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Materials Science in Semiconductor Processing

Density functional theory study of nitrogen-induced magnetism in rutile TiO_2

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ARTICLE INFO

ABSTRACT

We have investigated the structural, electronic, magnetic properties and chemical bonding of N-doped rutile TiO_2 by a first-principles ultrasoft pseudopotential of the plane-wave within the density-functional theory (DFT). We find the polarized holes above the Fermi level by 1.058 eV, indicating that the magnetic coupling is mediated by the deep hole doping. The asymmetrical spin of N-2p states are mainly responsible for the origin of the ferromagnetism. The polarized holes from the N $2p_\pi$ and the Ti 3d (E_g+B_{2g}) in D_{4h} induce the π bonding.

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1. Introduction

TiO_2 is a well-known material for its wide applications as photocatalysts [1–4], photovoltaic solar cells [5], diluted magnetic semiconductors (DMS) [6–10]. However, a relatively wide band gap requiring ultraviolet radiation for electronic activation limits its photocatalytic activity [11–14]. In order to enhance the visible-light absorption for energy conversion, e.g., water splitting to generate hydrogen, the band gap narrowing by doping is a feasible way. With respect to the doping schemes, lots of experimental and theoretical investigations have been addressed such as N dopant [15,16], S dopant [11], Te dopant [14], C dopant [17], and codopant [18,19]. Then, an interesting phenomenon appears. As we know, transition metal-doped TiO_2 induces stable ferromagnetism [20], which shows the potential application in spintronics. However, the nonmagnetic element-doped TiO_2 also results in ferromagnetism [6–10]. Why this phenomenon attracts wide attention? It is due to that those transition metals associated with secondary phases, precipitates, and metal clusters [9,21] bring us away from the origin of ferromagnetism in TiO_2 doping. Hence, the nonmagnetic elements doping will break new ground in the origin of ferromagnetism, which may provide new spintronic materials [10]. Li et al. [6] found that C_O and C_{Ti} in rutile TiO_2 induced magnetic moments of 2.0 μ_B/C and 0, respectively, and concluded that C-doped TiO_2 could be an important candidate for DMS. In N-doped anatase TiO_2, a total magnetic moment of 1.00 μ_B from an isolated N atom and the magnetic moments from the holes in N 2p π band have been reported [10]. Experimentally, the O substitution with N in rutile TiO_2 films was responsible for the origin of the ferromagnetism, and a magnetic moment of each substituted N was 0.9 μ_B [8]. However, this origin is still obscure due to that the defects, trace magnetic impurity contamination and nitrogen dopant can all bring on ferromagnetism [7]. Therefore, the origin of the ferromagnetism in N-doped rutile TiO_2 requires further theoretical investigation.

2. Computational methods

Study for the ferromagnetism of N-doped rutile TiO_2 was performed with the plane-wave ultrasoft pseudopotential method implemented in CASTEP [22]. The exchange-correlation interactions were treated by the generalized gradient approximation (GGA) with Wu-Cohen functional [23]. The plane-wave cutoff energy of 380 eV, the energy convergence threshold of 5.0×10^{-6} eV/atom, and the Brillouin-zone integration with $2 \times 2 \times 2$ Monkhorst-Pack meshes have been used. We constructed a $2 \times 2 \times 2$ supercell containing 48 atoms to analyse the origin of the ferromagnetism in N-doped rutile TiO_2 (N_O). Furthermore, we used the GGA+U (U=5.5 eV for the Ti-d)

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approach [24] to treat electronic correction.

3. Results and discussion

The space group and local symmetry of rutile TiO_2 are $P4_2/mnm$ and D_{4h}^{14}, respectively, which is shown in Fig. 1. The calculated lattice parameters of pure rutile TiO_2 are $a=4.6085$ Å and $c=2.9481$ Å, which are consistent with experimental data $a=4.5929$ Å, $c=2.9591$ Å [25] and $a=4.593659$ Å, $c=2.958682$ Å [26]. By optimizing the N-doped rutile TiO_2 supercell shown in Fig. 1, we obtain its lattice parameters $a=4.6143$ Å and $c=2.9470$ Å. We can see that the volume of N-doped rutile TiO_2 increases slightly due to the big atomic radius of N. In order to estimate the possibility of the reaction and the stability of the final compound, we use the bulk formation energy and the cohesive energy as follows:

$$E_f^b = \frac{1}{48}[E_{total}(TiO_2:N) - \frac{31}{2}E_{O_2} - \frac{1}{2}E_{N_2} - 16E_{Ti(crystal)}] \quad (1)$$

$$E_c = \frac{1}{48}[E_{total}(TiO_2:N) - 31E_{O(atom)} - E_{N(atom)} - 16E_{Ti(atom)}] \quad (2)$$

where $E_{total}(TiO_2:N)$ is the total energy of N-doped rutile TiO_2, E_{N_2}, E_{O_2} and $E_{Ti(crystal)}$ are the energies of N_2 and O_2 gas molecules as well as bulk Ti metal, $E_{O(atom)}$, $E_{N(atom)}$ and $E_{Ti(atom)}$ are the energies of O, N and Ti atoms, respectively. We obtain -3.403 eV/atom and -8.795 eV/atom for formation energy and cohesive energy, respectively, indicating that the reaction from pure elements to final compound is favorable and the N-doped rutile TiO_2 is energetically stable. Next, we use the impurity formation energy to analyse:

$$E_f^i = \frac{1}{48}[E_{total}(TiO_2:N) - E_{total}(TiO_2) - \frac{1}{2}E_{N_2} + \frac{1}{2}E_{O_2}] \quad (3)$$

where $E_{total}(TiO_2)$ is the total energy of pure rutile TiO_2. The obtained impurity formation energy is 0.102 eV/atom, showing that the doping reaction from reactants ($TiO_{2(crystal)}$ and N_2) to resultants (O_2 and N-doped TiO_2) is endothermic. In other words, the N-doped TiO_2 will separate to $TiO_{2(crystal)}$ and N_2 at equal O_2 and N_2 partial pressures.

We obtain that pure rutile TiO_2 is a direct-band semiconductor with 1.914 eV, which is lower than the experimental data due to the well-known underestimation of band-gap within the DFT-GGA
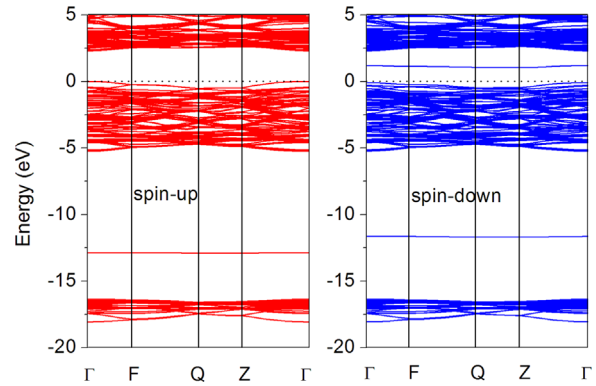

Fig. 2. Calculated band structure (GGA+U) of N-doped TiO_2.

calculations. For the N-doped rutile TiO_2, the calculated band structure (GGA+U) is shown in Fig. 2. The impurity bands having spin-down character are introduced by the unoccupied N-2p states, which appear above the Fermi level by 1.058 (GGA+U)/ 0.736 (GGA) eV. The impurity bands play an important role in enhancing photocatalysis and raising absorption region. The calculated total density of states (TDOS), partial density of states (PDOS) for the N dopant, the nearest neighboring Ti and O atoms of N-doped rutile TiO_2 are shown in Fig. 3. The N-2p and N-2s states are spin polarized, which show hybridization with Ti-3d states. The polarized holes and the asymmetrical spin of N-2p states are mainly responsible for the origin of the ferromagnetism in N-doped rutile TiO_2. In other words, the fully occupied spin-up bands and the partially occupied spin-down bands induce ferromagnetism, which cause the supercell magnetic moments of 1.0 μ_B (GGA+U)/ 1.0 μ_B (GGA). The calculated N spin moments are consistent with the experimental data [8], indicating that our results are believable. Moreover, Wang et al. [27] considered that the Ti ions around the N dopant resulted in the RTFM, where the N-doping causing the oxygen-vacancies have been taken into account. In order to study the magnetic coupling interaction [28–30] between two N impurities in N-doped rutile TiO_2, we further calculate two models with different N–N distances, where two N atoms substitute for O. The obtained magnetic moments of μ_N are 0.39 and 0.41 μ_B for the N–N distance of 3.991 and 7.209 Å, respectively, which are in agreement with previous data 0.43 and
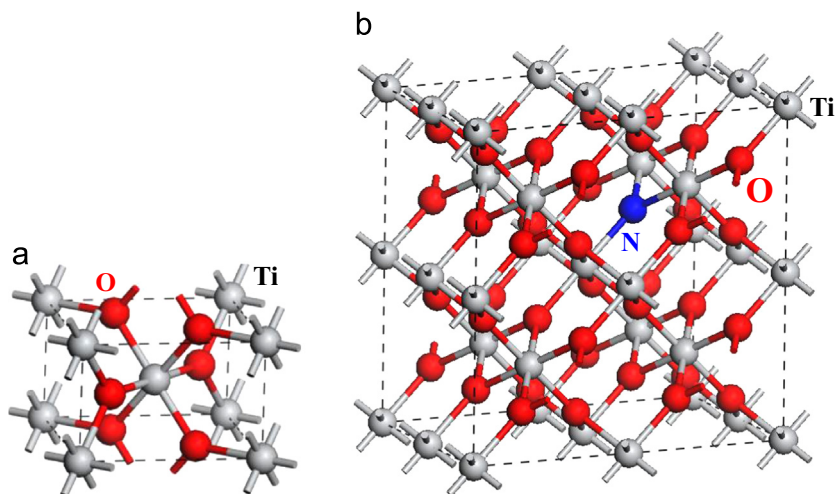

Fig. 1. Crystal structures: (a) pure TiO_2; (b) N-doped TiO_2.