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STRUCTURAL PROPERTIES OF NITROGEN DOPED ANATASE AND RUTILE TiO_2 THIN FILMS

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ABSTRACT

Anatase and rutile TiO_2 thin films have been doped by N ion implantation. The effect of N doping on the structural changes of TiO_2 thin films and its correlation to the optical and chemical properties of the films is investigated. The depth and concentration of the implanted N atoms is found not to exhibit substantial difference for anatase and rutile phases. The energy loss of the implanted N atoms correlates well to the energy gained by O and Ti atoms in the TiO_2 lattice. An increased number of O vacancies are found to be generated as compared to Ti for both anatase and rutile phases. The energy loss mechanisms of the implanted N atoms together with the O vacancy generation are found to be the major driving forces for facilitating enhanced optical and chemical properties of the TiO_2 thin films.

Indexing terms/Keywords

Anatase and Rutile TiO_2, Non-metal Doping, N Ion Implantation, Thin Film Growth, Optical and Chemical Properties

Academic Discipline And Sub-Disciplines

Science; Physics

SUBJECT CLASSIFICATION

Materials Physics; Thin Film Physics

TYPE (METHOD/APPROACH)

Monte Carlo based simulation and modeling

INTRODUCTION

Titanium dioxide is one of the widely studied metal-oxide systems owing to its superior optical, electrical and chemical properties [1–3]. In thin film form, the room temperature growth of TiO_2 often results in amorphous structure whereas its two crystalline polymorphs (known as anatase and rutile TiO_2), both exhibiting tetragonal structure, are possible to synthesize by modifying the growth conditions such as growth temperatures etc. [2,4]. In its anatase phase, the interesting chemical properties of TiO_2 makes it suitable for photocatalysis, self-cleaning and anti-fogging applications. The rutile TiO_2 exhibits high refractive index (~ 2.7 at 550 nm) and high dielectric constant (~ 80) and therefore it is widely used for optical and electrical applications [5].

The large band gaps of anatase (3.2 eV) and rutile (3.0) TiO_2 however limit its usage to highly demanding application of photochemical energy conversion since the excitation of electron-hole pair in TiO_2 with this large band gap is only possible through UV radiation which comprises only 4% of the solar spectrum [6,7]. It is therefore desirable for an efficient utilization of the material for photochemical conversion applications that the band gap of TiO_2 is reduced. Extensive research has been carried out in this regard by employing various strategies among them doping with metal has successfully demonstrated the reduction of the band gap by creating dopant induced band gap states. However, this approach, while facilitating an increased light absorption, does not provide free charge carriers and therefore results in severely affecting the photocatalytic activity [7].

Doping with non-metals such as N, C, S, F has shown to overcome the problems encountered by the metal doping [1]. The N-doped TiO_2 thin films have been found to exhibit enhanced visible light absorption as well as desirable photocatalytic activity [6,7]. The N doping brings about changes in the optical properties, charge transport properties as well as crystallinity of TiO_2 structure. The enhanced chemical and optical properties by N doping has been attributed to the creation of O vacancies in the films which facilitates mixing N 2p states with O 2p states as well as creating N-induced levels in the band gap [6].

In this work we investigate the effect of N doping on the structural changes of anatase and rutile TiO_2 thin films. We consider the plasma-assisted deposition process for TiO_2 and investigate the generation of O vacancies in anatase and rutile TiO_2 through doping of energetic N atoms using Monte Carlo based simulations.

FILM GROWTH AND SIMULATION

In order to investigate the effect of energetic N atom doping to TiO_2 thin films we consider 100 nm thick TiO_2 thin film in both anatase and rutile phases. The densities of the anatase and rutile thin films are 3.84 and 4.23 g/cm^3. The energy of the implanted N atoms is 500 eV. The concentration of implanted N atoms as well as the concentrations of film atoms (Ti and O) after the impact in the matrix are obtained as a function of the depth of the implanted and target species. The energy loss by the implanted N atoms and the recoil energies of N, Ti and O atoms along with the generation of O vacancies is determined. A correlation of these parameters with the structural changes and resulting properties of TiO_2 thin films is established. All the simulations are performed using SRIM [8].

RESULTS AND DISCUSSION

The concentration of N atoms doped into TiO_2 thin films as well as the depth-dependent concentration of Ti and O atoms in anatase and rutile TiO_2 thin film structures are presented in Fig.1. It is found that most of the N atoms having an energy of 500 eV are implanted to the depths of about 2 – 3 nm (Fig. 1a) whereas the maximum depths of the implanted N atoms is about 6 – 7 nm for both anatase and rutile phases. An overall slightly higher concentration is found for rutile phase as compared to the anatase phase. The similar trend is observed for Ti and O atoms (Fig. 1b) where a higher concentration of O atoms for both anatase and rutile phases is obtained as compared to Ti. The depths of 2 – 3 nm of N atoms shows that at an energy of 500 eV the doping of N atoms brings mainly the changes in the near surface region of the thin film (film thickness is 100 nm) which implies that in order to obtain the uniform an enhanced doping effect higher implantation energies for N atoms maybe required. However, since various energy loss mechanisms are at interplay during the film growth as well as during the implantation such as energy loss in the form of phonons that give rise to lattice vibration therefore the structural changes limited to near surface regions are likely to dominate for higher energy case as well.

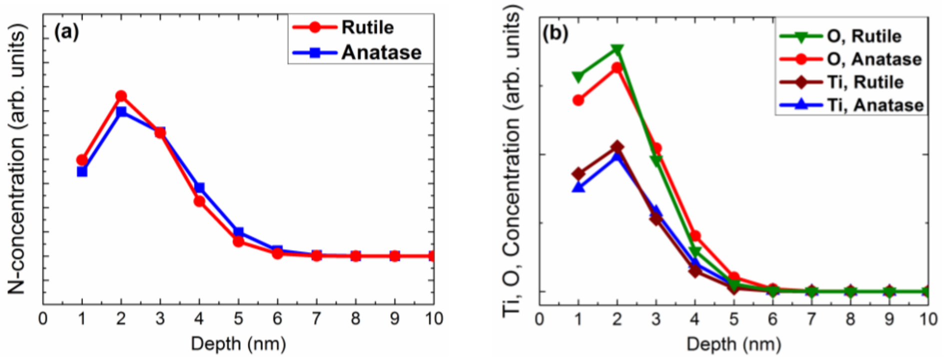

Fig. 1: The concentration of (a) implanted N atoms as well as (b) Ti and O atoms as function of depth for 500 eV N atoms doped in 100 nm TiO_2 thin film. For clarity, the ion ranges are shown up to only 10 nm.

The correlation between the energy loss by implanted N atoms and the energy gained by the film atoms i.e. Ti and O for anatase and rutile phases of TiO_2 thin film is presented in Fig. 2. It is observed that the energy absorbed by Ti and O atoms increase linearly with an increase in the energy loss of N atoms for both anatase (Fig. 2a) and rutile (Fig. 2b) cases. Higher energy absorption by O atoms is observed which is a consequence of lower mass and lower displacement energies of O atoms as compared to those of Ti atoms. The maximum energy loss for N atoms for the case of anatase phase is about 15 eV per ångstrom of film thickness per implanted N atom whereas slighter higher maximum energy loss (~ 16 eV) is obtained for rutile phase. Furthermore, a higher overall energy absorption is observed for both Ti and O atoms for rutile phase of TiO_2 thin film as compared to anatase phase. The higher energy loss and a subsequent higher energy absorption in the case of rutile phase is likely due to higher mass density of rutile thin film (4.23 g/cm^3) which gives a more densely packed lattice of Ti and O atoms as compared to anatase phase which has a lower mass density of 3.84 g/cm^3.

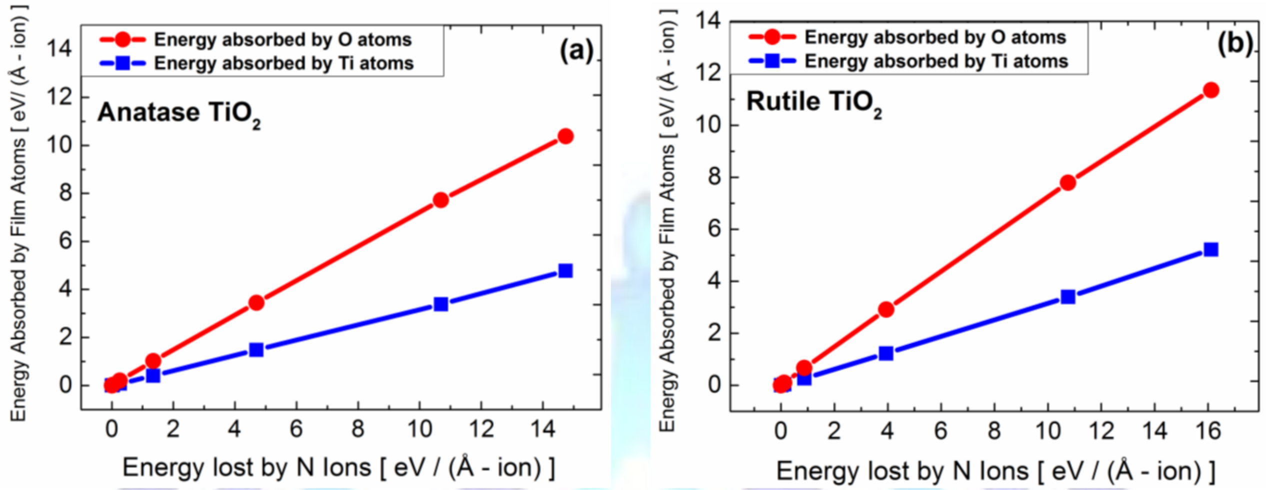

Fig. 2: A correlation between the energy loss by implanted N atoms with the energy absorbed by Ti and O atoms for 100 nm thick (a) anatase and (b) rutile TiO_2 thin film.

The number of O and Ti vacancies generated due to the implantation of N atoms in anatase and rutile TiO_2 thin films is presented in Fig. 3. For both anatase (Fig. 3a) and rutile (Fig. 3b) cases, the number of O and Ti vacancies increase with an increase in the energy loss of implanted N atoms. However, at about 10 – 11 eV, the number of vacancies start to saturate to some extent. An overall higher number of O vacancies in both anatase and rutile thin films are generated as compared to Ti vacancies which is likely due to lower displacement energies of O atoms as compared to Ti atoms. The vacancy generation indicates that the displaced O atoms form vacancy – interstitial pair and they can bond to other displaced O atoms in the lattice as well as to the implanted N atom [9]. The latter will result in the mixing of N 2p and O 2p states which gives rise to the enhanced photocatalytic activity as well as reduction in the band gap of TiO_2 thin films [6,10].

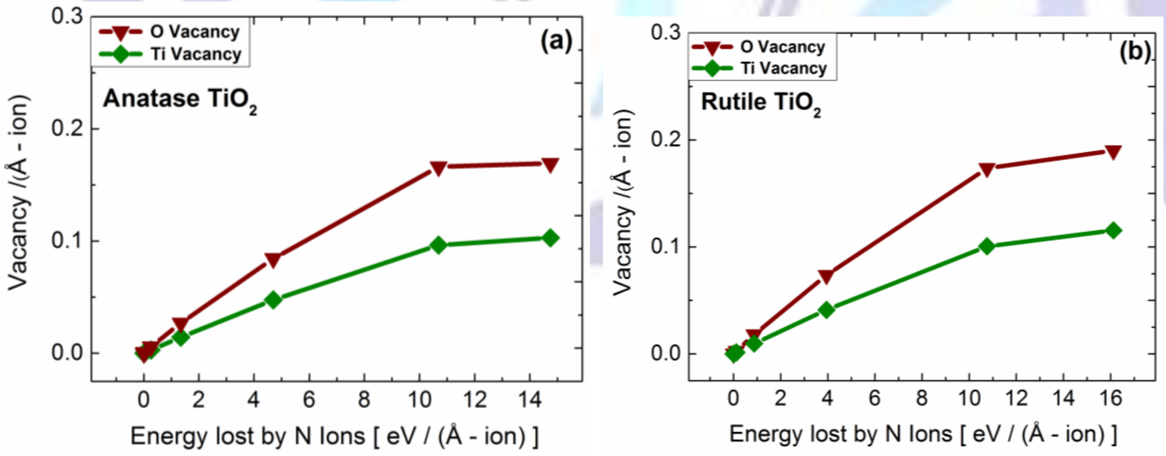

Fig. 3: The dependence of Ti and O vacancy generation on the energy loss by implanted N atoms in 100 nm thick (a) anatase and (b) rutile TiO_2 thin film.

CONCLUSIONS

The structural changes due to the implantation of energetic N atoms in anatase and rutile TiO_2 were investigated. The N atoms are found to implant and consequently bring about the structural changes in the near surface region of the films. O atoms in the films are found to absorb larger fraction of the energy that is lost by the implanted N atoms in the TiO_2 lattice. It is also found that the larger O vacancies are generated as compared to Ti which give rise to mixing of N and O 2p states and therefore facilitate enhanced optical and chemical properties of the TiO_2 thin films.

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