

# Nitrogen Incorporation(doping) in Metal Oxides

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## 1 Introduction

Various strategies have been pursued to make a typical semiconductor like Titanium dioxide( $\text{TiO}_2$ , Anatase or Rutile) to be photo-active in visible region which is normally in the unsubstituted state is active only in UV region. This has been associated with the band gap of both the forms of Titanium dioxide namely Rutile (band gap of 3.03 eV) and Anatase (band gap of 3.2 eV). In a recent publication, Scanlon et al., [1] have considered the band alignment of rutile and anatase and proposed that the electrons from the conduction band of rutile (obtained from the photo-excitation in Rutile is transferred anatase and thus the life time of the exciton is increased and hence the combination system is more active than the single polymorph of Titanium dioxide. This possibly provides an answer why P 25 Degussa sample of titanium dioxide is taken as reference for evaluating the photo efficiency of other semiconductors. The pictorial representation of the energy levels of this combined system as conceived by them(marked as b) and the representation which was hitherto believed (shown as a)is given in Fig.1.

## 2 Hetero atom substitution in Oxides

In recent times substitution of hetero-atoms mostly N, C, B. and S) in semiconducting oxides has been reported as a means of extending the wavelength of photon absorption by the semiconducting oxides[2]. This situation has also been recently reviewed with doubts on the nature of the substitution especially that of nitrogen either cationic or anionic, though most of the available literature assumes it to be anionic in place of oxide ions in the lattice[3]. Even though in reference 3, the authors have rased doubts about the

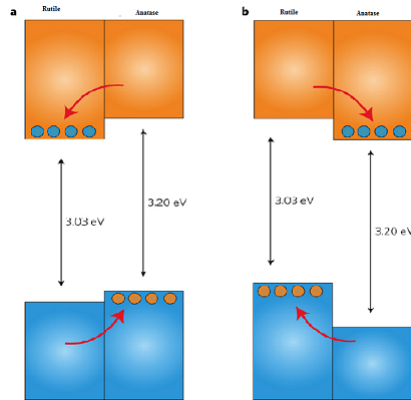


Figure 1: The proposed valence and conduction band alignments for the anatase and Rutile Interface, The direction of charge flow is indicated by the arrows; reproduced from reference 1.

valence state of incorporated nitrogen in oxide lattice, the evidences available so far seem to favour anionic state for the incorporated nitrogen atoms in the lattice. The points in favour of this postulate are:

1. The relative size of oxide anions and nitride anion.
2. The possibility of highest occupied states of nitride species overlapping with the valence band of the oxide ions thereby altering energetically the top of the valence band thus extending the photon absorption wavelength towards visible range.
3. The corresponding cationic vacancies can give rise to allowed energy states in the band gap thus accounting for the shift of the photon absorption wavelength.

It is therefore necessary to compare the band positions of pure semiconductor and nitrogen doped semiconductor. One such schematic diagram is shown in Fig.2. The essential features of this band diagram is that the top of the valence band is shifted to less positive value ( in electrochemical scale) or to less energy in absolute energy scale. Possibly the bottom of the conduction band is not altered much and it is in the same energy value of the pure semiconductor. The cationic vacancy states are now have allowed energy states in the band gap. A simple pictorial representation of this pictures is given in Fig.2. The possible supports for this model are as follows:

1. Nitrogen incorporated semiconductors showed photo absorption to longer wavelengths compared to the pure semiconductor.
2. Diffuse Reflectance Spectrum (DRS) of these samples showed enhanced absorption at higher wavelengths compared to the band gap excitation.

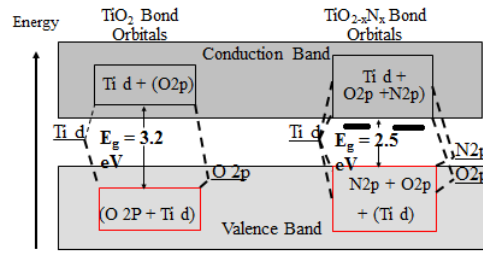


Figure 2: (A) represent the band positions for the pure semiconductor and B that for nitrogen doped semiconductor. Note the top of the valence band is shifted with respect to the pure semiconductor upwards(!)and additional energy states are introduced in the band gap

In Fig 3 the DRS spectrum of Nitrogen incorporated  $\text{TiO}_2$  is shown and it is seen that above the conventional band gap which is usually identified by the gradient changes, there is absorption in longer wavelengths as compared to pure  $\text{TiO}_2$  lending support that there are additional energy levels present in the band gap and this accounts for higher absorption in nitrogen doped semiconductors at higher wavelengths.

### 3 Alternate Model

The results considered in this presentation can also be treated in terms of another model. In the case of nano-state due to high surface, there will always be segregation of one phase over another phase as a result of surface free energy differences. This situation can be present in substituted systems since the substituents can segregate and thus give rise to core shell configuration such that the photon is absorbed in the shell and the exciton is transported to the core where the charge transfer reaction takes place. This situation may also be possible in nitrogen incorporated semiconducting oxides and thus one can also account for the observed enhanced photo-catalytic behaviour of substituted systems on this model. The band alignment concept put forth by Scanlon et al[1] may also be accountable by such a model. The message that we seem to draw is that the selection of materials for photo-electrochemical applications can be based on a configuration system with core and shell so that in one part the photon absorption takes place and the excited charge carriers move over to the other part thus increasing the life time of the charge carriers thus reducing the probability of recombination which is

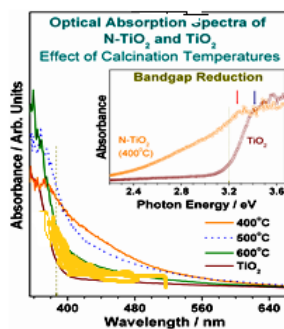


Figure 3: DRS spectrum of nitrogen doped  $\text{TiO}_2$  and one can see not only the band gap value is changed but also the photon absorption for doped semiconductors are higher at higher wavelengths as compared to Pure  $\text{TiO}_2$ . This observation may be true of most of the DRS reported in literature for nitrogen doped semiconductor **Note:** the yellow shaded region

otherwise the predominant route for the created charge carriers.

## Acknowledgment

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## References

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