

Suppression of Anatase to Rutile Phase Transformation of Niobium doped TiO₂ Synthesized by High Temperature Diffusion Technique

Ogacho A. Aa*,
Department of Physics, University of Nairobi, Box 30197 00100,
Nairobi, Kenya
aogachoa@uonbi.ac.ke

Ajuoga P b
Department of Physics, University of Nairobi
Box 30197 00100,
Nairobi, Kenya
bajuogapw@yahoo.com

Aduda B. Oc
Department of Physics, University of Nairobi
Box 30197 00100,
Nairobi, Kenya
c boaduda@uonbi.ac.ke

*Corresponding author email: ogachoa@uonbi.ac.ke

Abstract

The effects of niobium doping (for doping concentrations: 0.02 – 0.06 at. % Nb⁵⁺) on the crystal structure of TiO₂ 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 TiO₂, results which were attributed to Nb⁵⁺ substitution of lattice Ti⁴⁺.

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. TiO₂ naturally occurs in three crystalline phases, that is, rutile, anatase and brookite. Of the three phases, rutile 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, TiO₂ is a wide band gap material (3.0 eV - 3.2 eV for rutile and anatase phases of TiO₂ respectively). In a pure state TiO₂'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 ($> 600^{\circ}\text{C}$) 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, anatase 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 influence 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 $106\text{ }\mu\text{m}$ 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:TiO₂ 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 Nb₂O₅ / TiO₂ 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 TiO₂ 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].

Figure 1 shows a typical EDXRF results for the Nb: TiO₂ having 0.04 at. % Nb concentration confirming that the Nb doped TiO₂ sample powders contained Ti, Nb and O atoms. The non -labeled spectra are due to interference phenomena.

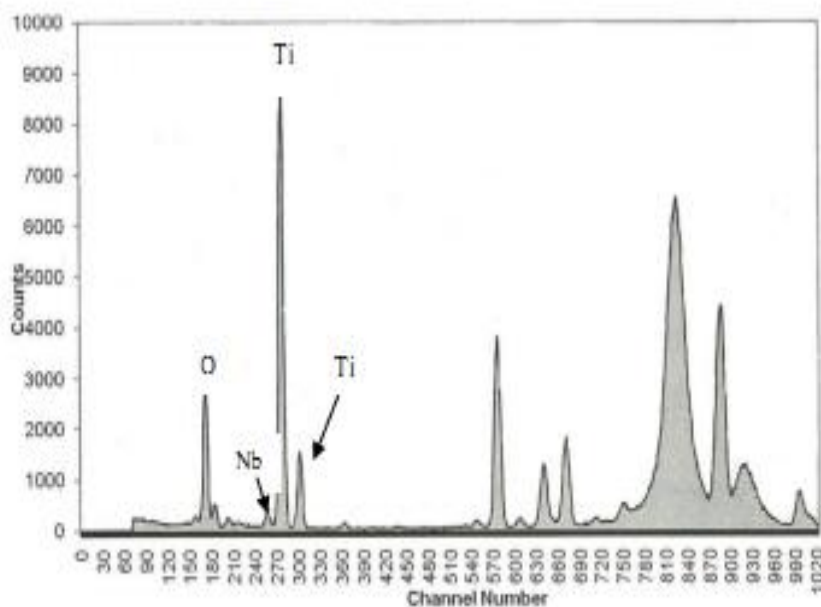


Figure 1: Energy Dispersive X-ray Fluorescence (EDXRF) spectra of niobium doped TiO₂ (The energy width: 1.33 eV/channel).

Figure 2 shows the normalized X-ray diffraction (XRD) spectrum of Nb: TiO₂ at various Nb doping concentrations. It is observed (Figure 2) that, both the anatase and rutile phases are present in all the niobium doped TiO₂, 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 TiO₂ to (211) being the most preferred anatase crystal phase structure in the doped samples.

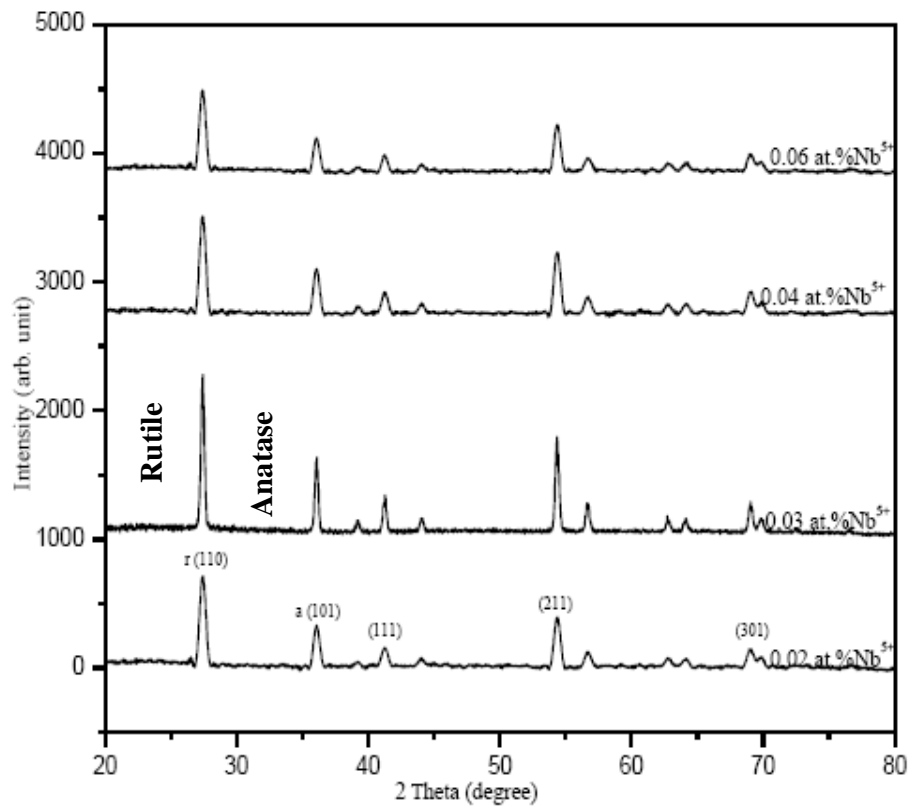


Figure 2: Typical X-ray diffraction spectra of niobium doped TiO₂ for niobium concentrations ranging from 0.02% to 0.06% atomic percent (with ‘r’ and ‘a’ representing rutile and anatase phases respectively).

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.

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

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 Scherrer’s equation (Eqn. 2) [Scherrer, 1918];

$$l = \frac{k\lambda}{\beta \cos\theta} \tag{2}$$

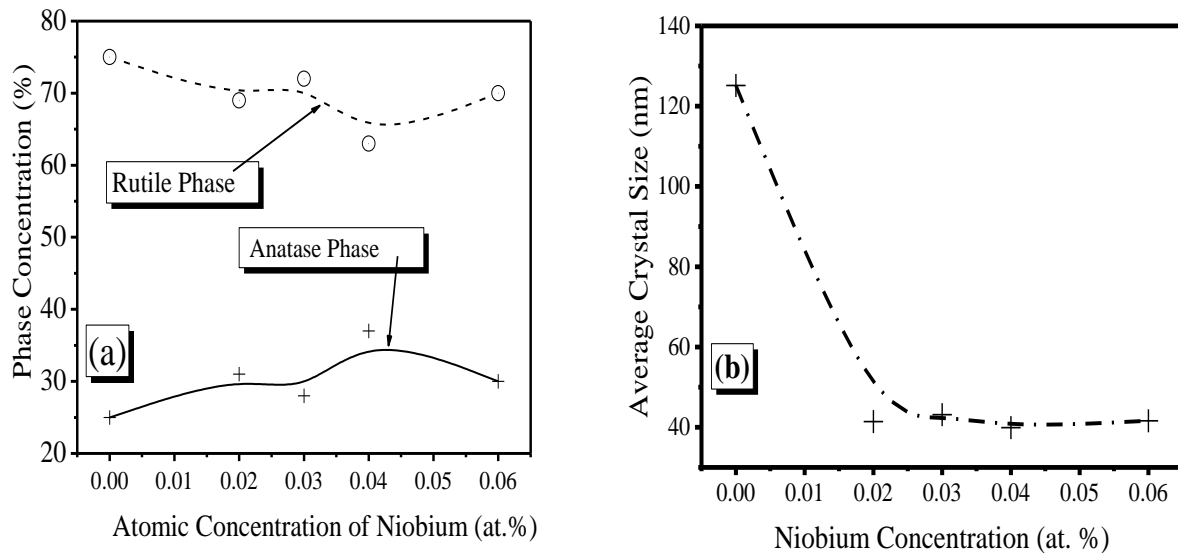


Figure 3: (a): Rutile and anatase phases' concentration and (b) average crystal sizes as a function of the niobium concentrations.

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 TiO₂ thermally treated at temperatures above 600°C [Sood and Gouma, 2013; Hari and Sunarto, 2010]. We proposed that, this is due to Nb⁵⁺ substitution for Ti⁴⁺ in the crystalline TiO₂ 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 phase transformation, retardation of grain 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 TiO₂ 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 TiO₂ 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 TiO₂ by niobium is possible and trace dopant Nb⁵⁺ 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 Nb⁵⁺ substitution for Ti⁴⁺ in the crystalline TiO₂ lattice.

5. Acknowledgements

The authors are grateful to the University of Nairobi for provision of research facilities and to the staff at the Department of Physics (University of Nairobi, Kenya) for their fruitful discussions and suggestions during the research and subsequent preparation of this paper. Last but not least, our sincere gratitude to the International Science Program (ISP) at Uppsala University (Sweden) for financial support.

References

1. **Anukuprasert T., Saiwan C. and Traversa E.**, The Development of Gas Sensor for Carbon Monoxide Monitoring using Nanostructure of Nb–TiO₂, *Science and Technology of Advanced Materials*, **6** (2005) 359 – 363.
2. **Bakardjieva S, Subrt J, Stengl V, Dianez M. J and Sayagues M. J.**, Photoactivity of anatase-rutile TiO₂ nanocrystalline mixtures obtained by heat treatment of homogeneously precipitated anatase. *Applied Catalysis B: Environmental* **58** (2005) 193 – 202.
3. **Basca R. R. and Kiwi J.**, Effect of rutile phase on the photocatalytic properties of nanocrystalline titania during the degradation of *p*-coumaric acid, *Appl. Catal. B.*, **16** [1] (1998) 19 – 29.
4. **Feroni M., Carotta M. C., Guidi V., Martinelle G., Rouconi F., Richard O., Van Dyck D. and Landuyt Van J.**, Structural Characterization of Nb–TiO₂ nanosized thick Films for Gas Sensing Applications, *Sensors and Actuators B*, **68** (2000) 140 – 145.
5. **Gamboa J. A. and Pasquevich D. M.**, Effect of Chlorine Atmosphere on the Anatase-Rutile Transformation, *J. Am. Ceram Soc.* **75** (1992) 2934 - 2938.
6. **Gopal M, Moberly Chan W. J and De Jonghe L. C.**, Room temperature synthesis of crystalline metal oxides. *J. Mat. Sci.* **32** (1997) 6001- 6008.
7. **Hanaor D and Sorrell C. C.**, Review of the anatase to rutile phase transformation, *J. Mat. Sci.* **46** (2011) 855 - 874
8. **Hanaor D. A. H., Assadi M. H.N., Aibng Yu, Li Sean, and Sorrell C. C.**, Ab Initio Study of Phase Stability in Doped TiO₂, *Computational Mechanics* **50** [2] (2012) 185 – 194.
9. **Hanaor D., Triani G and Sorrell C. C.**, Morphology and photocatalytic activity of highly oriented mixed phase titanium dioxide thin films, *Surface and Coatings Technology* **205** (2011) 3658 – 3664.
10. **Hari Sutrisno and Sunarto**, Polymorphic Transformation of Titanium Dioxide Caused by Heat Treatment of Protonic Leptdocrocite Titanate, *Indo. J. Chem.* **10** (2) (2010) 143 - 148
11. **Hurum D. C, Agrios A. G, Gray K. A, Rajh T and Thurnauer M. C.**, Explaining the enhanced photocatalytic activity of Degussa P25 mixed-phase TiO₂ using EPR. *J. Physical Chem B* **107** (2003) 4545 – 4549.
12. **Ihara T, Miyoshi M, Iriyama Y, Matsumoto O, Sugihara S**, Visible-light-active titanium oxide photocatalyst realized by an oxygen-deficient structure and by nitrogen doping, *Applied Catalysis B: Environmental*, **42** [4] (2003) 403 – 409.
13. **Iida Y. and Ozaki S.**, Grain Growth and Phase Transformation of Titanium Oxide During Calcination, *J. Am. Ceram Soc.* **44** (1961) 120 – 127.
14. **Jinsoo Kim, Ki Chang Song, Sandra Foncillas, Sotiris E. Pratsinis**, Dopants for synthesis of stable bimodally porous titania, *J. Eur. Ceramic Soc.* **21** (2001) 2863 - 2872
15. **Kumar K.N. P., Keizer K., Burggraaf A. J.**, Stabilization of the porous texture of nanostructured titania by avoiding a phase transformation, *J. Mat. Sci. Let.* **13** (1994) 59 – 61.
16. **Mattson Andreas, Michael Leideborg, Karin Larsson, Gunner Westin and Lars Osterlund**, Absorption and Solar Light Decomposition of Acetone on Anatase TiO₂ and Niobium Doped TiO₂ Thin films, *Journal of Physical Chemistry B*, **110** (2006)1210 –1220.
17. **Mohd Hasmizam Razali, Ahmad-Fauzi M. N., Abdul Rahman Mohamed, and Srimala** Morphological, Structural and Optical Properties Study of Transition Metal Ions Doped TiO₂ Nanotubes Prepared by Hydrothermal Method, *International Journal of Materials, Mechanics and Manufacturing*, **Vol. 1**, No. 4, (2013) 314 – 318.
18. **Nagaveni K., Hegde M. S., Ravishankar N., Subbanna G. N., and Giridhar Madras**, Synthesis and Structure of Nanocrystalline TiO₂ with Lower Band Gap Showing High Photocatalytic Activity , *Langmuir* **20** [7] (2004) 2900 – 2907.

19. **Ohno T, Sarukawa K and Matsumura M.**, Crystal faces of rutile and anatase TiO₂ particles and their roles in photocatalytic reactions. *New journal of chemistry* **26** (2002) 1167- 1170.
20. **Penn R. L. and Banfield J. F.**, Formation of rutile nuclei at anatase {112} twin interfaces and the phase transformation mechanism in nanocrystalline titania, *American Mineralogist* **84** (1999) 871 – 876.
21. **Ranjit K. T., Cohen H., Willner I., Bossmann S.**, Lanthanide oxide-doped titanium dioxide: Effective photocatalysts for the degradation of organic pollutants, *J. Mat. Sci.* **34** (1999) 5273 - 5280.
22. **Reidy D.J., Holmes J.D., Morris M.A.**, The critical size mechanism for the anatase to rutile transformation in TiO₂ and doped-TiO₂, *J. Eur. Ceram Soc.* **26** (2006) 1527 - 1534
23. **Riyas S., Krishnan G., Mohan Das P. N.**, Anatase - rutile transformation in doped titania under argon and hydrogen atmospheres, *Adv. Appl. Ceram.* **106** (2007) 255 – 264.
24. **Ruiz A., Dezanneau G., Arbiol J., Cornet A. and Morante J. R.**, Study of the Influence of Nb Content and Sintering Temperature on TiO₂ Sensing Films, *Thin Solid Films*, **436** (2003) 90 – 94.
25. **Scherrer Paul**, Bestimmung der Grösse und der Inneren Struktur von Kolloidteilchen Mittels Rontgenstrahlen, Nachrichten von der Gesellschaft der Wissenschaften, Göttingen, *Mathematisch-Physikalische Klasse* **2** (1918) 98 - 100.
26. **Schmitt M. and Aegerter A. M.**, Electronic Properties of Pure and Doped Nb₂O₅ Coatings and Devices, *Electrochemical Actuators*, **46** (2001) 2105 – 2111.
27. **Sclafani A and Herrman J. M.**, Comparison of the Photoelectronic and Photocatalytic activities of various anatase and rutile forms of titania, *J. Physical Chem.* **100** (1996) 13655 - 13661
28. **Scotter E., Vilanova X., Llobet E., Stankova M. and Correig X.**, Niobium doped Titania Nanopowders for Gas Sensor Applications, *Journal of Optoelectronic and Advanced Materials*, **7** [3] (2005)1395 – 1398.
29. **Serpone Nick**, Is the Band Gap of Pristine TiO₂ Narrowed by Anion- and Cation-Doping of Titanium Dioxide in Second-Generation Photocatalysts? *J. Phys. Chem. B*, **110** [48], (2006) 24287 – 24293.
30. **Sood S. M. S and Gouma P.**, Polymorphism in nanocrystalline binary metal oxides, *Nanomaterials and Energy*, Vol. 2 Issue No. NME2 (2013) 82–96; <http://dx.doi.org/10.1680/nme.12.00037>
31. **Spurr R. A and Myers H.**, Quantitative Analysis of Anatase-Rutile Mixtures with an X-Ray Diffractometer, *Analytical Chemistry* **29** [5] (1957) 759 – 761.
32. **Syarif D. G., Miyashita A, Yamaki T, Sumita T, Choi Y, Itoh H**, Preparation of anatase and rutile thin films by controlling oxygen partial pressure, *Appl. Surf. Sci.* **193**[1–4] (2002) 287 – 292.
33. **Zhang Yu-Hong, Reller Armin**, Phase transformation and grain growth of doped nanosized titania, *Mat. Sci. Eng. C* **19** (2002) 323 – 326.