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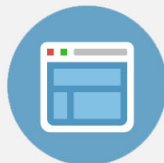
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Energy-level and optical properties of nitrogen doped TiO$_2$: An experimental and theoretical study

P. P. González-Borrero,[1,2,a] H. S. Bernabé,[2] N. G. C. Astrath,[2] A. C. Bento,[2] M. L. Baesso,[2] M. V. Castro Meira,[3,4] J. S. de Almeida,[3] and A. Ferreira da Silva[3]

[1]*Departamento de Física, Universidade Estadual do Centro-Oeste, 85040-080 Guarapuava, PR, Brazil*
[2]*Departamento de Física, Universidade Estadual de Maringá, 87020-900 Maringá, PR, Brazil*
[3]*Instituto de Física, Universidade Federal da Bahia, Campus Universitário de Ondina, 40210-340 Salvador, BA, Brazil*
[4]*CETEC-Universidade Federal do Recôncavo da Bahia, 44380 000 Cruz das Almas, BA, Brazil*

Photoacoustic spectroscopy was used to study nitrogen-doped titanium dioxide film. The energy positions of defect and impurity centre levels are reported. The energy levels were obtained using the excitation method and the mechanisms of the photoacoustic signal generation are discussed. The visible light absorption of the yellow film was explained considering electronic transitions between localized states within the band gap and the transitions from these states into the conduction band. Moreover, first principles calculations revealed that nitrogen doping and oxygen vacancies in titanium dioxide induce defect levels within the gap which account for the absorption in the visible light. © *2011 American Institute of Physics*. [doi:10.1063/1.3664104]

Titanium dioxide (TiO$_2$) has been extensively studied in the past few years for being extremely useful in many technological applications. It is one of the most promising photocatalysts for environmental cleanup, photogeneration of hydrogen from water, and solar energy utilization.[1,2] However, its wide band gap restricts its photoactivity to ultraviolet (UV) light. The band gap energy of rutile TiO$_2$ is about 3.0 eV and its fundamental band gap is direct.[3,4] It has been reported that nitrogen (N) doped TiO$_2$ (TiO$_{2-x}$N$_x$) films exhibit a narrower band gap.[1,5] Nitrogen doping alters the absorption of these films so that it extends through the visible (VIS) region. It has also been argued that these new spectral band is not a band-to-band transition but rather an excitation from localized states in the band gap to unoccupied states in the conduction band (CB).[6–8] Some of the disagreements in experimental findings may stem from sample-preparation procedures.[8] To clarify this scenario, theoretical investigations could be helpful to better understand the effect of impurity levels on the electronic and optical properties of N doped TiO$_2$.

Considering that the optical band-gap energy of these TiO$_{2-x}$N$_x$ oxides is a relevant parameter for determining the threshold at which the nitrogen doped films become photoactive, the optical absorption around the fundamental band edge is studied by means of photoacoustic spectroscopy (PAS) technique. This technique allows one to derive optical properties of materials such as semiconductors, the study of nonradiative relaxation processes and defect-related energy loss mechanism from the analysis of the PAS spectra. Since generation of the PA signal can be significantly modified depending on whether the measurements are performed with photon energy above or below the band gap, the information on the carriers can be readily obtained.[9–12]

The optical band-gap energy (E_g) can be obtained from PAS spectra using three methods, namely the derivative, the linear, and the excitation method. In the first, the E_g value can be obtained from the inflection point around the fundamental absorption edge.[10] In the second, E_g is considered as the absorption edge obtained from a linear fitting in the plot of the square of the absorption coefficient versus the photon energy for direct band gap, or the plot of the square root of the absorption coefficient versus the photon energy for indirect band gap.[13] In the third method, two photoacoustic spectra are used, being one with only the modulated light and a second with simultaneous excitation using also a continuous laser light. The E_g is the locus of the crossing point for both spectra.[11,12]

In this paper, the optical properties of a TiO$_{2-x}$N$_x$ film were both theoretically and experimentally investigated. The goal of this letter is to apply the excitation method for determining the energy levels, within the band gap of this film, directly from the experimental optical absorption from PA spectra. Additionally, first principles calculations are used to model the electronic structure and the absorption spectrum of TiO$_{2-x}$N$_x$.

The nitrogen doped TiO$_2$ film with $x = 0.01$ was produced by reactive DC magnetron sputtering without post-treatment. This film, with a thickness of (0.85 ± 0.05) μm, was deposited onto a glass substrate with a transparent and conducting layer of fluorine-doped tin oxide (8 Ω/square). The TiO$_{2-x}$N$_x$ film has a transparent yellowish color, which is consistent with the appearance of similar films reported in Ref. 1. Additional experimental details are described in Ref. 6.

The experimental setup is described in Ref. 11. The wavelength range was 300–800 nm. An Ar$^+$ ion laser tuned at 2.7 eV (457.9 nm) or 3.5 eV (351 nm) was used as the continuous light source. For the spectra with continuous light, possible contributions from the back scattering were corrected. Further details of experimental conditions can be found in

a)Electronic mail: gonzalez@unicetro.br.

Ref. 12. Here, in order to determine the E_g value of the nitrogen doped TiO$_2$ film, the excitation method was adopted.[11,12]

Fig. 1 shows the spectra for the TiO$_{2-x}$N$_x$ film, with and without excitation by continuous laser light, as a function of photon energy. The spectrum with modulated light depicts the threshold of the optical absorption band around 2.1 eV ($\sim$600 nm). This has a similar behavior to that obtained in Ref. 1. Using the dual wavelength excitation method, the optical band-gap energy was around 2.55 eV. It has been reported, employing UV-photoelectron spectroscopy, that for rutile nitrogen doped TiO$_2$, localized N 2p states extend about 0.4 eV into the band gap from valence band (VB) maximum.[8] Considering this energy value of the localized states and the energy gap of TiO$_2$ ($\sim$3.0 eV), it is reasonable to assume that $E_g \sim (2.55 \pm 0.05)$ eV is consistent with those in the literature. For this reason, this energy value was assigned to the electronic transitions from those localized states to the TiO$_2$ CB. It has also been claimed that the states arise from the substitutional N doping at oxygen (O) sites (N$_O$), and they extend up to $\sim$0.4 eV above the VB maximum.[8,14] Besides, it has been asserted that N doping contributes to the formation of oxygen vacancies (V$_O$) in TiO$_2$ lattice. These vacancies cause mid-gap states about 0.73-1.18 eV below the TiO$_2$ CB minimum.[15] Therefore, it can be inferred that the electronic transitions between localized states within band gap and the transitions from these states into conduction band could explain the visible light absorption of the yellow TiO$_{2-x}$N$_x$ film.

In order to have an understanding of the increasing and the decreasing of the obtained PA signal with the continuous laser light near the band gap as the excitation energy ($\hbar\omega$) varies when compared to the signal with only modulated light, two situations were analyzed as follow. First, when $\hbar\omega > E_g$, the modulated electrons are already in the conduction band when continuous light impinges on the sample. Hence, the continuous laser light may induce these electrons to absorb additional energy resulting in intraband transitions.
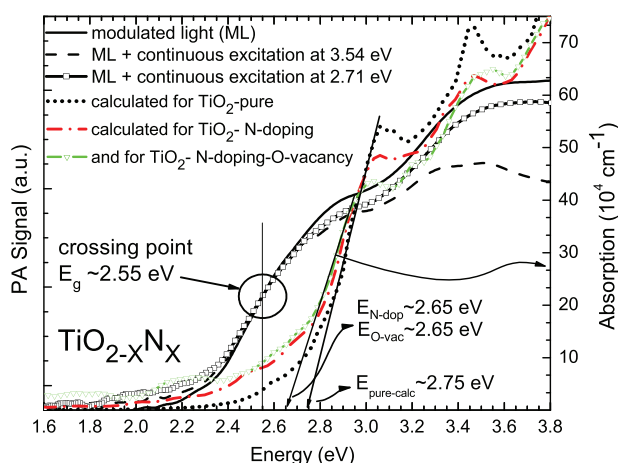
During this process, there is an increase in the nonradiative relaxation time and since the PA signal is inversely proportional to this time, the generated signal decreases (*cf.* Fig. 1). Second, $\hbar\omega < E_T$, in which E_T stands for the electronic transition energy: N$_O$ → V$_O$; N$_O$ → CB; VB → V$_O$, and VB → CB. In this case, the valence electrons and/or the electrons localized within the band gap do not undergo transitions to higher energy states because the energy of the modulated light is not enough to their excitation into localized states or into the CB. When continuous light, however, is switched on additional energy is given to the electrons from VBs and/or from localized states in the band gap, permitting them to be photoexcited to the V$_O$ states and/or to the CB. As an outcome of the higher probability of the modulated light to be absorbed by the excess of free carriers, a higher PA signal is generated. This PA-signal behavior, for energies higher or lower than E_g, is more evident when the continuous laser light has energy higher than E_g (*cf.* Fig. 1).

Furthermore, it has been observed that for a continuous laser light with lower excitation energies (2.54 and 2.41 eV) and at different excitation powers, the crossing point is only detected at the low-energy side of the PA spectra. The corresponding energy value of this point is about (2.26 ± 0.04) eV. This energy was associated to electronic transitions between localized states within band gap. Moreover, in the case of a continuous light of 50 mW at 2.41 eV, it was noted the presence of two crossing points. The results indicate that it is possible to detect different electronic transitions by using the excitation PAS method. For the sake of comparison, the energy levels of the TiO$_{2-x}$N$_x$ film has also been estimated applying the linear method for allowed direct transitions. The calculated values are at around 2.33 eV and 2.58 eV, which are close to the energy values obtained by the excitation method.

The electronic and optical properties of TiO$_{2-x}$N$_x$ were investigated by using first principles calculations in the framework of density functional theory (DFT) and based on the full-potential linearized augmented plane wave method (FP-LAPW) as implemented in WIEN2k code.[16] For the exchange-correlation functional, it was used the generalized gradient approximation (GGA).[17] The set of parameters used in the calculations can be found elsewhere.[18]

Rutile TiO$_2$ has a tetraganol crystal structure that belongs to the space group D_{4h}^{14}. To simulate the effect of nitrogen doping and the oxygen vacancies on TiO$_2$, it was started from the bulk lattice constants and constructed a $2 \times 2 \times 3$ rutile-like supercell containing 72 atoms. Initially, considering only the effect of substitutional nitrogen doping (i.e., N_O) by replacing the oxygen atom located in direct coordinates at (0.402, 0.402, 0.5) by a nitrogen atom and this change lowers the crystallographic symmetry to C_{2V}. Besides the N_O doping, it was also considered simultaneously the effect of oxygen vacancy by removing from the supercell another oxygen atom which was located at (0.598, 0.598, 0.5) and distant 2.546 Å from nitrogen. In this configuration, the crystallographic symmetry C_{2V} is preserved.

The optical properties of TiO$_{2-x}$N$_x$ were studied by calculating the absorption spectrum which is obtained directly from the electronic structure. In the calculations, it has been considered band-to-band (interband) transitions and also electronic transitions arising within the band; i.e., intraband
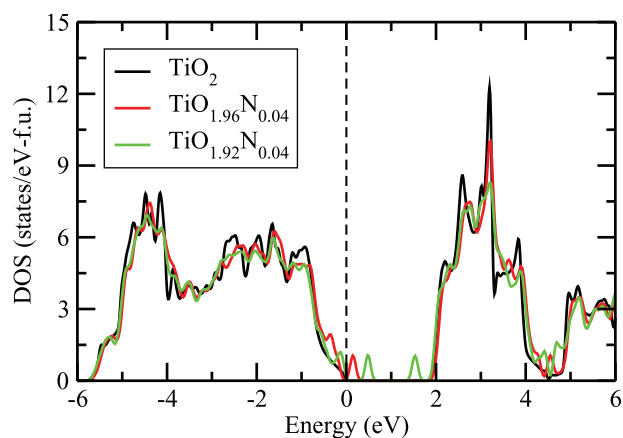

FIG. 1. (Color online) Room temperature PA signal of the TiO$_{2-x}$N$_x$ film as a function of photon energy. The continuous line represents the typical PA signal. The other curves stand for PA signal under both modulated and continuous excitation with 100 mW at 2.71 eV (dash) and 120 mW at 3.54 eV (dot) excitation. The direct optical band gap $Eg = (2.55 \pm 0.05)$ eV is obtained from the crossing point of PA signal with and without continuous excitation. For comparison, the calculated absorption spectra for TiO$_2$, TiO$_{1.96}$N$_{0.04}$, and TiO$_{1.92}$N$_{0.04}$ were also included.

FIG. 2. (Color online) DOS for TiO_2, $TiO_{1.96}N_{0.04}$, and $TiO_{1.92}N_{0.04}$. It shows the electronic transitions for the processes induced by UV-VIS irradiation of the N-doped $TiO_{2-x}N_x$ film. The valence band maximum (VBM) of TiO_2 is set to zero energy and it is indicated by a vertical dashed line.

transitions. Further details can be found in Refs. 19 and 20. Figure 1 also exhibits the theoretical absorption spectra of pure TiO_2 and of $TiO_{2-x}N_x$ with and without O vacancy. As it can be observed the absorption of $TiO_{2-x}N_x$ shows reasonable agreement with experimental PAS data. The calculated absorption edges of $TiO_{2-x}N_x$ are shifted toward lower energies (2.75 to 2.65 eV, see Fig. 1) compared to pure TiO_2 ($\sim$2.75 eV) because of the presence of defect levels within the gap. At higher energies, the absorption arise mostly from electronic transitions of the occupied O 2p states in the valence band and defect levels into the unoccupied Ti 3d states in the conduction band.

In Fig. 2, we clearly see the effect of nitrogen doping and oxygen vacancy in the calculated density of states (DOS) of TiO_2. For $TiO_{1.92}N_{0.04}$, the VB is formed mostly by the hybridization of occupied O 2p states and Ti 3d states. The localized states just above the VB maximum have predominant N 2p character whereas the localized states close to the CB minimum arise from the O vacancy. The CB is primarily determined by the unoccupied O 2p states and Ti orbitals with d character.

In conclusion, the optical band-gap energy of a $TiO_{2-x}N_x$ film has been investigated by means of PAS, using the excitation method. A E_g value of (2.55 $\pm$ 0.05) eV has

been obtained. This method allows determining directly not only the band-gap energy but also other transitions inside the band gap. Theoretical investigations based on density functional theory are used to explain the origin of the defect states within the gap of $TiO_{2-x}N_x$ and also to support the experimental findings.

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