

# First-principles calculations of Ti/N-codoping effect on electronic structures and optical properties of SiO<sub>2</sub>

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The electronic structures and optical properties of varies Ti/N-codoping SiO<sub>2</sub> are investigated for the first time using the first principles calculations based on density functional theory (DFT). The results indicate the introduction of doped ions reduce the band gap compared to the SiO<sub>2</sub> system, nearly by 1.4 eV on average, which may be partly attributed to the unoccupied N 2p states and the hybridization of Si 3s, 3p with N 2p and O 2p states. So Ti and N atoms may be possible doped elements for improving the optical properties of SiO<sub>2</sub> system.

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*Keywords:* First-principles, Ti/N, Electronic structure, Optical properties, Codoping

## 1. Introduction

Silicon dioxide (SiO<sub>2</sub>) has recently drawn much attention as a good luminous material because of its optical advantage, chemical stability and low cost. So far it has been widely used in the fields of military affairs, optical fiber, communication, laser technology and so on [1-2]. However, the intrinsic wide energy gap for SiO<sub>2</sub> (8.8eV) confines its applications to be less effectively utilized than expected. Therefore, many efforts have been made to break this limitation both by experimental [3-6] and theoretical methods [7-11], not just in the study of SiO<sub>2</sub>, but also in TiO<sub>2</sub>, ZnO, SrTiO<sub>3</sub> and other similar materials [12-23]. In these methods, doping luminous material with transition metal and nonmetal dopants was proved to be effective way to achieve the goal.

Some experimental studies have been carried out to prepare the doping SiO<sub>2</sub> by sol-gel method, Tb, Eu, Nd, Mn, Mg, S and other elements are introduced to modify the optical property of pure SiO<sub>2</sub>, the effects are obvious and the optical property can be improved in certain extent. Theoretical investigations have also been performed to study the energy band structure and structural properties of SiO<sub>2</sub> phase. The amorphous system of SiO<sub>2</sub> is obtained by molecular simulation and correlative comparison is made with the crystal system. In addition, the choice of ensemble and charge exchange in SiO<sub>2</sub> system are studied by molecular dynamic simulation, while the dielectric constant calculated agrees well with experimental value. So far, there are not enough investigations on understanding the reason of improved optical performance of doping SiO<sub>2</sub> deeply, meanwhile the first-principles study has been widely employed to know more about materials of similar performance. So more attention should be given on the underlying reason of the enhanced optical activity of SiO<sub>2</sub>.

In this work, we focus on the geometrical structures, electronic structures and optical properties of pure SiO<sub>2</sub>, varies Ti/N-codoping SiO<sub>2</sub>, which have been investigated

by the first-principles calculations based on DFT. Compared the calculated results with the experimental data and discussed the effects of Ti and/or N doping on the optical activity. It may be a good attempt to explain the reasons why the optical activity of SiO<sub>2</sub> could be improved significantly.

## 2. Computational details

The pure silicon dioxide supercell containing 108 atoms was adopted to study the doping effects on the electronic and optical properties as the initial model. We substituted a Ti atom and an N atom for a Si atom and an O atom respectively, to model the Ti-, N-and Ti/N-codoping. To make it clear, the pure structure and doped structures of different types were displayed in Fig. 1.

All DFT calculations were performed with the CASTEP code of plane-wave basis and ultrasoft pseudopotentials [24] as provided in the default library. The generalized gradient approximation with the Perdew-Burke-Ernzerhof functional [25] was employed to treat the electronic exchange and correlation potential. Reciprocal-space integration over Brillouin zone sampling was approximated through a careful sampling at a finite number of k-points using the Monkhorst-Pack grid [26]. In all the calculations, the kinetic energy cutoff was chosen as 380 eV and the parameters of the Monkhorst-Pack k-point was 2×2×1. The total energy was converged to lower than 5×10<sup>-6</sup> eV/atom. The Broyden-Fletcher-Goldfarb-Shanno method [27] was used to relax the crystal structure and the atomic coordinates fully until the force on each atom converged to less than 0.1 eV/Å. Higher cutoff energies and denser k-point grids were also employed to calculations, however, the overall results did not change much. So the parameters chosen above were suitable to the calculations. Then the electronic structures, density of states and optical properties were calculated on the basis

of the optimized supercells.

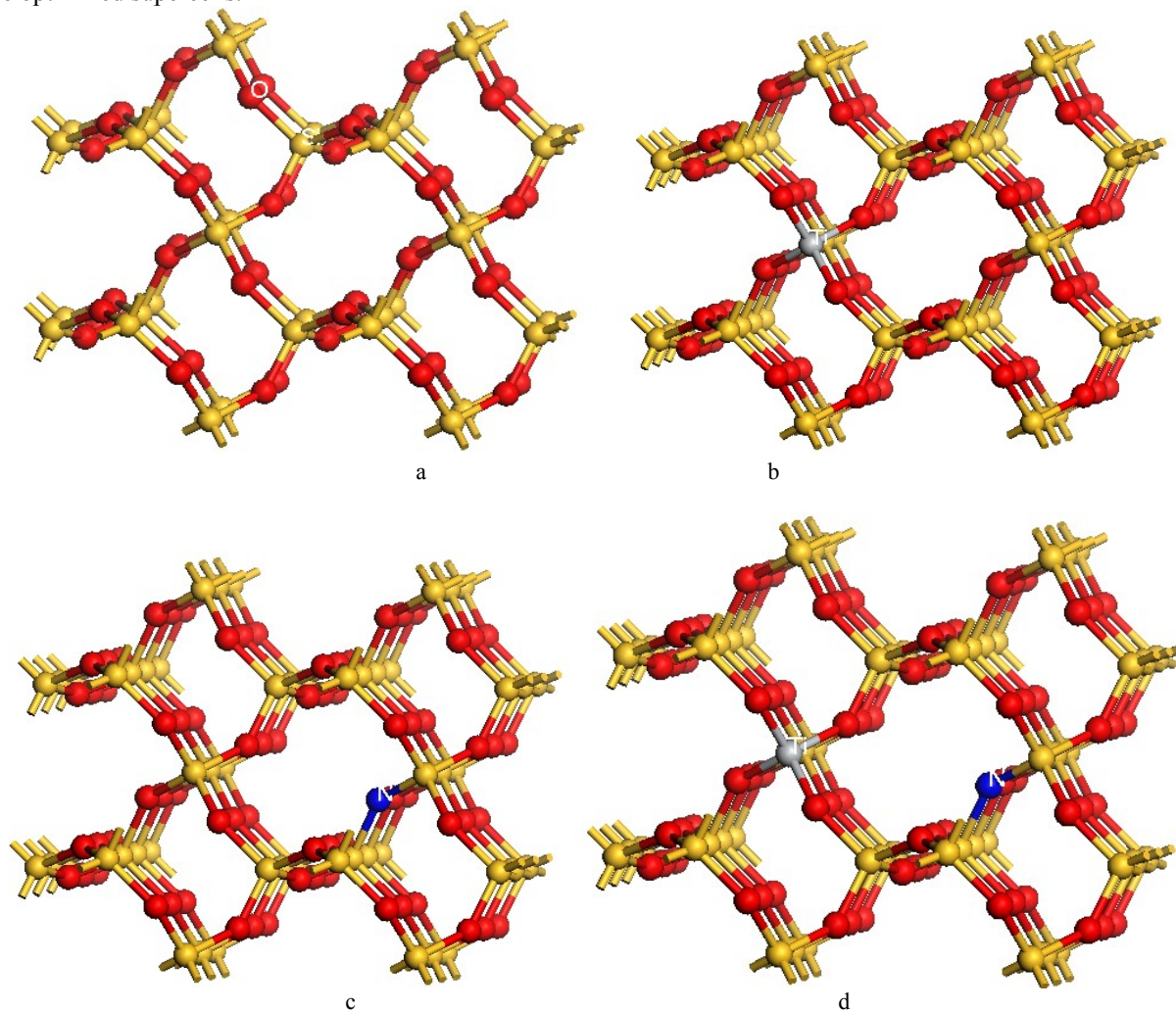


Fig. 1. Supercell models of  $\text{SiO}_2$ ; (a) pure; (b) Ti-doped, wt=2.2%; (c) N-doped, wt=0.65%; (d) Ti/N-codoped, wt=2.85%. The ion doping sites are marked with Ti and N. The grey and blue spheres represent the Ti and N atoms, respectively. While the red and yellow spheres represent the O and Si atoms.

### 3. Results and discussion

#### 3.1 Pure $\text{SiO}_2$

The calculated crystal parameters of pure  $\text{SiO}_2$  are  $a=b=4.913\text{\AA}$ , and  $c=5.4052\text{\AA}$ , which are in good agreement with ICSD file of  $\text{SiO}_2$  ( $a=b=4.91421\text{\AA}$ ,  $c=5.406\text{\AA}$ ). In addition, the band structure and density of states (DOS) of pure  $\text{SiO}_2$  containing 72 atoms are shown in Fig. 2 as standard references. From Fig. 2 (a), it can be found that the calculated band gap is 6.022 eV, which is lower than the experimental value of 8.8 eV [28].

Considering the limitation of DFT, the results obtained by us are acceptable and our calculation methods are reasonable. The DOS of total system in Fig. 2 (b) shows that the valence band consists of two groups with a bandwidth of about 20 eV. The lower valence band from -20 to -17 eV is derived from O 2s states, while the upper valence band from -10 to 0 eV mainly from O 2p states with large amounts of Si 3p states. The conduction band consists of Si 3d states and few O 2p states. This indicates that a strong covalence bond character between Si and O atoms, which is accepted by most theoretical researchers.

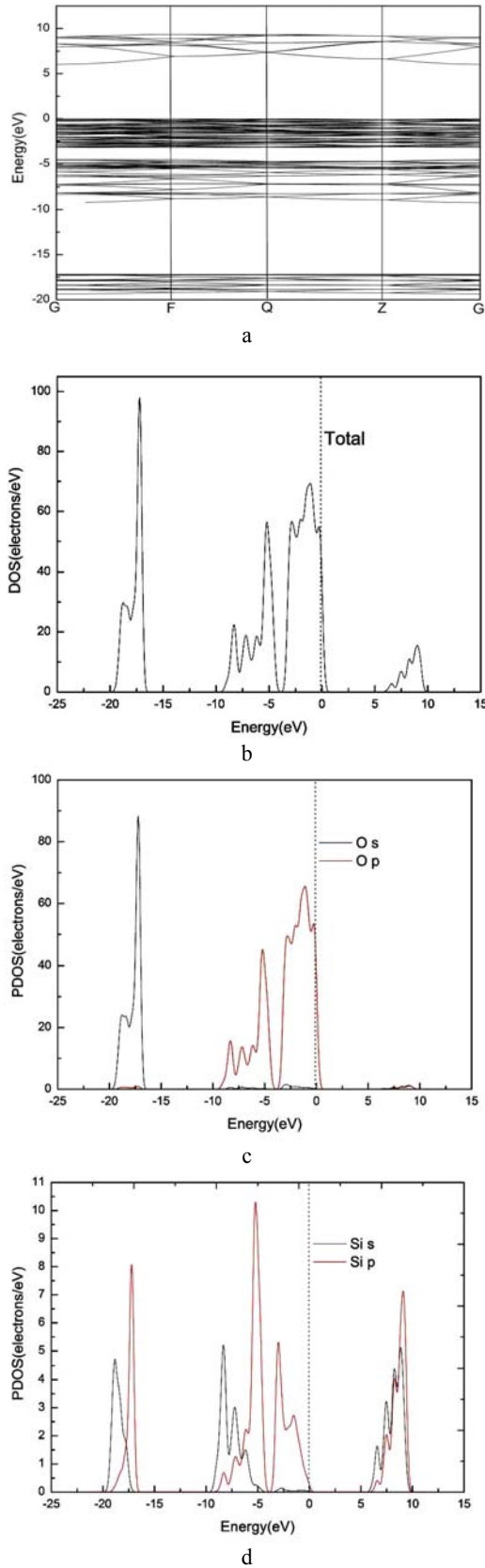


Fig. 2. Supercell models of SiO<sub>2</sub>; (a) pure; (b) Ti-doped, wt=2.2%; (c) N-doped, wt=0.65%; (d) Ti/N-codoped, wt=2.85%. The ion doping sites are marked with Ti and N. The grey and blue spheres represent the Ti and N atoms, respectively. While the red and yellow spheres represent the O and Si atoms.

### 3.2 Doped SiO<sub>2</sub>

To further study the doping effects of Ti and N on the SiO<sub>2</sub> systems, the electronic structures and optical properties are also calculated, which are given in Fig. 3-10. As it can be seen from these Figures, there are significant differences before and after doping. The adsorption coefficient spectrum ( $\alpha$ ), reflectivity (R), refractivity index (n), dielectric function ( $\epsilon_2$ ) and energy-loss function (L) are gained as follows, the relevant details can be found in references [29-30].

$$\alpha(\omega) = \sqrt{2}\omega[\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega)]^{1/2} \quad (1)$$

$$R(\omega) = \left| \frac{\sqrt{\epsilon_1(\omega) + j\epsilon_2(\omega)} - 1}{\sqrt{\epsilon_1(\omega) + j\epsilon_2(\omega)} + 1} \right|^2 \quad (2)$$

$$n(\omega) = [\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega)]^{1/2} / \sqrt{2} \quad (3)$$

$$\epsilon_2 = \frac{2e^2\pi}{\Omega\epsilon_0} \sum_{k,v,c} |\langle \psi_k^c | \hat{u} \times r | \psi_k^v \rangle|^2 \delta(E_k^c - E_k^v - E) \quad (4)$$

$$L(\omega) = \epsilon_2(\omega) / [\epsilon_1^2(\omega) + \epsilon_2^2(\omega)] \quad (5)$$

It can be found from Fig. 3 that the calculated band gap in N-doped, Ti-doped and Ti/N-codoped SiO<sub>2</sub> are 5.012 eV, 4.815 eV and 3.928 eV, respectively. All these figures are lower than that in pure system, which indicates that the narrowed band gap may reduce the photoelectron transition energy and make the optical absorption edge to visible light region available. In this circumstance, the optical properties of SiO<sub>2</sub> could be improved in certain extent, which agrees well with previous studies.

Fig. 4 shows the information about the total density of states (DOS) of doped models, while Fig. 5-7 give the part total density of states (PDOS), which can help us understand better how the band gap changes. It can be seen from Fig. 4 that there is no obvious shift in valence band maximum of all doped models, compared to that of pure SiO<sub>2</sub>, while the conduction band minimum decreases about 0.3 eV. In Fig. 5-7, we can find that N 2p states are not fully occupied after an N atom replacing an O atom, because the previous electronic balance is broken and deficient is produced in this N-doped system. As for the Ti-doped model, O 2p and Si 3p states mix together to a certain extent, which may improve the mobility of photo-generated hole, and thus improve its optical performance. In the case of Ti/N-codoped system, the band gap is further narrowed for the decline of the conduction band, and the electron transition energy from the valence band to the conduction band falls by almost 0.3 eV due to the codoping effects. The hybridization of Si 3s, 3p with N 2p and O 2p states can prolong the lifetime of photo-

generated holes and fill in the unoccupied N 2p states. According to the calculated band gap, DOS and PDOS, we can find a significant improvement in optical absorption edge for doping effects.

Fig. 8 presents the absorption coefficient spectrum of SiO<sub>2</sub> systems with four different structures. We can find that adsorption region is quite wide and mainly at the UV region as predicted [28]. Compared with pure SiO<sub>2</sub>, the absorption coefficient of doped SiO<sub>2</sub> increases rapidly and additional absorption in the visible region can be observed, which may be attributed to the N 3d impurity band and Ti 4s states. From Fig. 9, it can be seen that doping of Ti and/or N atoms mainly affects the optical properties in the low energy range, while in the high energy range the

curves are nearly the same for all the SiO<sub>2</sub> models. The reflectivity, refractivity index and energy-loss function of the targeted systems in the energy range of 0-30 eV are given in Fig. 10. After some fluctuations, the reflectivity and refractivity index reach their first peak at 8 eV and 10 eV, respectively. At the photon-energy range of 10-15 eV, the reflectivity goes up and down, then finally arriving at its second strongest peak, while the refractivity index changes from the strongest to the weakest. In the high photon-energy range (15-30 eV), an opposite trend appears in the two kinds of parameters. What is more, the energy-loss peaks at around 12 eV as shown which corresponds to the trailing edges in the reflectivity.

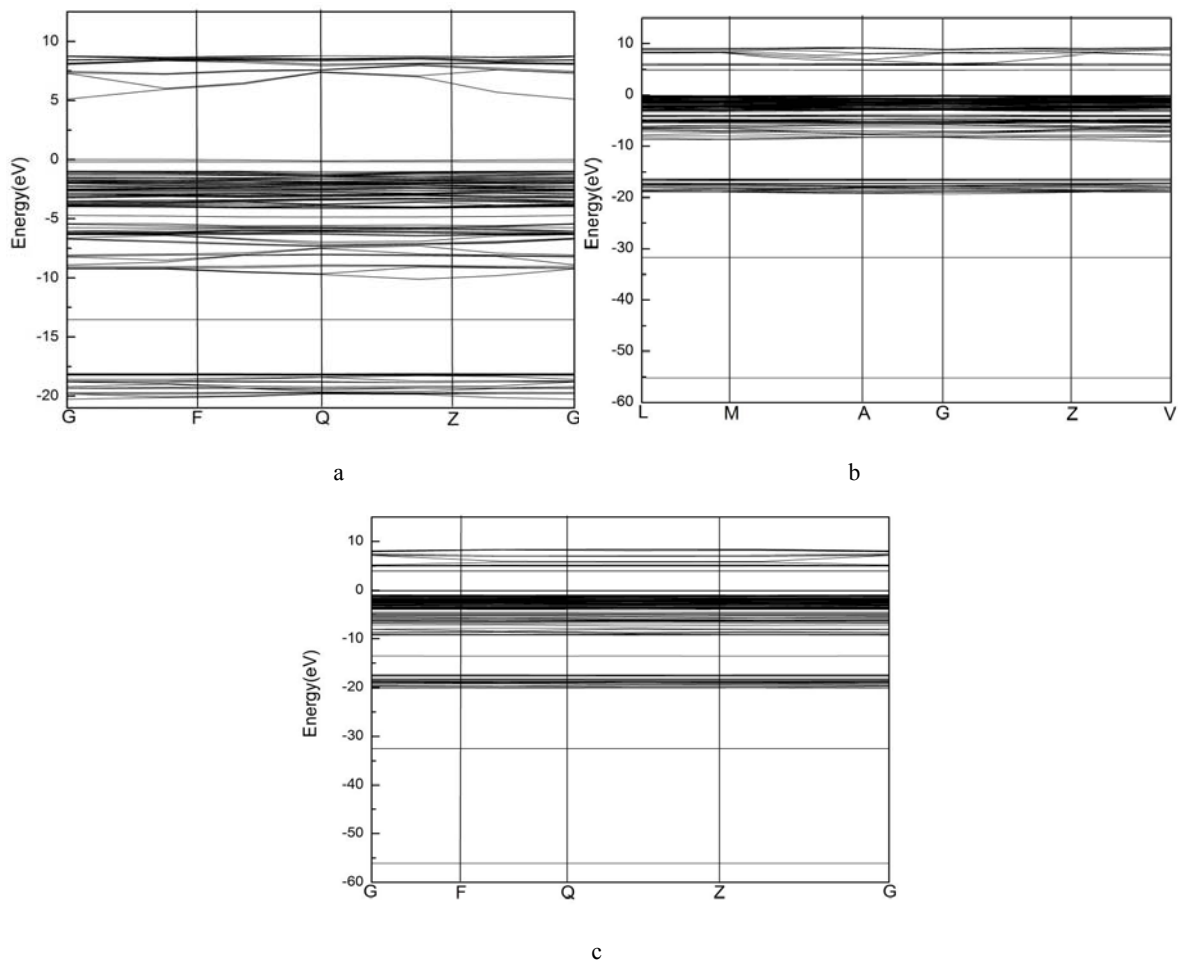
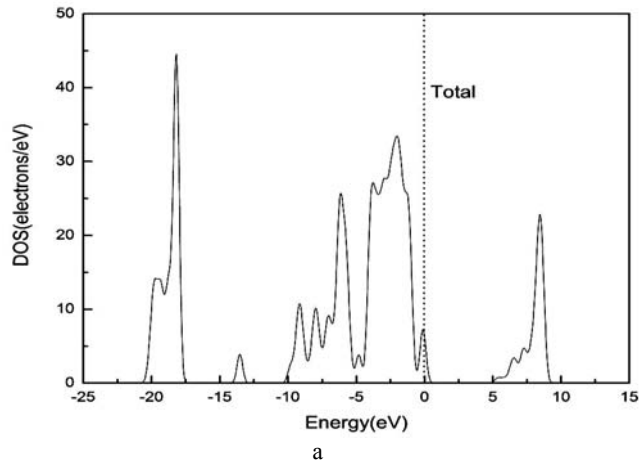
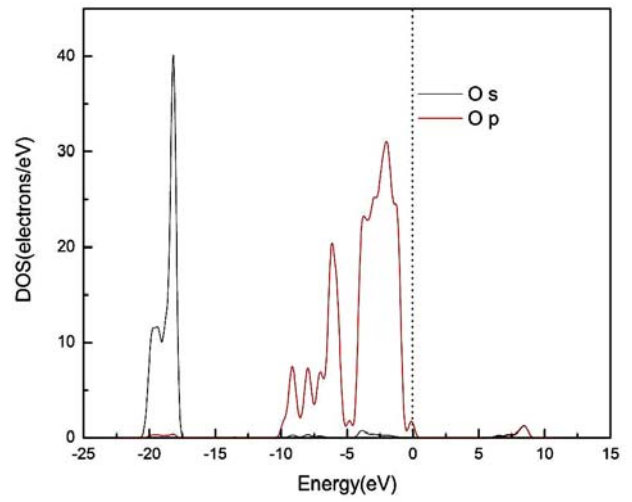


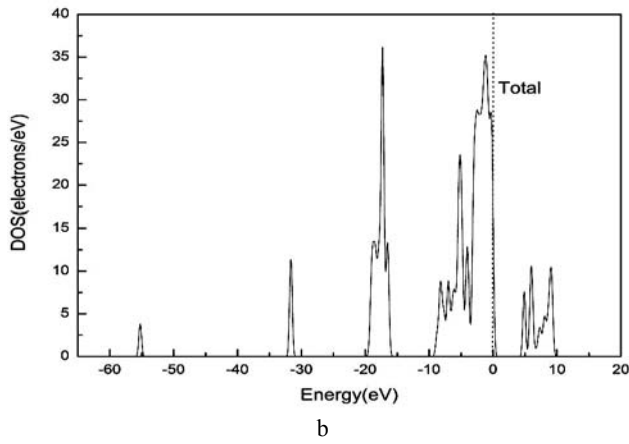
Fig. 3. Band structure of three different SiO<sub>2</sub> systems. (a) N-doped; (b) Ti-doped; (c) N/Ti-codoped.



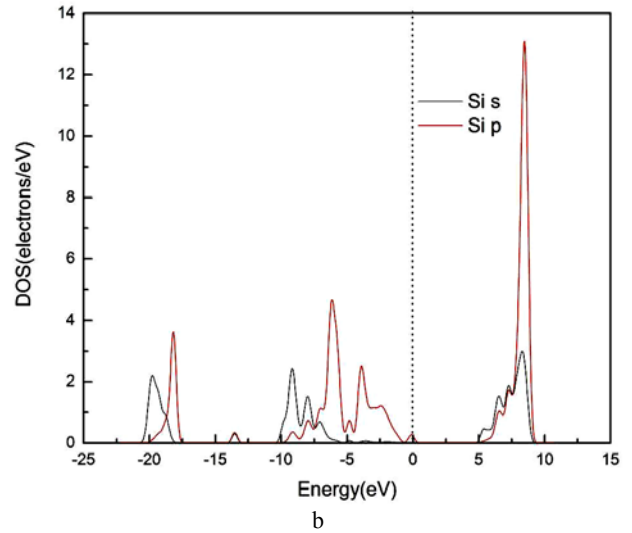
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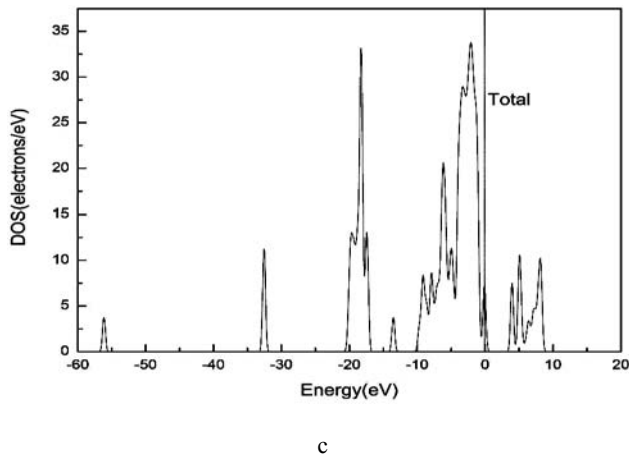
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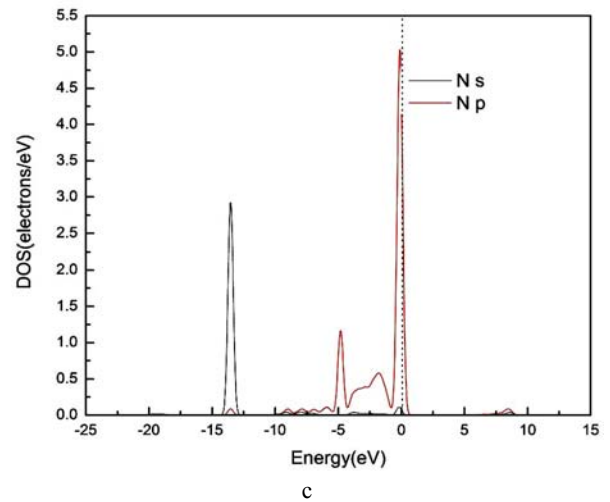
b



b



c



c

Fig. 4. DOS of different SiO<sub>2</sub> system. (a) N-doped; (b) Ti-doped; (c) N/Ti-codoped. The dashed lines at zero point energy are Fermi level.

Fig. 5. PDOS of N-doped SiO<sub>2</sub> system. The dashed lines at zero point energy are Fermi level.



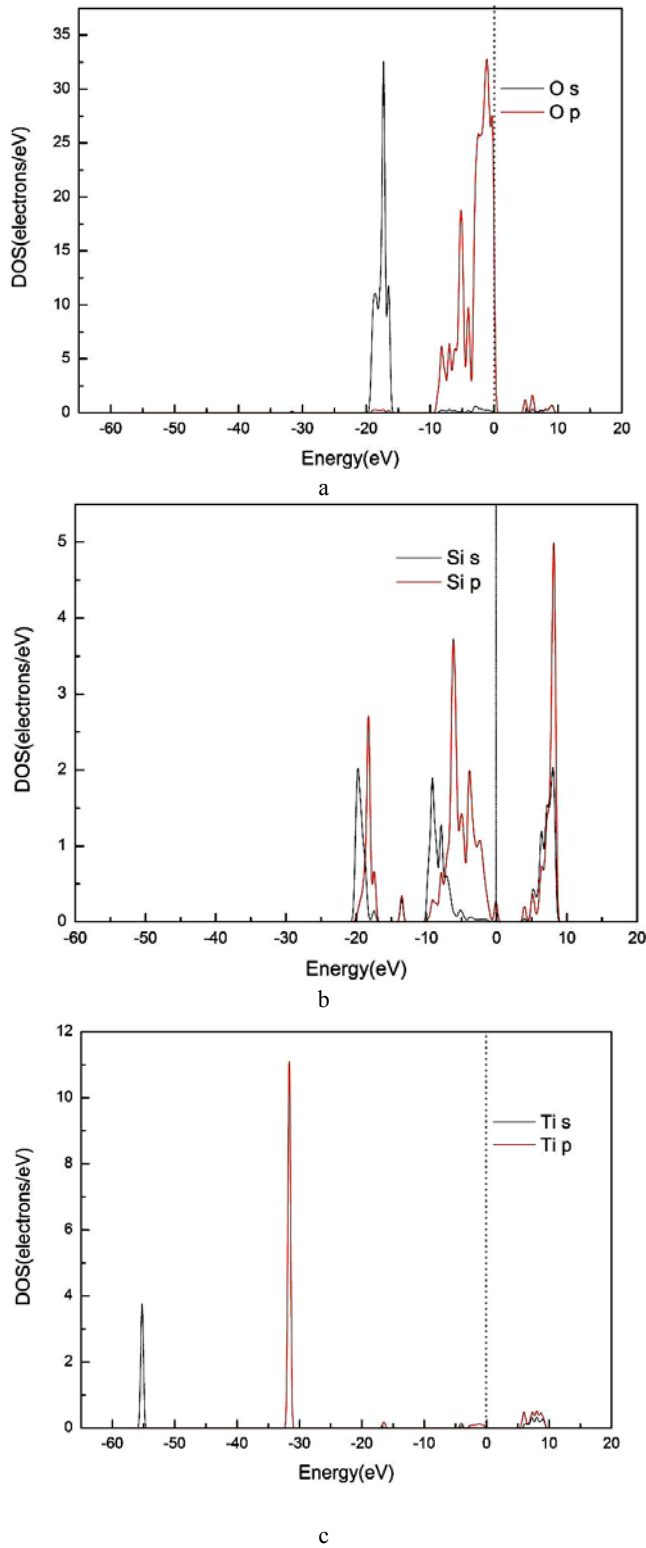


Fig. 6. PDOS of Ti-doped  $\text{SiO}_2$  system. The dashed lines at zero point energy are Fermi level.

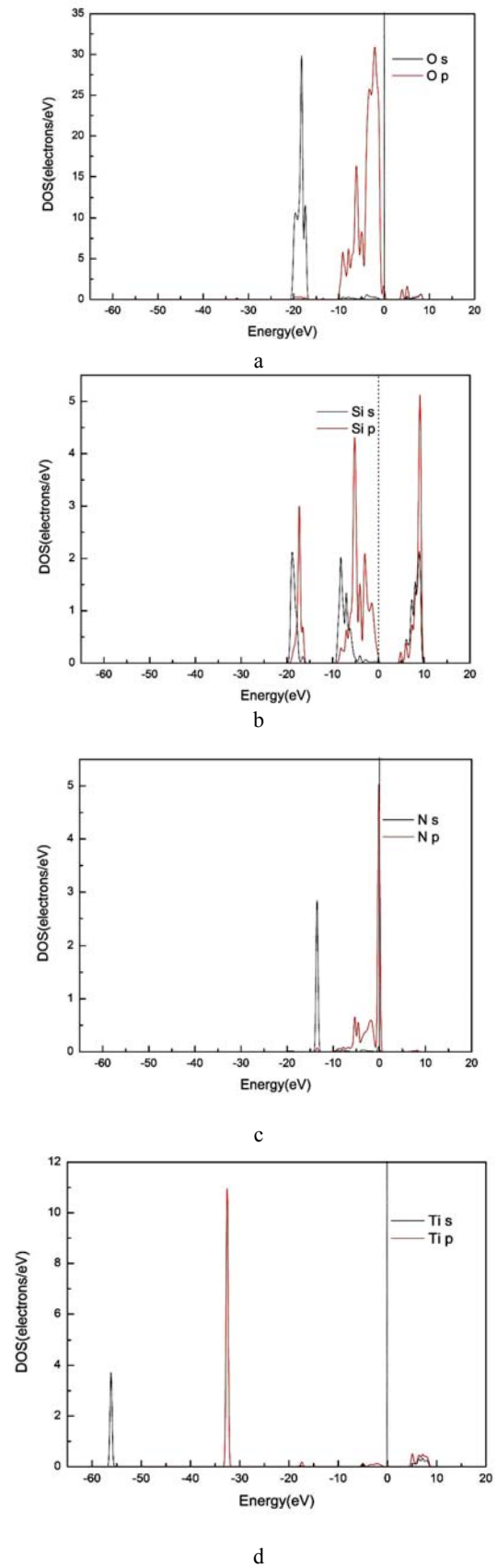


Fig. 7. PDOS of Ti/N-codoped  $\text{SiO}_2$  system. The dashed lines at zero point energy are Fermi level.

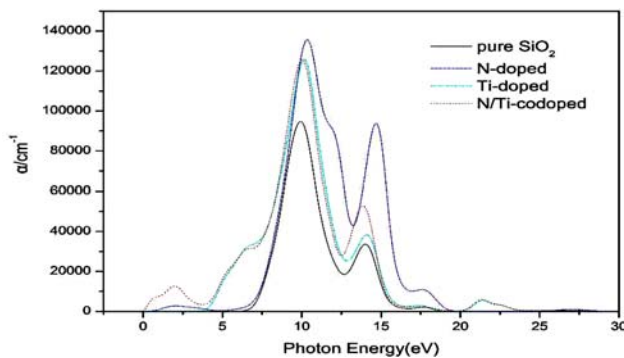


Fig. 8. The absorption coefficient spectrum of SiO<sub>2</sub> with four different structures.

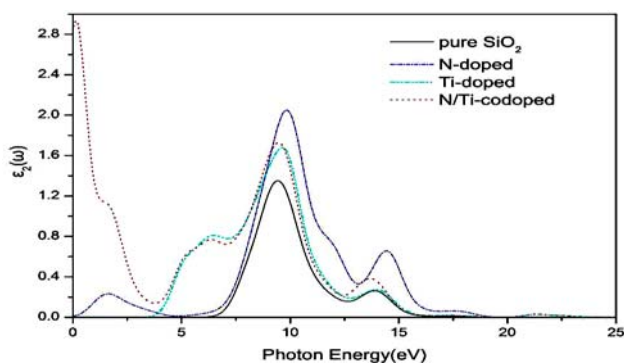


Fig. 9. Imaginary part of dielectric function of SiO<sub>2</sub> with four different structures.

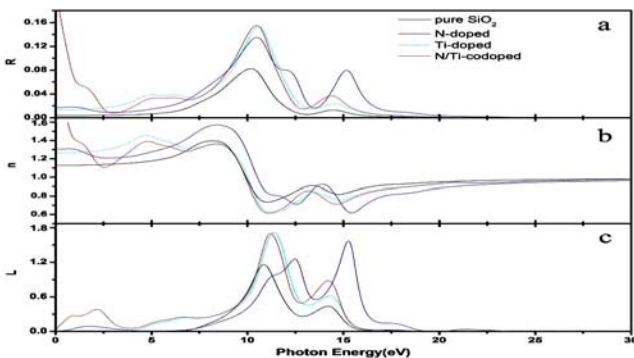


Fig. 10. The optical properties of four different SiO<sub>2</sub> systems. (a) reflectivity; (b) refractive index; (c) energy-loss function.

#### 4. Conclusions

Electronic structures and optical properties of pure SiO<sub>2</sub>, varies Ti/N-codoped SiO<sub>2</sub> have been calculated by first-principles methods. The results indicate that doping effects is obvious and the band gaps are all narrowed in three different doped systems. The unoccupied N 2p states may be a significant factor for this change in N-doped model. The hybridization of Si 3s, 3p with N 2p and O 2p states in Ti/N-codoped SiO<sub>2</sub>, as same the mixing of Si 3p and O 2p in Ti-doped system, would increase the mobility

and lifetime of photo-generated holes, and hence improve the optical properties to a certain extent. According to the research which provides a possible way to study the doping effects on SiO<sub>2</sub>, by theoretical means and can achieve satisfactory results, compared with the experimental data.

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#### References

- [1] J. Sarnthein, A. Pasquarello, R. Car, Physical Review Letters **74**, 4682 (1995).
- [2] C. D. Michele, P. Tartaglia, F. Sciortino, Journal of Chemical Physics **125**, 204710 (2006).
- [3] M. Langlet, C. Coutier, W. Meffre, M. Audier, J. Fick, R. Rimet, B. Jacquier, Journal of Luminescence **96**, 295 (2002).
- [4] M. Nogami, T. Yamazaki, Y. Abe, Journal of Luminescence **78**, 63 (1998).
- [5] N. Kamata, C. Satoh, K. Tosaka, K Yamada, Journal of Non-Crystalline Solids **293**, 595 (2001).
- [6] M. Morita, S. Kajiyama, D. Rau, T. Sakurai, M. Iwamura, Journal of Luminescence **102**, 608 (2003).
- [7] H.Y. Gou, F.M. Gao, J.W. Zhang, Computation Materials Science **49**, 552 (2010).
- [8] M.J. Pang, Y.Z. Zhan, H.Z Wang, W.P. Jiang, Y. Du, Computation Materials Science **50**, 3303 (2011).
- [9] P. Jund, R. Jullien, Physical Review B **59**, 13707 (1999).
- [10] K. Yamahara, K. Okazaki, K. Kawamura, Journal of Non-Crystalline Solids **291**, 32 (2001).
- [11] A. Takada, P. Richet, C.R.A. Catlow, G.D, Journal of Non-Crystalline Solids **345**, 224 (2004).
- [12] K. Yang, Y. Dai, B. Huang, Chemical Physics Letters. **456**, 71 (2008).
- [13] T. Lindgren, J. M. Mwabora, E. Avendano, J. Jonsson, A. Hoel, C. Granqvist, S. Lindquist, Journal of Physical Chemistry B **107**, 5709 (2003).
- [14] M. Zhang, L. Shi, S. Yuan, Y. Zhao, J. Fang, Journal of Colloid and Interface Science **330**, 113 (2009).
- [15] W. Dai, Z. H. Shui, K. Li, Computational and Theoretical Chemistry **967**, 185 (2011).
- [16] W. Dai, Z.H. Shui, INFORMATION-TOKYO **14**, 681(2011).
- [17] T. Yamamoto, Y.H. Katayama, Physica B **155**, 302 (2001).
- [18] P. Hu, W. Dai, Materials Research Innovations. **16**, 67 (2012).
- [19] A.A. Belik, T. Wuernisha, T. Kamiyama, K. Mori, M. Maie, T. Nagai, Y. Matsui, E.T. Muromachi, Chemistry of Materials **18**, 133 (2006).
- [20] P. Baetting, C.F. Schelle, R. LeSar, U.V.Waghmare, N.A. Spaldin, Chemistry of Materials **17**, 1376 (2005).

- [21] H. Wang, B. Wang, R. Wang, Q.K. Li, *Physica B* **390**, 96 (2007).
- [22] W. Dai, P. Hu, *Materials Research Innovations* **15**, 361 (2011).
- [23] S.K. Medeiros, E.L. Albuquerque, F.F. Maia Jr., E.W.S. Caetano, and V.N. Freire, *Chemical Physics Letters* **435**, 59 (2007).
- [24] D. Vanderbilt, *Physical Review B* **41**, 7892 (1990).
- [25] J.P. Perdew, K. Burke, M. Ernzerhof, *Physical Review Letters* **77**, 3865 (1996).
- [26] H.J. Monkhorst, J.D. Pack, *Physical Review B* **13**, 5188 (1976).
- [27] B.G. Pfrommer, M. Cote, S.G. Louie, M.L. Cohen, *Journal of Computational Physics* **131**, 233 (1997).
- [28] T. Tamura, S.J. Ishibashi, S.G. Tanaka, M. Kohyama, M.H. Lee, *Computation Materials Science* **44**, 61 (2008).
- [29] S. Saha, T.P. Sinha, *Physical Review B* **349**, 8828 (2000).
- [30] L.Y. Li, W.H. Wang, H. Liu, X.D. Liu, Q.G. Song, S.W. Ren, *Journal of Physical Chemistry C* **113**, 8460 (2009).

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