



Full Length Article

Exploring the work function variability and structural stability of VO₂ (1 1 0) surface upon noble metal (Ag, Au, Pt) adsorption and incorporation

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ABSTRACT

Vanadium dioxide (VO₂) has attracted great attention, with scientific and technological advances over the past few decades due to its reversible metal-insulator transition at 340 K. However, the high phase transition temperature (T_c) of VO₂ limits its practical applications. Our first-principles calculations show that VO₂(1 1 0) surfaces with adsorbed noble metals (Ag, Au, Pt) exhibit a lower work function compared with the clean surface and further induces a lower T_c due to charge transfer from the noble metals to the VO₂(1 1 0) surface. However, the work functions of the VO₂(1 1 0) surfaces after the incorporation of noble metals are higher than that of the clean surface. In addition, the results of formation energies of various configurations show that the VO₂(1 1 0) surface with the adsorption and incorporation of Ag is energetically more favorable than those with Au and Pt. Therefore, it may be concluded that the adsorption and incorporation of noble metals can not only tailor the work function of VO₂, in turn realizing the rational tuning of T_c of VO₂, but also stabilize the structures of VO₂ thin films. These results provide guidance for further exploration of VO₂-based optical switching devices and smart windows.

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1. Introduction

As a typical correlated oxide, VO₂ is one of the most promising thermochromic materials, with a reversible metal-insulator transition at the phase transition temperature (T_c) of 340 K [1]. From the high-temperature phase to the low-temperature phase, VO₂ exhibits a dramatic change in electrical and optical properties. Therefore, VO₂ is scientifically fascinating and technologically promising for many potential applications, such as optical switching devices and smart windows [2–11].

However, tuning T_c of VO₂ with respect to room temperature is still a topic for VO₂ studies. Recently, it was found that double-layered films for VO₂ combined with noble metals exhibited a decreased T_c , and even showed the improved optical properties due to the localized surface plasmon resonance of the noble metal nanoparticles (e.g., Ag, Au, Pt) [2–7]. Through a periodic array of subwavelength apertures, the transmitted-intensity ratio of Ag/

VO₂ double-layered film increases by a factor of 8 as VO₂ transits from the metal phase to the insulator phase [3]. Furthermore, optical properties related to transmission through the double-layered film, such as the absorption spectrum, can be tuned and controlled by changing the thicknesses of the VO₂ and Ag layers [8], or by an applied voltage [9]. In addition, a dual-functional sensor based on coupling between VO₂ nano-crystal films and Ag nanoparticles can probe fluorescence or Raman signals on the same substrate and these functions can be switched by changing the temperature [10]. The idea of constructed Au/VO₂ double-layered films has also gained widespread momentum because of the outstanding phase transition [11–21] and electrical transport properties [22,23]. By adjusting the threshold of laser power, the integration of Au and VO₂ resulted in regulation of the phase transition behavior of VO₂ and generated a 1.5-fold increase in its absorption coefficient [11]. It has been reported that Au-VO₂ films made via the sol-gel process [12], radio frequency-inverted cylindrical magnetron sputtering [14,17], or pulsed laser deposition method [15], exhibit the well-known metal-insulator transition. Moreover, they also display a variable hysteresis width, controlled by the size of Au nanoparticles [16] and the transmittance spectrum of VO₂ can also be

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modified by changing the Au mass thickness [18]. For example, Xu et al. [17] observed that the injected electrons flowing from Au atom to VO₂ can lower the T_c of VO₂, and initially proposed the effects of the lower work function of the metal. It should be noted that the screened coulomb interactions of localized electrons in the other transition metal oxides (e.g., MnO, FeO, CoO and NiO) also driven the phase-transition [24]. Furthermore, Reuter-Hack et al. found that the work function of Pt and TiO₂ particles decreases with increasing in temperature [25]. In addition, surface-doping with gold nanoparticles can be used to control the conductance of VO₂ nanowires [22]. In another example, Pt/VO₂ films not only exhibit a decreased T_c , but also show improved optical and electrical properties [2,23,26]. For instance, T_c of double-layered Pt/VO₂ film shows a decrease of 9.3 K, while its transmittance is enhanced from 25.1% to 37.9% at a fixed wavelength of 0.55 μm [2]. Through first-principles thermodynamic calculations, bulk VO₂ doped with 6.25% metals (such as Ag, Pt, Au) is proposed to be a potential choice for modulation of T_c and improvement of the optical spectrum [27]. Although most of these papers [2–23,25–27] on the metal-VO₂ interactions have focused on the behavior of nanoparticles or multilayers, these studies have provided important information on the adsorption site and structural energetics of a noble metal/VO₂ system [2,10,17]. Therefore, an atomic scale understanding of the interaction occurring between the single noble metal and VO₂ surface also requires calculations.

Recent reports suggest that T_c of VO₂ is related to its work function [28,29]. The work function of Au/VO₂ film, measured by Kelvin force microscopy, increases from 5.15 eV to 5.30 eV as the temperature increases from 300 K to 368 K [28]. In fact, by first-principles calculations, we recently found that the work function of the VO₂(1 0 0) surface can be tuned by Ag-adsorption due to the charge transfer from Ag to the surface, which increases the electron concentration in the VO₂ thin film and in turn regulates T_c of VO₂ [29]. Therefore, it is of vital importance to reveal the underlying micro mechanism on the single noble metal on VO₂ surface to the phase transition behavior for realizing the rational tuning of the T_c .

In the present paper, we use first-principles calculations to systematically investigate the work function variability and structural stability of rutile VO₂(1 1 0) surface with adsorbed and incorporated noble metals (Ag, Au, Pt). Further, we attempt to reveal the correlation between T_c and work function of noble metals/VO₂ double-layered films, and analyze the reasons for the decrease in the work function of noble metals (Ag, Au, Pt) adsorbed on VO₂ film.

2. Computational details methodology

Density function theory (DFT) calculations were performed, based on the generalized gradient approximation (GGA) of Perdew Burke Ernzerhof (PBE) [30,31], as implemented in the Vienna *ab initio* simulation package (VASP) code [32,33]. Given the existence of strong on-site Coulomb repulsion among the V-3d electrons, the Hubbard parameter U was added to the PBE functional [34], in which only the difference ($U_{\text{eff}} = U - J$) between the Coulomb repulsion U and screened exchange J must be specified. Despite the fact that the choice of U was often adjusted to match existing experimental quantities, the Dudarev DFT + U method had been shown to reasonably describe the electronic structure and strong correlation of VO₂ [35–37]. For instance, our first-principles calculations showed that hydrogen is an efficient dopant which can stabilize the metallic VO₂ phase at ambient temperature [38] and that the T_c of VO₂ can be regulated by constructing an Ag/VO₂ double film [29]. Therefore, in the present calculations, the effective parameters U and J , were specified as 4.0 eV and 0.6 eV, respectively [29,35–39].

The valence electron configurations for V, O, Ag, Au, and Pt were considered as $3d^34s^2$, $2s^22p^4$, $4d^{10}5s^1$, $5d^{10}6s^1$, and $5d^96s^1$, respectively. The energy cutoff for the plane-wave was set to 530 eV and a $2 \times 2 \times 1$ Monkhorst-Pack k -point mesh was used. This set of parameters was used to ensure that the total energies converged to 10^{-5} eV/unit cell. The Hellmann-Feynman forces were converged to less than 0.01 eV/Å. For calculations of the electronic density of states, a $4 \times 4 \times 1$ k -point mesh is used for rutile VO₂(1 1 0) surface and the linear tetrahedron method with Blöchl corrections. The climbing-image nudged elastic band (CI-NEB) method [40] was used to search for the saddle points and minimum energy path as well as to determine the diffusion barrier height.

To investigate the work function variability and structural stability upon incorporation and adsorption of X ($X = \text{Ag, Au, Pt}$) on a rutile VO₂(1 1 0) surface, we construct a $p(4 \times 2)$ ($p = \text{primitive}$) unit cell. As shown in Fig. 1(a), for a VO₂(1 1 0) surface incorporated with noble metals X ($X = \text{Ag, Au, Pt}$), the X atoms at V-substitution sites are denoted as $(n_1/n_2/n_3)$, where n_1 , n_2 and n_3 represent the numbers of X atoms in the first, second, and third V-atomic layers, respectively. Note that only configurations with the X/V ratio of 1.59% [12] are considered in the present calculations. As shown in Fig. 1(b), possible adsorption sites on the rutile VO₂(1 1 0) surface include: (1) 2-fold coordinated O atoms in the topmost atomic layer (O_{br}), (2) 3-fold coordinated O atom in the second atomic layer (O_{3c}), (3) 5-fold coordinated V atoms in the second atomic layer (V_{5c}), (4) 6-fold coordinated V atom in the second atomic layer (V_{6c}), (5) hollow one (H_1), and (6) hollow two (H_2). The possible adsorption sites on the rutile VO₂(1 1 0) surface are considered similar to those on the rutile TiO₂(1 1 0) [41] and rutile VO₂ surfaces [29,42], showing that our models are reliable.

Based on the optimized rutile VO₂ (VO₂(R)) lattice parameter of 4.552 Å, the $x[0 0 1]$ and $y[1 \bar{1} 0]$ dimensions on the VO₂(R) (1 1 0) surface are fixed at 11.408 Å and 12.875 Å, respectively. In fact, convergence tests on the surfaces with $p(2 \times 2)$ versus $p(4 \times 2)$ supercells yield similar results, with adsorption energy differences within 0.016 eV/f.u., 0.030 eV/f.u., and 0.010 eV/f.u. for Ag, Pt, and Au, respectively. It is noted that eV/f.u. denotes eV/formula unit. Slabs of various configurations are modeled, with a thickness of 12.22 Å, and containing 64 VO₂ formula units and a vacuum layer of 18 Å. The vacuum layer guarantees that no interactions between the slab and its periodic images perpendicular to the surface. To simulate bulk VO₂, the bottom five layers are fixed (see region enclosed by a dashed line in Fig. 1(a)) and the remaining layers are allowed to relax. The energies of isolated noble metal (Ag, Au, Pt) atoms are calculated by putting one noble metal atom in a cubic box with the size of 15 Å \times 15 Å \times 15 Å by VASP.

The adsorption energy (E_{ads}) is calculated by the following formula

$$E_{\text{ads}} = E_{X/\text{VO}_2} - E_{\text{VO}_2} - E_X, \quad (1)$$

where E_{X/VO_2} , E_{VO_2} and E_X are the total energies of X ($X = \text{Ag, Au, Pt}$) adsorbed on the VO₂(1 1 0) surface, clean VO₂(1 1 0) surface, and isolated X ($X = \text{Ag, Au, Pt}$) atom, respectively.

To compare the relative structural stability of various configurations of X ($X = \text{Ag, Au, Pt}$) adsorbed on and incorporated into the VO₂(1 1 0) surface at different growth conditions, the formation energies (E_f) [43] are calculated as

$$E_f = E_{\text{total}} - E_{\text{ref}} - \Delta n_V \mu_V - \Delta n_X \mu_X - \Delta n_O \mu_O, \quad (2)$$

where E_{total} is the total energy of the configuration under consideration, E_{ref} is the total energy of the clean VO₂(1 1 0) surface, μ_i is the chemical potential of the i th species, and Δn_V , Δn_X and Δn_O are the number of excess or deficient V atoms, X atoms and O atom, respectively; When the i th species is added to or removed from

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