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DFT study of electronic structure and optical properties of VO_2 and Ag/VO_2

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The electronic structure and optical properties of VO_2 and Ag/VO_2 were studied via density functional theory (DFT). The calculation results show that the interaction between Ag and O is stronger than that between V and O. There exists not only the covalent bonding but also ionic bonding in Ag–O bond. The band gap of Ag/VO_2 is smaller than that of VO_2, while the dielectric constant, conductivity, and intensity of optical absorption of Ag/VO_2 is larger than those of VO_2.

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1. Introduction

Vanadium dioxide has been widely studied because of the reversible metal-to-insulator transition (MIT) since it had been studied for the last half-century, the phase transition temperature is about 340 K [1–2]. It is monoclinic (M1) phase and infrared-transmitting semiconductor below the T_{MIT} (metal–insulator transition temperature). On the contrary, it can transform to the infrared-reflecting tetragonal rutile phase above the T_{MIT} [3–6]. The underlying mechanism of the MIT in VO_2 is considered as the Mott-Hubbard-like [7] driven by electron-electron correlation or Peierls-like [8] driven by electron-phonon interactions, which continues debating. The arrangement of the atomic structure and the properties will be changed when the transition happens, optical and electronic properties have a great change after and before the phase transition. These fascinating characteristics make VO_2 a further application in thermodynamic window coating, smart optoelectronic switcher, memory material, actuators, photonics technologies, and diffractive elements, and so on [9–11]. However, some drawbacks in properties and practical applications need to be resolved, such as high critical temperature, low visible transparency, limited solar-energy modulation efficiency [12].

Critical temperature can be altered via stress, doping, graining or incorporation of all factors. Doping is a most effective path to change the T_{MIT}. The T_{MIT} will be reduced when the high valence ions (Nb^{5+}, Mo^{5+}, W^{6+}) were doped to the VO_2, while the T_{MIT} will be increased if the low valence ions (Al^{3+}, Cr^{3+}, Ga^{3+}) were doped. Some characteristics have different changes along with the change of T_{MIT}, such as crystalline structure, color, optical properties, and electrical properties. Phase transition temperature will keep the linear relationship with the doping contents performance. Research had shown that the metal–insulator transition temperature and phase structure could be tuned by the Al-doping concentration [13]. Moreover, the phase transition temperature will decrease when oxygen vacancy is introduced into the VO_2 thin film [14]. Nonmetal elements (F, Cl, Br, I) can also do the same work, the band gap of F-doped VO_2 is lower than that of pure VO_2 [15].

In the last few years, some studies have shown that noble metal-doped VO_2 films can improve their optical performances [16,17]. Ag is one of the best noble metals with electrical and thermal conductivity. Zhang et al. investigated the optical transmission and absorption of Ag/VO_2 over a wide temperature range and the phase-transition temperature of Ag/VO_2 over a range of structural changes via simulations. They found that the optical absorption and transmission could be tuned by changing the thickness of the Ag layer[18]. However, the mechanism that doping Ag can change optical properties and phase-transition temperature of VO_2 remains unclear to date. In this paper, electronic structures and optical properties of pure VO_2 and Ag-doped VO_2 were studied using the DFT method, including energy gap, density of states, Mulliken population, dielectric function, conductivity, and optical absorption. This study can provide important insight into the mechanism that the structure and optical properties of VO_2 can be changed by doping methods.

2. Computational methods

The CASTEP package (Cambridge sequential total energy package) was used for this calculation. DFT calculation is based on the crystal structure optimized by molecular dynamics module. Generalized-gradient-approximations (GGA) in the form of the Perdew–Wang 91 (PW91) exchange-correlation functional was used. The interactions between valence electrons and ionic core were represented by ultrasoft pseudoptentials. Based on the test results, a plane wave cut-off energy of 350 eV, and a 1 × 1 × 1 uniform Monkhorst−Pack k grid were used for M1 phase. We used a simplified version of the rotationally invariant LDA+U method where the adopted values of U were set at 2.5 eV for the vanadium d electrons. Using BFGS algorithm, optimization parameters: atomic energy convergence criteria is 1×10^{-5} eV/atom, the interaction force between atoms convergence criteria is 0.05 eV/nm, the crystal stress convergence criteria is 0.05 GPa, the atom maximum displacement convergence criteria is 0.001 Å.

3. Computational models

The M1 phase VO_2 possesses a space group of P21/c. The lattice constants are 5.734 Å, 4.517 Å, 5.375Å, respectively. Each vanadium atom coordinates with adjacent six oxygen atoms and one vanadium atom, while each oxygen atom coordinates with adjacent three vanadium atoms (Fig. 1). The model of Ag/VO_2 was obtained from optimum unit cell and was modeled using a supercell approach (2 × 2 × 2), which is shown in Fig. 2. For comparative purposes, the electronic structure and optical properties of undoped VO_2 were obtained by calculating supercell VO_2.

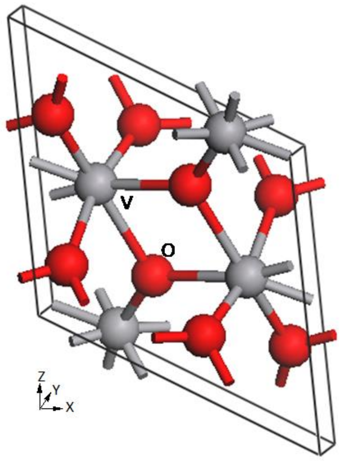

Fig. 1. Cell model of VO_2

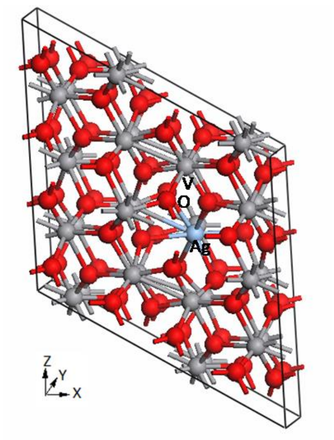

Fig. 2. Model of Ag/VO_2

3.1. Energy band structure and density of states

The band structures of VO_2 (Fig. 3(a)) and Ag/VO_2 (Fig. 3(b)) are showed in Fig. 3. Band gaps of VO_2 and Ag/VO_2 are 0.115 eV and 0.024 eV, respectively, which are small to the theoretical value (0.7 eV)[19]. Smaller band gap values are caused by DFT in GGA functional, which is insufficient to process inter-electron exchange interaction and does not affect the analysis of energy gap results. In a word, the band gap of Ag/VO_2 is far smaller than the pure VO_2, which suggests that the doped VO_2 has a better metallicity.

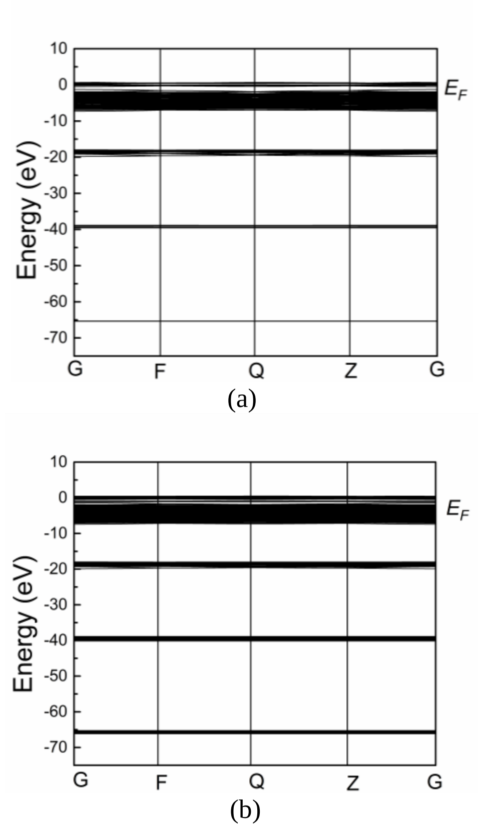

Fig. 3. Band structures of supercell VO_2 (a) and Ag/VO_2 (b)

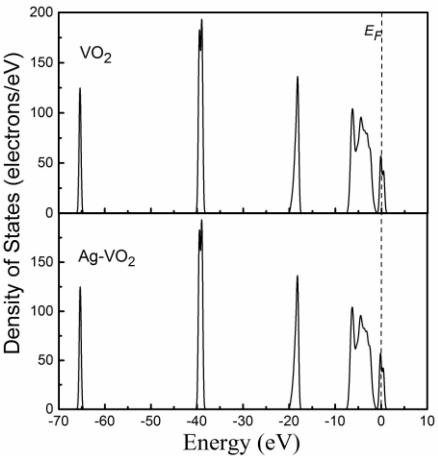

Fig. 4. Total densities of states for VO_2 and Ag/VO_2

Fig. 4 shows the total densities of states of VO_2 and Ag/VO_2. According to Fig. 4, the curves of total density of states for VO_2 and Ag/VO_2 are very similar. Fig. 5 shows the partial densities of states of V atom for VO_2 (a) and Ag atom for Ag/VO_2 (b). It is very obvious that density of states of vanadium atom are mainly made up of four groups. The first group between -67 eV and -65 eV is from V 4s orbital. The second group between -40 eV and -37 eV is from V 4p orbital. The third group between -7 eV and 0 eV is mainly made up of V 3d orbital. The conduction band is made up of V 3d orbital. Density of states of Ag is made up of Ag 4d orbital with few Ag 5s orbital, which are located in the range of -0.7 eV to 0 eV.

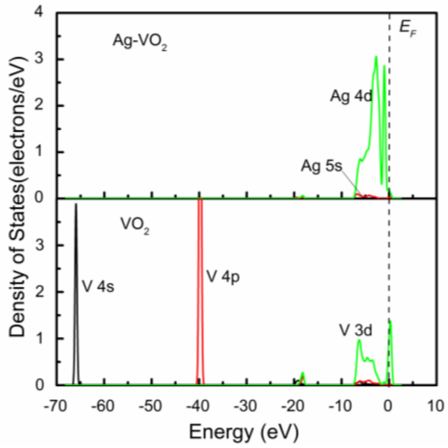

Fig. 5. Density of states of supercell VO_2 and Ag/VO_2

Fig. 6 shows DOS results of interactions between vanadium atom and oxygen atom for VO_2, and between silver atom and oxygen atom for Ag/VO_2. Near the Fermi level it is mainly that the O 2p interacts with V 3d for VO_2, while O 2p interacts with Ag 4d for Ag/VO_2. DOS of Ag 4d for Ag–O is larger than that of V 3d for V–O bond, which shows that silver is more active than vanadium. In addition, the overlap of O 2p and Ag4d orbitals is larger than that of O 2p and V 3d orbitals. These results show that the interaction between oxygen and silver is stronger than that between oxygen and vanadium.

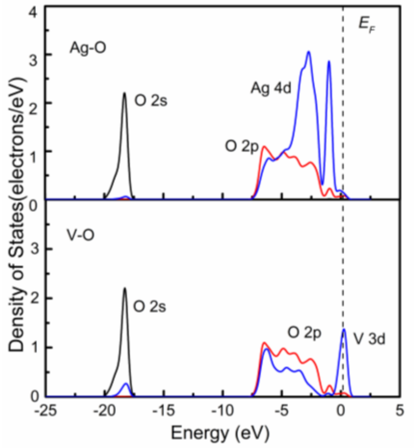

Fig. 6. DOS results of O atom and V atom for VO_2, O atom and Ag atom for Ag/VO_2

3.2. Mulliken population analysis

Table 1 shows Mulliken bond population values of O–V bond (VO_2) and Ag–O bond (Ag/VO_2). It is observed that the population values of Ag–O bond is much smaller than that of V–O bond, which shows that covalent bond between silver and oxygen is smaller than that between vanadium and oxygen. According to Fig. 6, the interaction between silver and oxygen is stronger than that between vanadium and oxygen, indicating that Ag–O contains the stronger ionic bond.

Table 1. Mulliken bond populations of VO_2 and Ag/VO_2

Bond	Population	Length (Å)
O1– V1	0.66	1.7219
O1– Ag1	0.08	2.2560

3.3. Optical properties

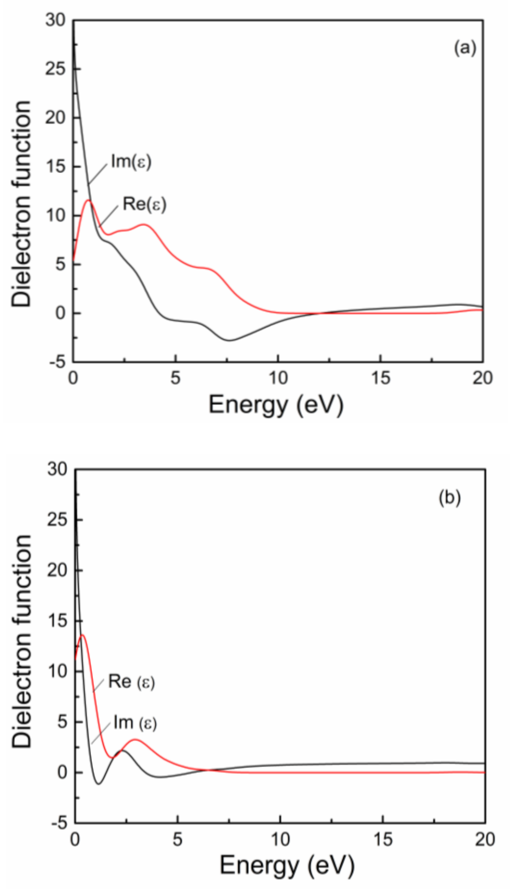

Fig. 7. Dielectric functions of VO_2 (a) and Ag/VO_2(b)

The dielectric functions of VO_2 and Ag/VO_2 are showed in Fig. 7. The formula of dielectric function is shown as follows:

$$\varepsilon(\omega)=\varepsilon_1(\omega)+i\varepsilon_2(\omega) \tag{1}$$

Where $\varepsilon_1(\omega) = \mathrm{Re}\,\varepsilon(\omega)$, $\varepsilon_2(\omega) = \mathrm{Im}\,\varepsilon(\omega)$, $\mathrm{Re}\,\varepsilon(\omega)$ is real part of dielectric function and $\mathrm{Im}\,\varepsilon(\omega)$ is imaginary part of dielectric function, ω is frequency. From the Fig. 7, the dielectric function of Ag/VO_2 is different from VO_2. The dielectric peak of Ag/VO_2 shifts towards the low energy compared to VO_2, and the peak intensity of the imaginary part increases, while that of the real part decreases.

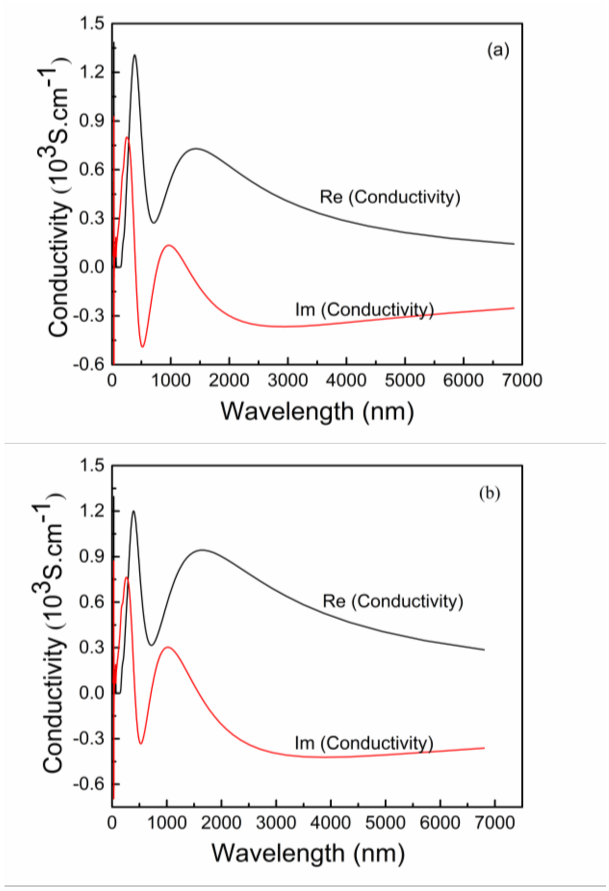

Fig. 8. Conductivities of VO_2 (a) and Ag/VO_2 (b)

Fig. 8 shows the conductivities of VO_2 and Ag/VO_2. It is very obvious that the conductivity of Ag/VO_2 is larger than that of VO_2, especially those around 1000 nm (imaginary part). The conductivity of polarization current and the dielectric function are related through Eq. (2):

$$\sigma_{\mathrm{p}} = \omega\varepsilon_2(\omega) \tag{2}$$

According to Eq. (2), the conductivity is proportional to the imaginary part of dielectric function, which is in good agreement with the results of dielectric function (Fig. 7) and also with those of band structures in which band gap of Ag/VO_2 is smaller (Fig. 3). The conductivity of Ag/VO_2 increases with a decrease in band gap. When light is irradiated to a material, the photon energy larger than the band gap can excite electron-hole pair and cause an increase in carrier concentration, resulting in increasing conductivity.

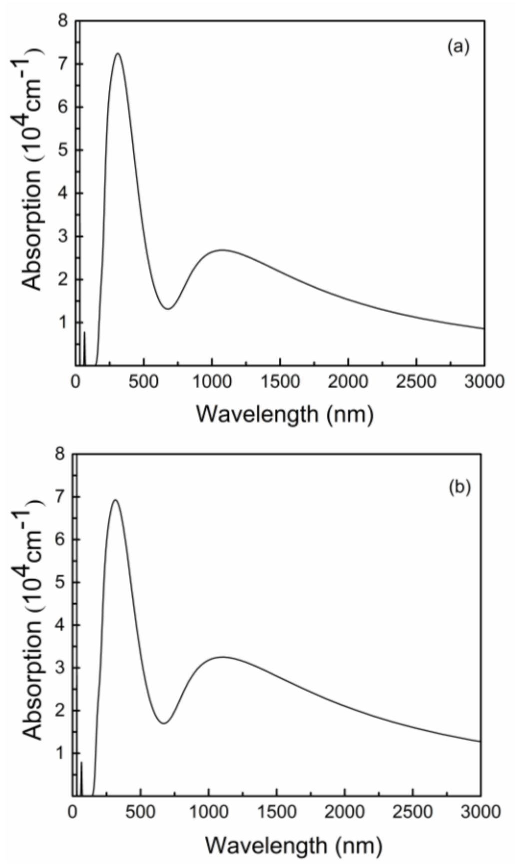

Fig. 9. Optical absorption of VO_2 (a) and Ag/VO_2 (b)

The absorption spectra of VO_2 and Ag/VO_2 are displayed in Fig. 9. The intensity and corresponding wavelength of absorption peak for Ag/VO_2 are lower than those of VO_2, but the intensity of absorption peak for Ag/VO_2 near 1150 nm is larger than those of VO_2 and the larger wavelength of absorption peak for Ag/VO_2 means a red-shift relative to VO_2. Zhang's research showed that the absorption of Ag/VO_2 enhances with the increase of the Ag thickness, regardless of semiconductor state or metallic state. There exists a good absorption near 1000 nm when the thickness of the Ag layer is 15 nm[14]. Hence, the band gap of Ag-VO_2 is smaller than that of VO_2, which is in good agreement with the results of band structure (Fig. 3). On the other hand, optical absorption coefficient is proportional to the imaginary part of dielectric function, which is also in well agreement with our results. In this study, the peak intensity of the imaginary part of dielectric function for Ag/VO_2 was found larger, resulting in the increase of intensities of the optical absorption.

4. Conclusions

The electronic structure and optical properties of VO_2 and Ag/VO_2 were studied by DFT method. The interaction between Ag and O is stronger than that between V and O. There are both covalent bonding and ionic bonding in Ag−O bond. The band gaps of VO_2 and Ag/VO_2 are 0.115 eV and 0.024 eV, respectively. In other words, when Ag is doped in the VO_2, the band gap becomes small, while the dielectric constant, conductivity, and intensity of optical absorption get larger.

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