that the emission band in the visible range is very broad,

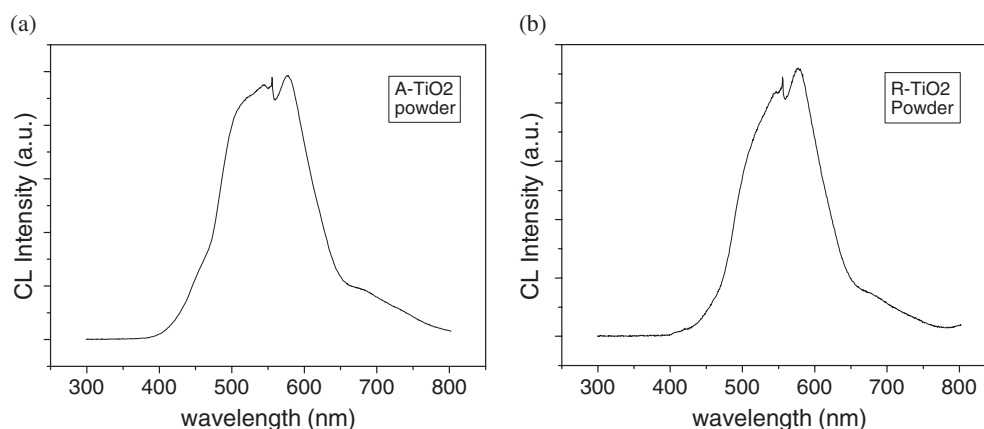


Figure 1. CL spectra of initial powders of (a) anatase and (b) rutile titanium oxide phases.

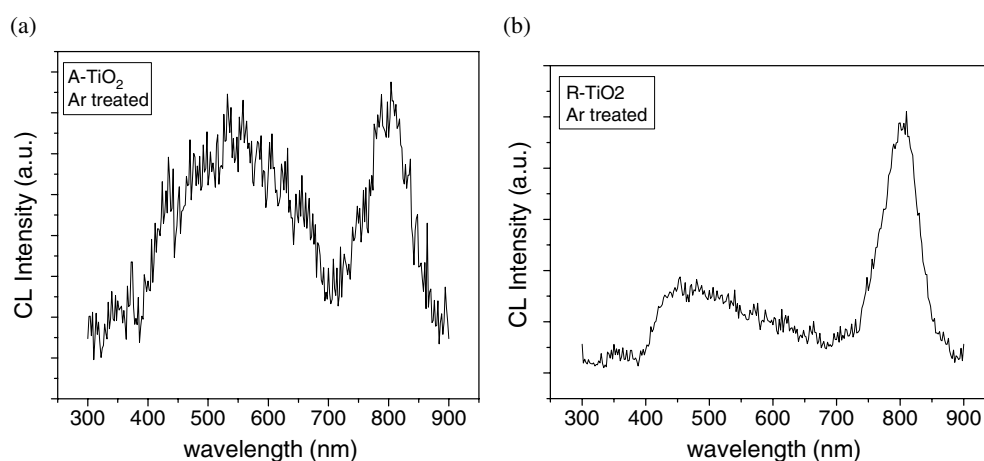


Figure 2. CL spectra from the (a) anatase and (b) rutile phases of the TiO₂ samples formed by treatment of powder at 1100 °C in argon.

with the intensity maximum situated at 550 nm, and that an intense and well resolved band appears, peaked at 820 nm. The green emission is even less intense in the case of the rutile phase, and the maximum is shifted to the blue region, with a peak at 450 nm (figure 2(b)). The main emission peak is situated at 800 nm.

After annealing in air at 1100 °C the dominant emission is infrared with higher intensity in the case of rutile. This treatment causes the quenching of the green emission in anatase and rutile samples, as can be observed in the spectra presented in the figures 3(a) and (b). The dominant infrared emission is also characteristic for the films annealed at 1500 °C, with the particularity that the emission band, peaked at 800 nm, is very sharp for rutile, while a broader band, peaked at 820 nm, appears for the anatase samples.

Previous studies have shown that the structural differences of the two phases of TiO₂, rutile and anatase, govern the differences in their electrical and optical properties [1, 7]. In the polymorph phases the titanium oxide presents different interconnections of the TiO₆ octahedra, leading to different structures and symmetries. Accordingly, the electronic band structures of the two phases and the related optical properties are expected to be different.

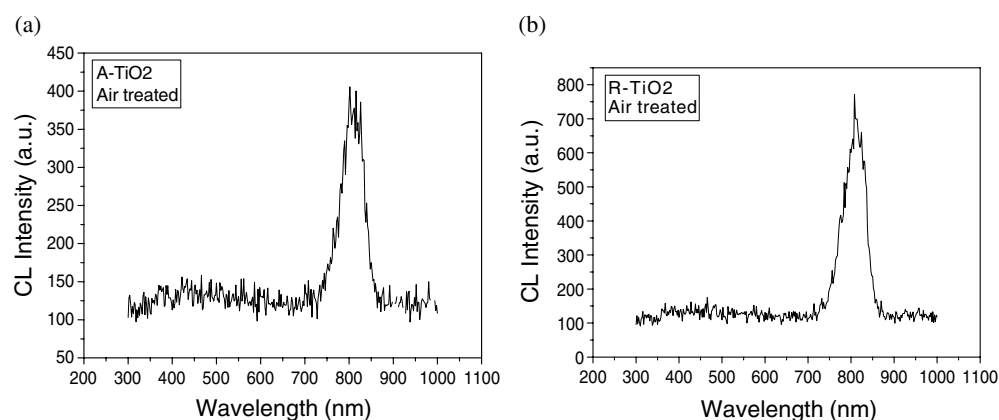


Figure 3. CL spectra from the (a) anatase and (b) rutile phases of the samples formed by treatment of powder at 1100 °C in air.

In the basic cell, each Ti^{4+} ion is surrounded by an octahedron of six O^{2-} ions. Structural defects can be formed by losing an oxygen atom, and the defect states associated with Ti^{3+} ions appear to be introduced in the band gap at 0.7–0.8 eV below E_F [8]. Luminescence transitions associated with Ti^{3+} interstitial ions in rutile single crystal were reported, with the emission at about 820 and 850 nm [9].

These results suggest that the observed evolution of the luminescence emission during the sintering process is related to the formation of Ti^{3+} ions and the associated defect states. The process is thermally assisted and the CL spectra show that the concentration of the emitting centres is rather constant once established at 1100 °C, without marked increase at higher temperatures, up to the 1500 °C used for sintering the polycrystalline materials. The structural differences between the starting titanium oxide powders, anatase and rutile, confirmed in the XRD spectra, do not appear to influence the initial CL emission (see figures 1(a) and (b)). It was previously reported that green photoluminescence emission is observed in amorphous TiO_2 thin films and is due to the Stokes shift caused by relaxation processes in the lattice [10, 11]. In our case, it is possible that a common radiative centre is involved in the green emission observed in figure 1, whose excitation conditions are not influenced by energy transfer from the matrix. A model proposed in order to explain the green luminescence of ZnO suggests a radiative transition between a shallow donor associated with an oxygen donor and a deep level associated with a metal ion vacancy [12].

The intensity of the green band decreases and quenches in competition with the infrared emission that appears after sintering in argon and in air. Its intensity does not increase during the treatment in oxygen, which suggests that the surface defects of the crystallites are related to the shallow donors. The CL spectra of the anatase and rutile polycrystalline samples sintered in argon are presented in figures 2(a) and (b). The luminescence emission in the visible region, 440–650 nm, appears as a broad band with unresolved peaks in the spectra of the samples treated in argon and is almost quenched in the spectra of the samples sintered in air (figures 3(a) and (b)). It can be considered that different defect centres are formed during the treatment in the two atmospheres, and that they act as radiative and nonradiative centres. The sintering treatment in air induces a higher concentration of nonradiative centres than the sintering treatment performed in argon. Previous studies report the presence of shallow traps or deep defect levels associated with the presence of oxygen vacancies which are formed in reduced or oxidized rutile crystal and in TiO_2 films [9, 13]. The energies of the shallow traps

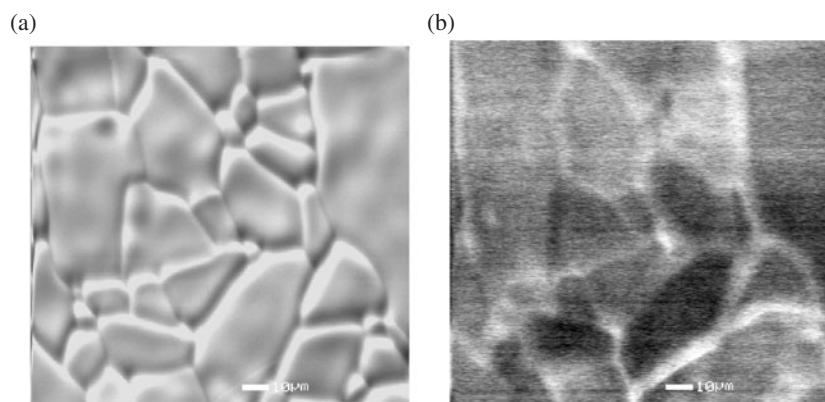


Figure 4. (a) A SE image of the anatase sintered in argon at 1500 °C. (b) A CL image in the visible range of the area shown in (a).

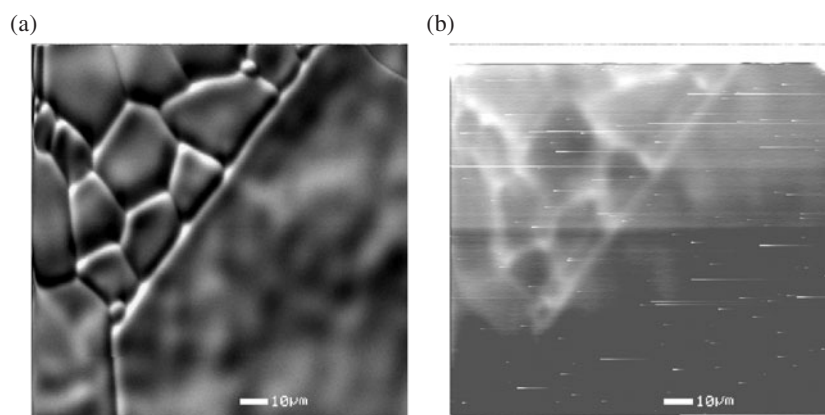


Figure 5. (a) A SE image of the anatase sample sintered in argon atmosphere at 1500 °C. (b) An infrared CL image of the area shown in (a).

range from 0.27 to 0.87 eV below the conduction band. The shallow traps act as radiative or nonradiative centres depending of their electronic charge. When the oxygen is absorbed at the sample surface, it traps the electrons, and the shallow traps can act as radiative centres. In our experiment, the treatment in oxygen at 800 °C of the sample sintered in argon showed that some of the defect centres are sensitive to oxygen. Blue luminescence peaked at 450 nm becomes the dominant emission in the visible region after treatment in oxygen, suggesting that the de-excitation process is assisted by a shallow trap associated with a vacancy of oxygen. The SEM CL images of the polycrystalline samples show that the regions of the grain boundaries appear brighter, with a higher concentration of the emitting centres in comparison to the grain region. Figure 4 shows a CL image of an anatase sample formed by thermal treatment at 1500 °C in argon. The grain boundaries are observed as luminescent regions and also some of the grains show luminescence emission. SEM CL infrared images of the same sample presented in figure 5 show that the infrared emission is preferentially localized at the grain boundaries. The particularities of the octahedral crystal field around the Ti ion could determine the splitting of associated electronic levels and appropriate emission bands, observed mainly in the spectra of anatase phase films (see figure 2(a)).

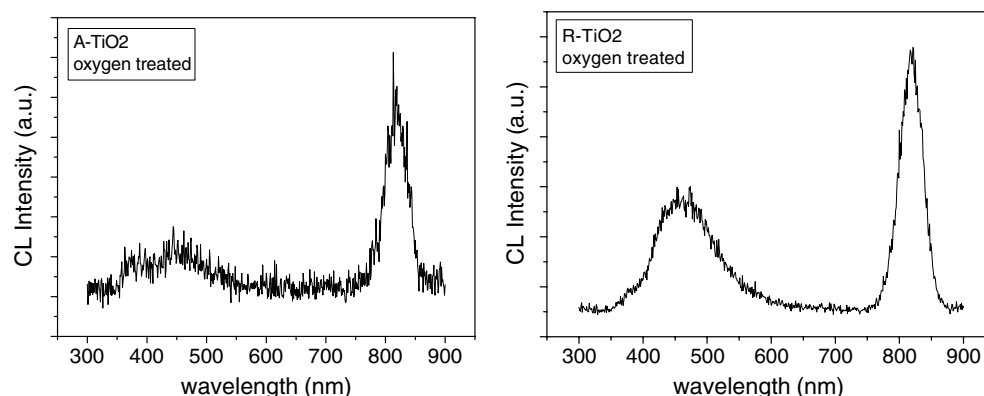


Figure 6. CL spectra of (a) anatase and (b) rutile samples treated for 30 min in oxygen atmosphere.

The annealing in oxygen atmosphere does not lead to the removal of Ti^{3+} centres. A sharp and intense band peaked at 820 nm is still present in the spectra of both anatase and rutile samples after annealing in oxygen atmosphere for 30 min at 800 °C (figures 6(a) and (b)) and even after 2 and 8 h of treatment. However, annealing in oxygen atmosphere induces changes of the luminescence emission in the visible range. Some weak bands are present in the spectrum of anatase (figure 6(a)) with peaks at 380, 450 and 520 nm. The intensity of the band at 450 nm presents a noticeable increase for rutile, relative to the case of anatase, as can be seen in the spectrum shown in figure 6(b).

Previous studies suggest that only grains with a certain orientation are preferentially reacting with oxygen. In particular, several studies on (110) rutile surface reactivity have shown that in the presence of oxygen, the surface reconstruction is achieved by the growth of various types of structure [3, 14, 15]. The changes in the (110) surface lead to a structure of terraces that is formed after annealing in oxygen at elevated temperatures [16]. Typically, the dimensions are: tens of ångströms wide; monatomic step height. Other structures consist of hexagonal shaped interconnected rosettes, with the width equal to that of the substrate unit cell along the [110] direction, that is 6.5 Å. This is a metastable phase that transforms into a stable structure after treatment at high temperatures or long time treatments [14, 17]. The terrace structure formation is related to the presence of titanium ions in interstitial positions after previous reducing treatments [6, 18]. The preferential sites for the formation of the surface structures are the regions with large concentrations of Ti^{n+} interstitial centres. The process is activated at about 470 K [12] and the elevated temperatures lead to three- or two-dimensional growth of the structures, depending on the atom mobility.

SEM micrographs of the rutile sample treated in oxygen for 30 min at 800 °C show the presence of protrusions growing with an irregular distribution in the grains (figure 7(a)). After 2 h of treatment in oxygen atmosphere, the surface reconstruction takes place by terrace growth. SEM and AFM images show that not all the grains are reacting with oxygen, or at least the terraces are not present in all the grains. An SEM image of rutile after 2 h of treatment in oxygen (figure 7(b)) shows the terrace structure. Figure 8(a) shows an AFM image of the same sample with terraces localized near to or at the grain boundaries. An AFM image of interconnected terraces is presented in the figure 8(b). A profile line of the image of figure 8(b) shows that the steps height is increasing from the first step to the top structure and the step sizes are, sequentially, 20, 60 and 90 nm (figure 8(c)).

The presence of protrusions and terrace structures suggests that an excess concentration of Ti^{3+} interstitial ions generated during sintering is involved in the surface reconstruction

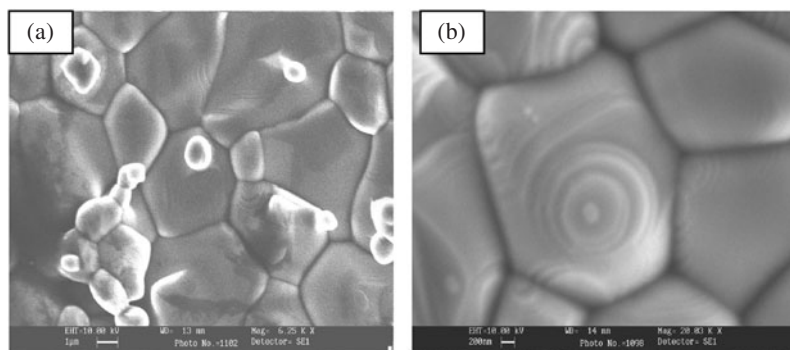


Figure 7. SEM secondary electron images of a rutile polycrystalline sample treated in O₂ for (a) 30 min, (b) 120 min.

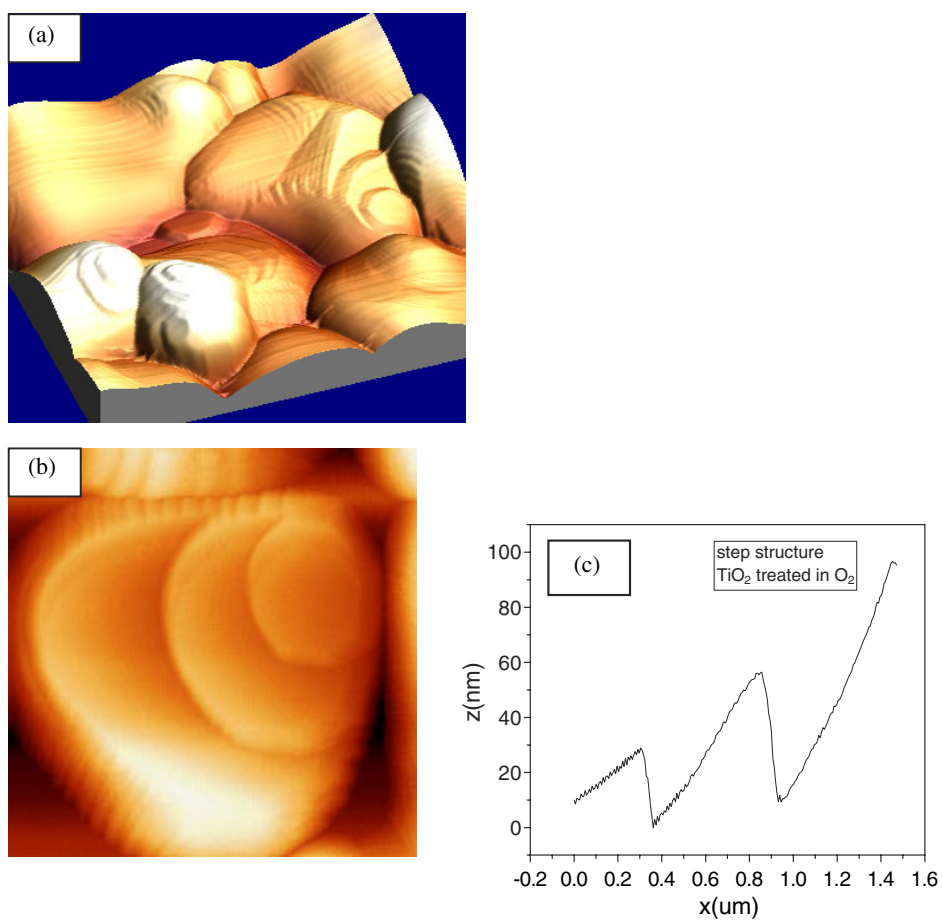


Figure 8. (a) An AFM image of an interconnected terrace structure grown on the surface of rutile after treatment in O₂ for 2 h at 800°C; (b) detail of the terraces; (c) a profile of the structure presented in (b).

(This figure is in colour only in the electronic version)

taking place during annealing in oxygen. However, the accumulation of such ions at the grain boundaries and in certain grain regions remains after treatment in oxygen. The associated energy levels in the band gap act as radiative recombination centres, leading to a characteristic infrared emission.

4. Conclusions

The influence of temperature and treatment atmosphere on the structure and optical properties of TiO₂ sintered samples was analysed by means of XRD, SEM, AFM and CL in SEM. Samples sintered at 1100 °C present luminescence emission in the visible and infrared regions. The infrared band, peaked at 800–820 nm, is the main emission band appearing in the spectra of the polycrystalline samples obtained in the temperature range 1100–1500 °C. The luminescence is associated with the presence of Ti³⁺ interstitial ions appearing to form at these annealing temperatures. The luminescence emission is mainly localized at the grain boundary regions. Some of the grains appear as luminescent regions as well. Light emission in the visible region shows a reduced intensity and is almost quenched if the samples are formed in air. However, the intensity of the emission band at 450 nm increases with treatment in oxygen. After treatment in oxygen, the surface reconstruction results in the formation of a terraced structure with preferential sites localized in the grain boundary regions.

Acknowledgments

This work was supported by MCYT (Project MAT2000-2119). RP thanks MCYT for a research grant from the NATO scientific programme.

References

- [1] Diebold U 2003 *Surf. Sci. Rep.* **48** 53
- [2] Asari E and Souda R 2003 *Vacuum* **68** 123
- [3] Gan S, Liang Y and Baer D R 2000 *Surf. Sci.* **459** L498
- [4] Fujino T, Katayama M, Inudzuka K, Okuno T and Oura K 2001 *Appl. Phys. Lett.* **79** 2716
- [5] Nörembrger H, Tanner R E, Schierbaum K D, Fischer S and Briggs G A D 1998 *Surf. Sci.* **52–60** 396
- [6] Bennett R A, Poulston S, Stone P and Bowker M 1999 *Phys. Rev. B* **59** 10341
- [7] Tang H, Prasad K, Sanjines R, Schmid P E and Levy F 1994 *J. Appl. Phys.* **75** 2042
- [8] Sanjines R, Tang H, Berger H, Gozzo F, Margaritondo G and Levy F 1994 *J. Appl. Phys.* **75** 2945
- [9] Ghosh A K, Wakim F G and Addiss R R Jr 1969 *Phys. Rev.* **184** 979
- [10] Deb S K 1972 *Solid State Commun.* **11** 713
- [11] Tang H, Berger H, Schmidt P E and Levy F 1993 *Solid State Commun.* **87** 847
- [12] Reynolds D C, Look D C, Jogai B, Van Nostrand J E, Jones R and Jenny J 1998 *Solid State Commun.* **106** 701
- [13] Rothschild A, Levakov A, Shapira Y, Ashkenasy N and Komem Y 2003 *Surf. Sci.* **456** 532
- [14] Li M, Hebenstreit W and Diebold U 1998 *Surf. Sci.* **414** L951
- [15] Epling W S, Peden C H F, Henderson M A and Diebold U 1998 *Surf. Sci.* **412/413** 333
- [16] Li M, Hebenstreit W, Gross L, Diebold U, Henderson M A, Jennison D R, Schultz P A and Sears M P 1999 *Surf. Sci.* **437** 173
- [17] Diebold U, Anderson J F, Ng K O and Vanderbilt D 1996 *Phys. Rev. Lett.* **77** 1322
- [18] Onishi H and Iwasawa Y 1996 *Phys. Lett.* **76** 791