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# Effect of niobium on the structure of titanium dioxide thin films

L. Sheppard [a,*], T. Bak [a], J. Nowotny [a], C.C. Sorrell [a], S. Kumar [b], A.R. Gerson [b,c], M.C. Barnes [d], C. Ball [e]

[a] Centre for Materials Research in Energy Conversion, School of Materials Science and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia
[b] Ian Wark Research Institute, University of South Australia, Australia
[c] Applied Center for Structural and Synchrotron Studies (ACeSSS), Mawson Lakes, SA 5095, Australia
[d] Center for Microstructure Science of Materials, School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea
[e] Australian Nuclear Science and Technology Organisation, Department of Materials Science and Engineering, Lucas Heights, Menai, NSW 2234, Australia

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**Abstract**

This paper reports the effect of niobium on the structure of titanium dioxide ($TiO_2$) thin films deposited on glass. The results obtained indicated that the direct current (DC) co-sputtering of Ti and Nb onto glass substrates in the presence of oxygen results in the formation of Nb-doped anatase thin films with strong preferential orientation. In the concentration range between 0 and 40 at.% Nb, niobium is incorporated into the $TiO_2$ lattice according to a substitution mechanism, entering Ti sites in the cation sub-lattice. No evidence exists for a solubility limit <40 at.% of Nb under the applied deposition conditions, however, it is not believed that an equilibrium situation prevails. Lattice charge compensation was concluded to occur by the formation of cation vacancies for samples with up to 10 at.% Nb, and by $Ti^{3+}$ or $Nb^{4+}$ ions for the samples with ≥15 at.% Nb, the latter in conjunction with cation vacancy compensation.


*Keywords:* Growth mechanism; X-ray diffraction; Sputtering; Titanium oxide

## 1. Introduction

For some time, $TiO_2$ has been a prime candidate for photo-electrodes for photo-electrochemical hydrogen generation from water using solar energy [1]. This is due primarily to its resistance to photo-corrosion. However, the performance of $TiO_2$-based photo-electrodes has been low owing to the unsuitability of several functional properties, which are pertinent to this application. Fortunately, the functional properties of $TiO_2$ can be widely modified by changes to its oxygen non-stoichiometry and/or through the incorporation of aliovalent cations forming donors or acceptors.

With respect to the use of dopants, the mode of incorporation and their solubility limit are crucial to their impact on the associated properties. In this paper, Nb doping in $TiO_2$ is of interest. In the literature, there are conflicting reports on the solubility range of Nb into the $TiO_2$ lattice and the effect of Nb on properties of the Nb-doped $TiO_2$ [2]. The observed differences may be caused by the fact that the studied specimens were not in thermodynamic equilibrium and therefore, not well defined.

In analogy to $BaTiO_3$, the diffusion rate of Nb in the $TiO_2$ lattice is expected to be very low [2,3]. Therefore, solid solutions of Nb in $TiO_2$ are expected to form only at elevated temperatures at which the mobility of the cation sublattice is sufficiently high. Preliminary data indicate that Nb may be incorporated rapidly into the $TiO_2$ lattice above 1500 K [4]. A similar effect has been reported for Nb-doped $BaTiO_3$ [2].

The aim of this study was to examine the effect of Nb on the crystalline structure of "as-deposited" Nb-doped $TiO_2$ thin films and to assess the extent of Nb incorporation. In particular, this study focused on the X-ray diffraction (XRD) data of $TiO_2$ thin films doped with up to 40 at.% Nb. The mode of Nb incorporation was assessed by examining the changes to the lattice parameters as a function of the Nb concentration. Also considered is the state of the films in terms of thermodynamic equilibrium.

* Corresponding author. Tel.: +61 2 9385 6459; fax: +61 2 9385 6467.
*E-mail address:* l.sheppard@student.unsw.edu.au (L. Sheppard).

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## 2. Low temperature crystalline thin film deposition

For thin film deposition from a gas phase, it is generally accepted that the growth mechanism results from the reaction or interaction of the substrate with atoms/molecules in the gas phase. On the other hand, the theory of charged clusters (TCC) considers such thin films to consist of a self-assembly of charged clusters, which have nucleated and grown in the gas phase before migrating to the substrate [5–8]. These clusters form the fundamental growth unit of the resulting thin film. Hence, according to the TCC, the structure and properties of the cluster will largely determine the structure and properties of the resulting thin film.

Cluster charging occurs due to the presence of an ionizing source, such as plasma, and plays a role in determining the cluster size and crystallinity [5–8]. By controlling the residence time in the gas phase, the cluster size can be controlled [7,8], and the deposition of a crystalline film at low temperatures (approaching room temperature) becomes possible. Furthermore, controlling the size of the charged cluster enables the deposition of films with a controlled crystal morphology [5–8]. The ability of clusters to deposit and epitaxially realign to a larger crystal has been explained by [5–10]. Although the TCC is accepted in the sputtering process, its application to the deposition of novel materials is relatively new. To the best of the authors' knowledge, there is only one paper that has reported the application of the TCC to the deposition of crystalline $TiO_2$ at low substrate temperatures [8]. In the present paper, the structure and morphology of crystalline Nb-doped $TiO_2$ thin films with up to 40% Nb deposited on will be considered within the framework of the TCC.

## 3. Experimental details

Thin films of undoped and Nb-doped $TiO_2$ were deposited on glass substrates using the DC magnetron sputtering. The sputtering system (70 cm × 70 cm × 60 cm) involved a 180 mm Ti (purity 99.9%) sputtering target, with sputtering performed in an argon/oxygen mixture, at the flow rate of 40 sccm Ar and 20 sccm oxygen, used to strike the plasma. A constant oxygen flow rate was maintained while the Ar flow rate was altered to adjust for pressure. The oxygen flow rate was chosen through preliminary experiments, which showed that at this flow rate there was sufficient oxygen to react with all of the Ti sputtered. The chamber was sequentially pumped down with a roughing pump (Leybold Trivac), and then by a diffusion pump (Javac Australia) with a rotary backing pump (Leybold Trivac). The base pressure in the chamber was $5 \times 10^{-4}$ Pa. After the gas was introduced into the chamber, the pressure increased to 0.27 Pa. The gas flow rate was controlled using standard mass flow controllers.

The power used for deposition of the $TiO_2$ thin films was 400 W. The voltage was 485 ± 5 V and the current was 0.825 A. The experiments involved sputtering of a Ti target with the dopant material being placed on the target and a thin film being deposited on a substrate attached to an electrically floating substrate holder. To control the amount of Nb being sputtered, a set number of 1-cm-long Nb wires were placed equidistant from each other on the target. The glass substrates were placed 30 mm away from the target. The deposition times at 400 W were 120 min. The thickness of the deposited films was 1000 ± 150 nm. The temperature of the substrate was always <400 K.

The compositions of the films on the glass substrates were determined by energy dispersive spectroscopy (EDS) using a scanning electron microscope (SEM-Philips XL30 FEGSEM). The accelerating voltage was 20 kV, and the precision of the EDS was ~±0.5 at.%. The Nb concentration in the films was found to increase by close to 1 at.% for each 1-cm Nb wire placed on the target. EDS was also performed on the glass substrates and revealed the major components to be: Si 67.3, Na 15.8, Ca 8.7, Mg 5.1 and Al 1. 9 at.%. None of these elements were detected in any of the $TiO_2$ thin films.

Using Cu Kα radiation and parallel beam geometry, with a fixed glancing angle of incidence of 3° $\theta$, XRD patterns were recorded from 20° to 60° at a scan rate of 0.02° 2$\theta$/min, using a Philips powder X-ray diffractometer.

## 4. Results

Fig. 1 shows the XRD patterns of the Nb-doped $TiO_2$ thin films. All the patterns are consistent with the anatase structure. The only lines that could not be attributed to the anatase structure were two lines in the pattern from the film involving 10 at.% of Nb, which indicated the presence of some rutile in this sample. No other crystalline phases were detected in any of the samples. The broad hump in the background centered at ~26°, which appeared with varying intensity but identical shape in all the patterns except for the pattern from the sample with no Nb, is probably due to penetration of the X-ray beam into the glass substrate.

Although the positions of the lines are as expected from anatase (with small variations in the cell parameters), the relative intensities of the lines vary greatly between the patterns. This is due to the strong preferred orientation within the samples, as was expected from the SEM micrographs shown in Fig. 2. Since this preferred orientation is the dominant factor affecting the intensities of the lines it is impossible to draw any conclusions regarding the atomic arrangement within a unit cell from the line intensities.

The line positions were obtained by profile fitting using the XFIT program [11] and cell parameters were obtained by least square analysis, which minimised the sum of the squares of the weighted deviations of the observed from the calculated line positions: the weighting was in accordance with the accuracy of the measurement of line positions returned by XFIT [11]. The only significant source of systematic error in line positions with parallel beam geometry (and a good diffractometer) is the zero offset, which arises when the Soller slits that define the acceptance angle of the detector are not aligned with the incident beam when at the zero position of the scale. For the data reported here, the zero offset was not recorded, but was known to be ~1°. An estimate of the zero offset can be obtained for each data set by treating it as a variable in the least squares analysis, but naturally