Suppression of Anatase to Rutile Phase Transformation of Niobium doped TiO_2 Synthesized by High Temperature Diffusion Technique

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Abstract

The effects of niobium doping (for doping concentrations: 0.02 – 0.06 at. % Nb^{5+}) on the crystal structure of TiO_2 prepared by high temperature diffusion method were investigated. The samples were characterized using energy dispersive X-ray fluorescence (EDXRF) and X- ray diffraction (XRD) spectroscopy to investigate the chemical compositions, phase compositions and crystallinity of the thin films respectively. Despite the expected high reutilization at high temperatures (>600°C), XRD results confirmed a significant suppression of anatase to rutile phase transformation at even a higher synthesis (850°C) temperature. Grain growth retardation was also observed in niobium doped TiO_2, results which were attributed to Nb^{5+} substitution of lattice Ti^{4+}.

Key words: Anatase, rutile, phase transformation, grain growth

1. Introduction

Research on titanium dioxide light absorption has for the past four decades attracted considerable attention for possible broad applications in solar cells, photo catalysis, gas sensors, etc. TiO_2 naturally occurs in three crystalline phases, that is, rutile, anatase and brookite. Of the three phases, ruitle is the most thermodynamically stable at room temperature. Although anatase phase is the most kinetically stable phase of titania, both anatase and brookite phases transform to rutile at higher temperatures (> 600°C) [Sood and Gouma, 2013; Hari and Sunarto, 2010]. However, TiO_2 is a wide band gap material (3.0 eV - 3.2 eV for rutile and anatase phases of TiO_2 respectively). In a pure state TiO_2's application is only limited to the less abundant ultra violet (UV) part of the larger solar spectrum.

Despite the fact that rutile has a lower band gap (~3.0eV) compared to anatase (~ 3.2 eV), anatase exhibits better photovoltaic activity due to its higher specific surface area [Sclafani and Herrmann, 1996]. In spite of irreversible transformation of anatase at elevated temperatures (> 600°C) to equilibrium rutile phase, most applications of TiO_2 still require this metastable anatase phase instead of the equilibrium rutile phase due to the high specific surface area of anatase phase [Basca and Kiwi, 1998]. The good news is that, in most synthesis procedures, it is the less constrained long-range ordered molecular construction of the 4-edge-sharing TiO_6 octahedra anatase that crystallizes first since its crystallization requires less energy than rutile phase [Hanaor and Sorrell, 2011; Gopal *et al*., 1997].

However, some applications require a mixed phase composition of anatase and rutile which give superior photovoltaic performances compared to a single phase of either anatase or rutile [Ohno *et al*., 2002; Bakardjieva *et al*., 2005; Hurum *et al*., 2003]. Additionally, where high temperature synthesis is used or when titania derived devices are to be used in high temperature environments such in gas sensing and in porous membrane gas separators [Kumar *et al*., 1994; Penn and Banfield, 1999; Jonsoo *et al*., 2001], control of the transformation kinetics of anatase to rutile phases is critical. This is because, under such high temperature application environments, phase transformation may occur with adverse effects on the performance of these devices.

The anatase to rutile transition kinetics is affected by a number of variables such as presence of impurities and dopants, in addition to samples preparation procedures. Presences of impurities or dopants may imply lattice distortions thus affecting the degree of crystallinity. Anatase to rutile transformation usually result in significant grain growth [Iida and Ozaki, 1961; Zhang and Reller, 2002], while thermal gradient enhances surface nucleation of rutile phase. However, anatsae to rutile phase transformation can be impeded (or enhanced) by manipulating the arrangement of the atoms in the anatase or rutile lattices.

Depending on the valency and atomic radii of a dopant, it can occupy either an interstitial or a lattice site. Interstitial or lattice dopants in titania have various effects such as band gap narrowing [Serpone, 2006; Nagaveni *et al*., 2004], creation of mid gap states [Ranjit *et al.*, 1999], carrier generation and transport improvements, and hindrance or enhancement of phase transformation leading retardation or quickening of grain growth in titania [Reidy *et al*., 2006]. A dopant occupying an anatase lattice site, will influences the level of oxygen vacancies thereby either enhancing or impeding anatase transition to rutile. Enhanced transformation is achieved through lattice relaxation via increased oxygen vacancies. This can be easily done through firing under high vacuum or under very low oxygen partial pressure [Gamboa and Pasquevich, 1992; Syarif *et al*., 2002]. Therefore careful control of oxygen sublattice vacancies related defects is critical [Riyas *et al*., 2007; Ihara *et al*., 2003]. Substitutional dopants on the other hand, may destabilize or stabilize anatase phase [Hanaor *et al*., 2012] depending on their sizes. In this work, we report a systematic description of suppression of anatase to rutile phase transition as well as retardation of grain growth in TiO_2 thin films doped by niobium by high temperature diffusion technique.

2. Experimental Procedures

Thin films were prepared via high temperature diffusion. To obtain the desired Nb^{5+} concentration in the TiO_2 matrix, calculated masses of Nb_2O_5 (99.9% purity, Aldrich) were weighed and mixed with 10g of TiO_2 (Degussa P-25). Distilled water (50.00 cm^3) was then added to the mixtures in 100 cm^3 beakers. The slurries formed were then gently heated to 80°C under continuous stirring until nearly all the water evaporated. The solid residues were further dried in a furnace at 110°C for about 10 hours. Using a mortar and pestle, the solids were crushed into fine powders which were sieved using a 106 µm pore size sieve. These powders were calcined (heat treated) in a furnace (Nabertherm - 30) fitted with a programmable controller at a temperature of 850°C for 5 hours to achieve appreciable high temperature thermal diffusion assisted doping of TiO_2 by niobium (Nb).

To get a colloidal solution of $Nb:TiO_2$, specific masses of $Nb:TiO_2$ powder prepared as described above, were mixed with the same mass of de - ionized water. The mixtures were then ground for 10 hours using an agate mortar to a uniform paste. These pastes were further diluted with w:w triton water (Triton X–100 Aldrich) solution to 36% w:w with respect to the $Nb:TiO_2$. A few drops of 0.5M nitric acid were added to facilitate the dispersion of the Nb:TiO_2 particles thus reducing particles agglomeration. The resulting gels were then stirred with a magnetic stirrer overnight and were then stored under refrigeration (at < 5°C). Thin films were then deposited by spin-coating (P67080, Cookson Electronics–USA) at spin speed of 2000 rev/min. onto cleaned microscope slides. The thin films were annealed at 450°C at a heating rate of 1.5°C/minute for 5 hours then allowed enough time (over 24Hrs) to cool to room temperature (23°C).

3. Results and Discussions

The Nb_2O_5 / TiO_2 mixtures fired at 850°C for five hours, turned from white to slightly yellow in color. The slight yellowish coloration may be attributed to polaron absorption due to niobium doping into the TiO_2 lattice, an indication that appreciable doping had taken place, agreeing with earlier independently reported observations by a number of authors [Feroni *et al.*, 2000; Ruiz *et al.*, 2003; Scotter *et al.*, 2005; Mattson *et al.*, 2006]. As the crystalline order increases, the absorption band becomes broader and shifts towards larger wavelength giving rise to the slight yellow color [Schmitt and Aegerter, 2000].

Figure1 shows a typical EDXRF results for the Nb: TiO_2 having 0.04 at. % Nb concentration confirming that the Nb doped TiO_2 sample powders contained Ti, Nb and O atoms. The non -labeled spectra are due to interference phenomena.

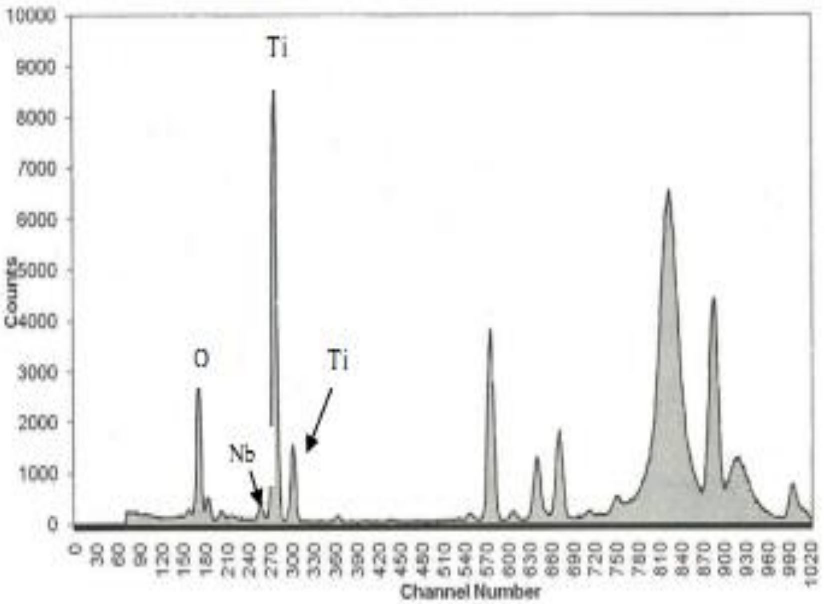

Figure 1: Energy Dispersive X-ray Fluorescence (EDXRF) spectra of niobium doped TiO_2 (The energy width: 1.33 eV/channel).

Figure 2 shows the normalized X–ray diffraction (XRD) spectrum of Nb: TiO_2 at various Nb doping concentrations. It is observed (Figure 2) that, both the anatase and rutile phases are present in all the niobium doped TiO_2, albeit with varying concentration depending on the concentrations of niobium dopants. It is noticed that, the anatase phase crystals' orientations also changed from (101) being more preferred in pure TiO_2 to (211) being the most preferred anatase crystal phase structure in the doped samples.

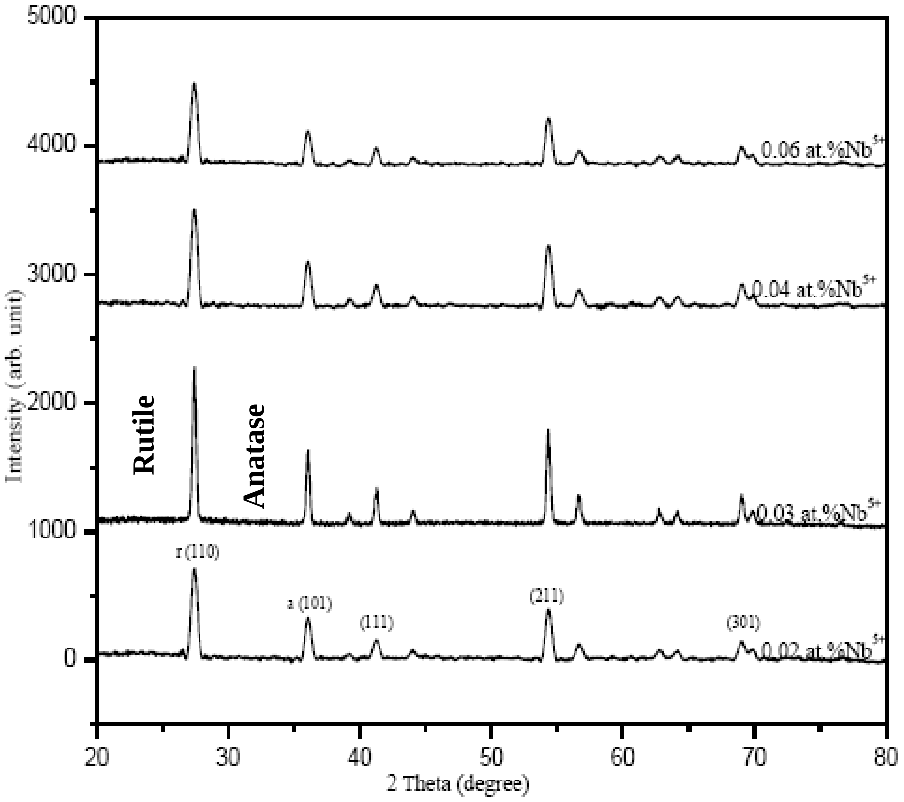

Figure 2: Typical X-ray diffraction spectra of niobium doped TiO_2 for niobium concentrations ranging from 0.02% to 0.06% atomic percent (with '*r*' and '*a*' representing rutile and anatase phases respectively).

The mean percentage content of anatase phase in the composite were calculated from the XRD data (Figure 2) with the aid of Spurr and Myer equation (Eqn. 1) [Spurr and Myers, 1957] and the results plotted in Figure 3.

$$x_A = \left(1 + 1.26\frac{I_R}{I_A}\right)^{-1} \qquad (1)$$

where x_A is the weight fraction of anatase in the doped powder, while I_A and I_R are the x-ray intensities of anatase and rutile peaks respectively. The average grain/crystal sizes "l" as a function of niobium concentration were calculated from the XRD data using Scherer's equation (Eqn. 2) [Scherrer, 1918];

$$l = \frac{k\lambda}{\beta\cos\theta} \qquad (2)$$

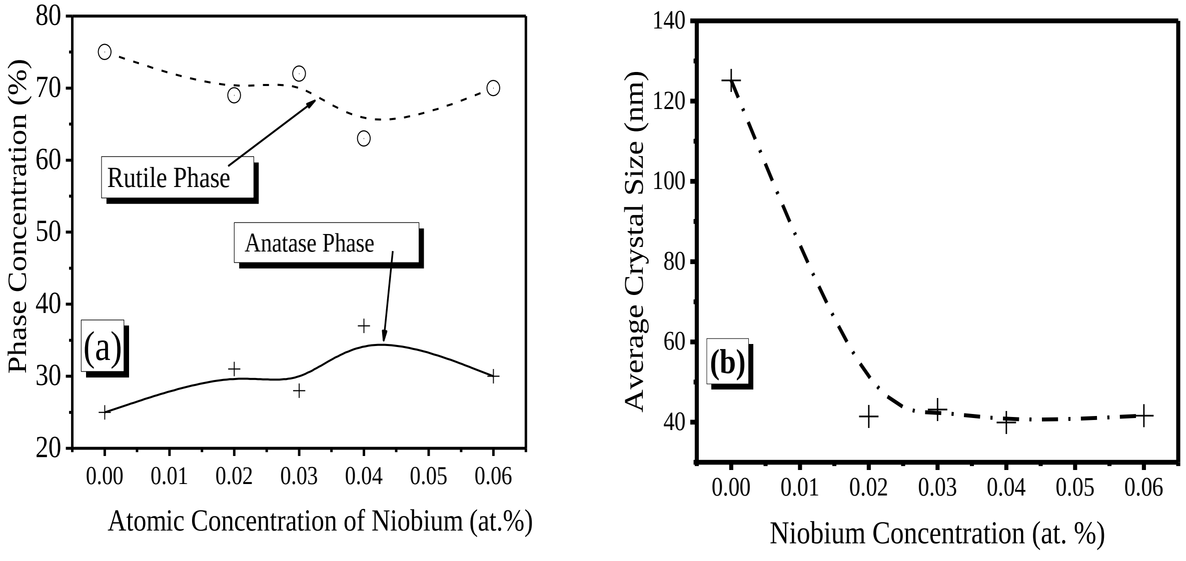

Figure 3: (a): Rutile and anatase phases' concentration and (b) average crystal sizes as a function of the niobium concentrations.

From Figure 3(a), significant suppression of anatase to rutile phase transformation for Nb trace concentrations up to 0.03 at. % Nb is observed. This happened, disregarding the expected high rutilization rates expected in TiO_2 thermally treated at temperatures above 600°C [Sood and Gouma, 2013; Hari and Sunarto, 2010]. We proposed that, this is due to Nb^{5+} substitution for Ti^{4+} in the crystalline TiO_2 lattices thus hindering anatase to rutile phase transformation. Similar observations were reported by Anukunprasert's group [Anukunprasert *et al.*, 2005]. In addition to suppressed anatase to rutile phrase transformation, retardation of gain growth at the doping is clearly noticeable (Figure 3(b)). The calculated particle sizes were found to be ranging between 39.92 and 43.14 nm in doped samples compared to undoped TiO_2 thin films which had a mean crystal sizes well above 125 nm. This result is consistent with other previously reported observations [Mohd *et al.*, 2013] where doping of TiO_2 by various transition metals had shown significant reduction of crystal sizes. This result is a clear indicator that niobium doping significantly retarded grain growth thereby increasing the specific surface area of the particles. Larger specific areas' particle is one of the ideal properties required in materials used in photovoltaic applications.

4. Conclusions

The results of this study showed that high temperature doping of TiO_2 by niobium is possible and trace dopant Nb^{5+} concentrations suppressed anatase to rutile phase transformation despite the expected high rutilization at a high calcination temperatures (above 600°C). Crystal sizes obtained from x-ray diffraction spectra showed an increase in surface areas manifesting retardation of grain growth. These results attributed to a possibly Nb^{5+} substitution for Ti^{4+} in the crystalline TiO_2 lattice.

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