Ab-initio Calculation of Structural and Electrical Properties of Amorphous TiO₂

Binay Prasai, Bin Cai, and D. A. Drabold Department of Physics and Astronomy, Ohio University, Athens, OH 45701, USA

M. Kylee Underwood and James P. Lewis Department of Physics, West Virginia University, Morgantown, WV 26506, USA

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Abstract

We used first-principle simulation methods to generate amorphous TiO_2 (a- TiO_2) models and obtained chemically-ordered amorphous networks. We analyzed the structural and the electronic properties of the resulting computationally generated structures. We propose that two peaks found in the Ti-Ti pair correlation correspond to the edge-sharing and the corner-sharing Ti-Ti pairs. Resulting coordination numbers for Ti (6) and O (3) and the corresponding angle distributions suggest that local structural features in bulk crystalline TiO_2 are retained in our a- TiO_2 models. The electronic density of states and the inverse participation ratio reveal that highly-localized tail states at the valence band edge are due to the displacement of O atoms from the plane containing three neighboring Ti atoms; whereas, the tail states at the conduction band edge are localized on over-coordinated Ti atoms. The Γ -point electronic gap of approximately 2.0 eV is comparable to calculated results for bulk crystalline TiO_2 .

Introduction

There is great pressure for society to discover alternative energy sources. Similarly, harmful environmental impacts (*e.g.* increasing levels of carbon dioxide) resulting from the use of fossil fuels also require significant investigation of new materials which may reduce carbon dioxide into potentially useable products. Since the discovery of titanium dioxide's ability to split of water by photocatalysis under ultraviolet light by Fujishima and Hondo [1], enormous efforts have been devoted to the understanding of titanium dioxide and its potential applications to energy and environment (see Ref. [2] for a recent review). Widely used as a pigment in sunscreen and white paint, titanium dioxide may prove to be an economical material for use in photovoltaic, photocatalytic, and sensing applications [2].

The majority of studies on titania are based upon three crystalline structures (anatase, rutile, and brookite), as well as in multiple forms (bulk, nanoparticle, thin film, *etc.*). However, titania is obtained in poor crystalline or amorphous powder form. Various methods have been employed to enhance the crystalline quality of titania(*e.g.* Ref. [3]) without considering potential benefits of the amorphous phase (a-TiO₂). However, recent research, including the results presented herein, has focused on understanding both the structural and electronic properties of amorphous titania with the hope that the desirable properties of TiO₂ can be found in the less processed, thus cheaper, form of the material [4-9]. For example, a-TiO₂ has been synthesized as

a tinted or enhanced photocatalyst [10, 11], used to purify dye-polluted water [12], and applied to resistive random access memory applications [13]. As more synthesis techniques, like those of Battiston *et al.* [14] and Zhao *et al.* [15], are developed to create amorphous TiO_2 thin films, amorphous titania will be used in more applications traditionally reserved for crystalline TiO_2 or other more expensive amorphous films. Through our research we aim for a deeper understanding of the energetic and electronic properties of a- TiO_2 while confirming structural properties to aid in the development of these materials as a viable solution to current energy and environmental issues.

Methods

Our goal is to create appropriate a-TiO₂ computer models for future analysis of the structural and electronic-structural properties. At this stage, we use VASP (a density functional code with a planewave basis) [16-18] to generate smaller (96-atom and 192-atom) model structures of a-TiO₂. We used the local density approximation (LDA) and Vanderbilt ultra-soft pseudopotentials [19] for generating our a-TiO₂ models. A 450 eV energy cutoff was used. We performed all molecular-dynamics simulations (with 1.6 fs time step) using periodic boundary condition at constant volume for annealing, equilibrating and cooling, as well as a zero pressure conjugate gradient (CG) for relaxation. The details of these simulations to generate the amorphous structures are presented herein.

We consider a 192-atom model (64 Ti atoms and 128 O atoms) using a mass density of 3.8 g/cm³ in order to obtain the correct cubic supercells; a smaller 96-atom supercell was created by using a subset of the 192-atom system after some initial molecular-dynamics simulations. The final models were then prepared by using the method of melt quenching [20]. Using this approach, we annealed the 192-atom model and then we equilibrated at 2500K for 8ps, well above the melting point (2116K). We cooled this liquid TiO₂ system to 2200K (slightly above the melting point) over 4.8ps, and then we again equilibrated for another 4.8ps. After these initial annealing and cooling simulations, we further cooled the TiO₂ system to 1100K at the rate of 75K/ps. At this stage in the procedure, we were able to observe primary structural features of a-TiO₂. After we equilibrated the system for another 2ps at 1100K, we further cooled the model to 300K at the rate of 200K/ps. After equilibrating for another 3.4ps at 300K, we quenched the model to its final ground state, fully optimized, structure. Two 96-atom model systems were prepared, using the same method as for the 192-atom model system, using two different rates of cooling (90K/ps and 75K/ps) between 2200K and 1100K. The densities of all amorphous models were calculated after the zero pressure relaxation; we find that the density of the 96-atom model I (90K/ps cool rate) is 3.59 g/cm³; the density of the 96-atom model II (75K/ps cool rate) is 3.56 g/cm^3 ; and that the density of the 192-atom model, is 3.73 g/cm^3 .

After creating the a-TiO₂ models, we study the atomic structure through a set of measurements consisting of pair correlation functions, coordination statistics, angular distributions and structure factors. A pair correlation function, also known as a radial distribution function, is a position distribution function based on the probability of finding atoms at some distance r from some particular atom. The pair correlation function can be written as

$$g(r) = \frac{1}{\rho^2 V r^2} \sum_{i, i \neq j} \delta(r - r_{ij}) \qquad (1)$$

Here, ρ and V are the number density and volume respectively of the model, and r_{ij} is the distance of one atom (a_i) from any other atom (a_j). The pair correlation function describes the average distance between atoms. A subset of this calculation is the partial pair correlation function which will tell us the average distance between two atoms of particular species (*i.e.* the average distance between two titanium atoms). In addition to the structural information provided by pair correlation functions, coordination statistics, angular distributions and structure factors provide insights to a local topology for an atom.

We analyze the electronic structure by calculating and plotting the electronic density of states (EDOS), atom or orbital site projected density of states (PDOS), and inverse participation ratio (IPR) of each individual site. The EDOS is defined as

$$g(E) = \sum_{i=1}^{N_{basis}} \delta(E - E_i)$$
(2)

This calculation provides the information about the electronic band gap between the valance band edge and the conduction band edge which determine the electronic properties of the materials. The PDOS gives information about the defects or irregularities in the topology by evaluating the contribution of individual atomic-like orbitals to the complete electronic density states. The PDOS function can be expressed as

$$g_n(E) = \sum_{i=1}^{N_{basis}} \delta(E - E_i) \left| \left\langle \phi_n \mid \Psi_i \right\rangle \right|^2$$
(3)

where $g_n(E)$ is site projected DOS for the orbital site *n*, f_n is the local orbital, and Y_i is the *i*th eigenvector with eigenvalue E_i . We use IPR analysis to investigate the localization of the tail states near the gap region. The IPR for a system with *N* atoms is calculated by the expression

$$I(E) = N \sum_{i} q(i, E)^{2}$$
(4)

where q(i,E) is the charge localized on an atom site *i* for a state with energy *E*. The degree of localization for a given electronic eigenstate is measured by the I [21]; I=1 for highly localized states and N^{-1} for extended states, where *N* is the number of atoms in a given system.

Results and Discussion

Partial Pair Correlation Functions

We used partial pair correlation functions (PPCF) to examine the local bonding environment of atoms in a-TiO₂. For all computational models, the PPCF confirmed a chemically ordered system with no homopolar bonding (Fig 1). This system displays high level order in the local environment of the atoms marked by sharp initial peaks for all models, but confirms amorphous disorder at long distances as evidenced by a reduction of discernable structure in the PPCF with increasing distance.

Of particular interest are the two distinct initial peaks found for all models in the Ti-Ti pair correlation function. These two peaks, also found in experiment, are attributed to two different environments for Ti atoms. The first peak corresponds to edge-sharing Ti-Ti pairs, whereas the second peak corresponds to corner-sharing Ti-Ti pairs. Although there is little variation in peak position between all three models for the first peak, the Ti-Ti distance is overestimated compared to the value of 3.0 Å obtained by Petkov et al[4]. By normalizing the PPCF for Ti-Ti, we were able to calculate the fraction of edge-sharing Ti-Ti pairs denoted by this first peak as 0.29, 0.30, and 0.38 for the 96-atom model I, 96-atom model II, and 192-atom model, respectively. For the second peak position we observe larger variation between the three models (3.48 - 3.59 Å). Similarly, the width of the initial peak in the O-O pair correlation function also suggests both edge-sharing and corner-sharing environments for neighboring oxygen atoms. Again, the calculated O-O first peak position is slightly over-estimated in all three models compared to the experimental value of 2.67 Å[4]. Conversely, the calculated first peak position in the Ti-O correlation of 1.92 Å is slightly less than the experimental Ti-O average bond distance of 1.96 Å. More detailed information on measured nearest neighbor bond distances is presented in Table 1. While all computational observations are consistent with experiment, we attribute all variation among the models with each other and as compared to experiment to any error given by the model densities.



Figure 1. Partial pair correlation functions for Ti-O, Ti-Ti, and O-O coordination of the three a-TiO₂ models (96atom model I, 96-atom model II, and 192-atom model) are plotted.

	Ti-O	Ti	-Ti	0-0
96-atom model I	1.92	3.08	3.48	2.85
96-atom model II	1.91	3.07	3.53	2.83
192-atom model	1.94	3.13	3.59	2.74
Experiment. [4]	1.96	3.00	3.55	2.67

Table I. Mean nearest neighbor bond lengths (Å) in a-TiO₂

From the PPCF data, we found the coordination numbers of Ti to be 5.47, 5.50, and 5.76, and the coordination numbers of O to be 2.73, 2.74, and 2.88 for the 96-atom model I, 96-atom model II, and the 192-atom model, respectively. These results are consistent with the experimental coordination numbers of Ti ($5.6 \pm 10\%$) and O ($2.8 \pm 10\%$)[4]. Complete coordination statistics are presented in Table 2. This information reveals that the local structure of aTiO₂ resembles that of crystalline TiO₂ where Ti atoms prefer to bond with six oxygen neighbors that form an octahedral structure, and O atoms prefer 3 titanium atoms as neighbors.

Table II. Coordination statistics for a-TiO₂ (in %).

	Ti ₄	Ti ₅	Ti ₆	Ti ₇	Ti ₈	O ₂	O ₃	O_4	O ₅	N _{Ti}	No
96-atom model I	6.3	46.9	40.6	6.2		34.4	57.8	7.8		5.47	2.73
96-atom model II	3.1	53.1	37.5	3.1	3.1	29	67.7	3.2		5.50	2.74
192-atom model		34.4	56.3	7.8	1.6	24.2	64.1	10.9	0.8	5.76	2.88
Experiment. [4]										5.6	2.8

Angle Distributions

We plot and analyze the Ti-O-Ti and O-Ti-O angle distributions of all three a-TiO₂ models to gain a better understanding of the physical structure of the simulated structures, (plotted in Fig. 2). When compared to the angle distributions for the rutile and anatase TiO₂ bulk crystalline structures, we observed that, though shifted, many dominant Ti-O-Ti and O-Ti-O angular features are preserved in the amorphous form of TiO₂. For comparison, the peaks for the Ti-O-Ti angle in anatase are 101.9° and 156.2° and in rutile are 98.8° and 130.6°; the peaks for the O-Ti-O angle in anatase are 78.1°, 92.4°, 101.9° and 156.2° and in rutile are 90°, 81.2°, 98.2° and 180°[21]. We observe interesting features which appears unique to the a-TiO₂ models. For instance, in the plotted Ti-O-Ti angle distribution, all of the a-TiO₂ models show a large initial peak positioned near 98°. We attribute this peak to Ti-Ti edge sharing pairs described by the first peak in the Ti-Ti pair correlation function. The subsequent peaks are therefore attributed to Ti-Ti corner-sharing pairs. The non-uniformity between models of these other peaks is consistent with the variation between models in the position of the second peak in the Ti-Ti pair correlation function. Similarly, we observe an initial peak in the O-Ti-O angle distribution near 75° for all three models and we attribute this peak to O-O edge-sharing pairs while subsequent peaks correspond to O-O corner-sharing pairs. For all models, we attribute significant differences in the second peak position and beyond to variation between models in the O-O pair correlation function.



Figure 2. Angle distributions are plotted for the three a-TiO₂ models (96-atom model I, 96-atom model II, and 192atom model). For comparison, the peaks for the Ti-O-Ti angle in anatase are 101.9° and 156.2° and in rutile are 98.8° and 130.6°; the peaks for the O-Ti-O angle in anatase are 78.1°, 92.4°, 101.9° and 156.2° and in rutile are 90°, 81.2°, 98.2° and 180°[21].

Partial Static Structure Factors

We also compared partial static structure factors for all three models and present the results in Fig. 3. The partial structure factors are consistent for all three models. These structure factors do not show any significantly sharp peak between 1 Å⁻¹ and 2 Å⁻¹ and confirm the absence of a significant first sharp diffraction peak (FSDP). Thus, the results from the structures of our three a-TiO₂ models demonstrate that our models exhibit strong amorphous characteristics.



Figure 3. Partial static structure factors are plotted for the three a-TiO₂ models (96-atom model I, 96-atom model II, and 192-atom model).

Electronic Structure

We describe the main features of the electronic structure by analyzing the electronic density of states (EDOS), projected density of states (PDOS), and inverse participation ratio (IPR) of each individual site for each of the three a-TiO₂ models. Fig. 4 shows the total EDOS of all three models with the Fermi level shifted to 0 eV. Except for slight variations, all of the three EDOS have very similar features. For a deeper understanding we also analyzed the PDOS for all three a-TiO₂ models. For illustration purposes we present the species PDOS and the orbital PDOS in Fig. 5. The lowest conduction band levels are mainly dominated by 3d-like states of Ti as in bulk TiO₂ (both rutile and anatase). Also, similarly to the bulk results, the valence band near the Fermi level has contributions from both 3d-like states of Ti and 2p-like states of O with oxygen 2p-like state dominating the tail region. Interestingly, we find that the Γ -point electronic gap of approximately 2.0 eV is comparable to calculated results for bulk crystalline TiO₂ as determined from LDA planewave calculations [22].



Figure 4. Electronic density of states (Γ point) are plotted for the three a-TiO₂ models (96-atom model I, 96-atom model II, and 192-atom model). Fermi level is at 0eV.



Figure 5. Partial electronic density of states (Γ point) for the 192-atom a-TiO₂ model. The other two 96-atom a-TiO2 models yield similar results (not shown for simplicity).

We used Inverse Participation Ratio analysis to investigate the localization of the tail states near the band gap[23]. Fig.6 illustrates the IPR for all three models. Except for the 96-atom model II, we observed that the valence tail states are highly localized. These valence tail states are localized on O-2p orbitals whereas conduction tail states are localized on Ti-3d orbitals. We analyzed the topology of the atoms associated with the tail states as indicated in the figure. All of the O atoms associated with the selected valence tail states (a-d) are three-fold coordinated, whereas the Ti atoms associated with the conduction tail states (e-g) are six-fold coordinated. However, the O atom is displaced from the plane containing the neighboring Ti atoms, forming a pyramidal structure. This means that the over-coordinated Ti is the cause of the conduction tail states, whereas the positional disorder of O is the reason for the valence tail states.



Figure 6. Inverse participation ratios are plotted for the three a-TiO₂ models (96-atom model I, 96-atom model II, and 192-atom model). Fermi level is shifted to 0 eV.

Conclusion

We created different a-TiO₂ models (two with 96 atoms and one with 192 atoms) by computational cooking and quenching using the 'melt-quench' method, and we were able to reproduce structural properties for a-TiO₂ as provided by experimental methods. Most of the Ti and O atoms tend to be six-fold and three-fold coordinated, respectively, showing the similar local structure to crystalline form TiO₂ (both in the anatase and rutile structures). We found an Γ point band gap which is comparable to calculated results for bulk crystalline TiO₂. The IPR analysis showed that the valence tail states result from the positional disorder of O atoms whereas the conduction tail states result from over-coordinated Ti atoms.

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References

- 1. Fujishima, A. and K. Hondo, *Electrochemical photolysis of water at a semiconductor electrode*. Nature, 1972. **238**: p. 37-38.
- 2. Chen, X. and S.S. Mao, *Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications.* Chem. Rev., 2007. **107**(7): p. 2891-2959.
- 3. Yin, H., Y. Wada, T. Kitamura, S. Kambe, S. Murasawa, H. Mori, T. Sakata and S. Yanagida, *Hydrothermal synthesis of nanosized anatase and rutile TiO₂ using amorphous phase TiO₂*. J. Mat. Chem., 2001. **11**(6): p. 1694-1703.

- 4. Petkov, V., G. Holzhüter, U. Tröge, Th. Gerber, and B. Himmel. *Atomic-scale structure of amorphous TiO₂ by electron, x-ray diffraction and reverse Monte Carlo simulations*. J. Non-Cryst. Sol., 1998. **231**(1-2): p. 17-30.
- 5. Zhang, H. and J.F. Banfield, *Kinetics of Crystallization and Crystal Growth of Nanocrystalline Anatase in Nanometer-Sized Amorphous Titania.* Chem. Mater., 2002. **14**(10): p. 4145-4154.
- 6. Hoang, V.V., *Structural properties of simulated liquid and amorphous TiO*₂. Phys. Stat. Sol. B, 2007. **244**(4): p. 1280-1287.
- 7. Hoang, V.V., H. Zung, and N.H.B. Trong, *Structural properties of amorphous TiO*₂ *nanoparticles*. Eur. Phys. J. D, 2007. **44**(3): p. 515-524.
- 8. Zhang, H.Z., B. Chen, and J.F. Banfield, *Atomic structure of nanometer-sized amorphous TiO*₂. Phys. Rev. B, 2008. **78**(21): p. 214106.
- 9. Hoang, V.V., *The glass transition and thermodynamics of liquid and amorphous TiO*₂ *nanoparticles.* Nanotech., 2008. **19**(10): p. -.
- 10. Zou, J.A., J.C. Gao, and F.Y. Xie, An amorphous TiO_2 sol sensitized with H_2O_2 with the enhancement of photocatalytic activity. J. Alloy. Compd., 2010. **497**(1-2): p. 420-427.
- 11. Randorn, C., J.T.S. Irvine, and P. Robertson, *Synthesis of visible-light-activated yellow amorphous TiO*₂ *photocatalyst*. Int. J. Photoenergy, 2008: p. 426872.
- 12. Kanna, M., S. Wongnawa, S. Buddee, K. Dilokkhunakul, and P. Pinpithak, *Amorphous titanium dioxide: a recyclable dye remover for water treatment.* J. Sol-Gel Sci. Tech., 2010. **53**(2): p. 162-170.
- 13. Jeong, H.Y., J.Y. Lee, and S.Y. Choi, *Interface-Engineered Amorphous TiO₂-Based Resistive Memory Devices*. Adv. Funct. Mat., 2010. **20**(22): p. 3912-3917.
- 14. Battiston, G.A., R. Gerbasi, A. Gregori, M. Porchia, S. Cattarin, and G.A. Rizzi, *PECVD* of amorphous TiO₂ thin films: effect of growth temperature and plasma gas composition. Thin Sol. Films, 2000. **371**(1-2): p. 126-131.
- 15. Zhao, Z.W., B.K. Tay, and G.Q. Yu, *Room-temperature deposition of amorphous titanium dioxide thin film with high refractive index by a filtered cathodic vacuum arc technique*. Appl. Opt., 2004. **43**(6): p. 1281-1285.
- 16. Kresse, G. and J. Furthmuller, *Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set.* Comput. Mat. Sci., 1996. **6**(1): p. 15-50.
- 17. Kresse, G. and J. Furthmuller, *Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set.* Phys. Rev. B, 1996. **54**(16): p. 11169-11186.
- 18. Kresse, G. and J. Hafner, *Ab initio molecular-dynamics for liquid-metals*. Phys. Rev. B, 1993. **47**(1): p. 558-561.
- 19. Vanderbilt, D., *Soft self-consistent pseudopotentials in a generalized eigenvalue formalism.* Phys. Rev. B, 1990. **41**(11): p. 7892.
- 20. Drabold, D.A., *Topics in the theory of amorphous materials*. Eur. Phys. J. B, 2009. **68**(1): p. 1-21.
- 21. Howard, C.J., Sabine, T. M. and Dickson, F., *Structural and thermal parameters for rutile and anatase*. Acta Cryst., 1992 **47**: p. 462–468.
- 22. Mo, S.-D. and W. Ching, *Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite.* Phys. Rev. B, 1995. **51**(19): p. 13023-13032.
- 23. R. Atta-Fynn, R., Biswas, P., Ordejon, P. and Drabold, D. A. Systematic study of electron localization in an amorphous semiconductor, Phys. Rev.B, 2004 **69**, 085207