Consecutive Insulator-Metal-Insulator Phase Transitions of Vanadium Dioxide by Hydrogen Doping

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Abstract

We report modulation of a reversible phase transition in VO$_2$ films by hydrogen doping. Metallic and insulating phases are successively observed at room temperature as the doping concentration increases. The polarized charges induced by doped hydrogens gradually occupy V3$d$-O2$p$ hybridized orbitals and consequently modulate the filling of the VO$_2$ crystal conduction band-edge states, which eventually become saturated and therefore evolve into new valence band-edge states. A clear linear relationship between H-concentration and V3$d$ orbital occupancy were found. These results suggest the exceptional sensitivity of VO$_2$ electronic properties to electron concentration and orbital occupancy, providing key information for the phase transition mechanism.
Since Mott predicted the first-order metal-insulator transition (MIT) behavior several decades ago, the underlying physics of how electron-electron interactions affect electronic structures of strongly correlated systems has become a hot field of condensed matter physics. As a typical correlated oxide, monoclinic vanadium dioxide (M-VO₂) undergoes a MIT process from metal to insulating state at the critical temperature near 68°C [1,2]. This transition is believed to be driven by the Mott transition associated with electron-electron correlations [3–5] or the Peierls transition involving electron-phonon interactions [6,7], although the actual MIT mechanism is still under debate.

Regulating electronic density through atomic doping is an effective way to modulate the balance between competing phases in strongly correlated materials [8,9]. It is reported that hydrogen incorporated into M-VO₂ crystals can stabilize the metallic VO₂ phase at room temperature [10-14] and further lead to an insulating phase in the high doping regime [15]. Fig. 1(a) shows both the normal temperature-triggered MIT (from insulating M-VO₂ to metallic rutile VO₂ (R-VO₂)) as well as the phase transitions driven by reversible hydrogen doping. Different from the temperature induced MIT, the metallic H-VO₂ (H-VO₂(M)) is produced by light doping concentration in HₓVO₂ (0< x < 1), while further hydrogenation treatment up to the saturation point of HVO₂ leads to a new insulating H-VO₂ (H-VO₂(I)) state.

Explained in the context of crystal-field theory [16,17], the H-doping induced band structure evolutions is represented in Fig. 1(b). For the pure M-VO₂ crystal, the Fermi level is located in the ~0.6eV insulating gap between the edge states of d// and d//*/π* orbitals. Under low H-doping treatment, the conduction band-edge states of d//*/π* are partially filled, resulting in a metallic state. Upon further hydrogenation, the d//* band become fully occupied, producing new valence band-edge states. This leads to a new insulating gap and an insulating H-doped VO₂ crystal. As electron-electron correlations and electron-lattice interactions are always relevant, the variation of electronic structure also influences the crystal lattice structure, such as the V-V bonds. However, largely due to the difficulties of characterizing the dynamic doping process from incompletely hydrogenated states to the maximally H-doped
state, previous work focused on the phenomena of doping-induced property variations, and thereby did not arrive at a clear mechanism for the doping-based transitions.

In this letter, we report in-situ synchrotron based characterization to directly monitor the dynamics of H atom doping in VO₂ crystals. This characterization captures the lattice/orbital variations as well as the band structure evolution during the reversible phase transitions. Based on the experimentally determined geometric details, first-principle theoretical studies show the gradual filling of conduction band-edge states with nearly linear dependence on H-doping level, which was unattainable in previous works. The underlying mechanism for the doping-driven insulator-metal-insulator phase transitions is thus revealed, indicating the filling-based evolution of the semiconductor conduction band-edge states to valence band-edge states.

The 50 nm M-VO₂/Al₂O₃ (0001) epitaxial films were deposited by an rf-plasma assisted oxide-MBE method [18]. Metallic H-VO₂ (M) and insulated H-VO₂ (I) films were obtained by hydrogenation for different time in Ar/15% H₂ gas mixture with Au particles as the catalyst [12, 15]. From the in-situ R-T measurement in vacuum conditions, the insulating H-VO₂ (I) gradually became a metallic sample as shown in Fig.1 (c). This metallic state was quite stable in vacuum. Upon further annealing of this metallic H-VO₂ (M) sample in air, the material will gradually revert to its initial monoclinic structure as shown in Fig.1 (d). In fact, if conducting the R-T tests in air, the phase transformation of the hydrogenated VO₂ film from the insulating state to metallic state, and then back to the initial (monoclinic) insulator state could be observed (Fig.S1 in Ref. [19]). This suggests that the hydrogenated VO₂ film is more stable in vacuum than in the air condition.

The chemical states of the hydrogenated VO₂ were examined by X-ray photoelectron spectroscopy (XPS) in Fig.2 (a). There exist double peaks for V2p3/2 at 516.0 eV and 517.1 eV, which are assigned to V⁴⁺ and V⁵⁺ states, respectively [20,21]. The O₁s peak at 530.1 eV is from vanadium oxide and the peak at 531.9 eV originates from the –OH species [12,22,23]. For hydrogenated VO₂, the -OH peak is much stronger than V-O peak, indicating the formation of -OH bonds [22,23]. After
annealing the H-VO₂ samples in air for 30 min, the –OH peak decreases substantially and the sample almost reverts to the undoped M-phase. We can then estimate the hydrogen concentration by XPS peak fitting (Fig.S2 in Ref. [19]) and obtain the stoichiometric values of H₀.₆₄VO₂ for the metallic H-VO₂ (M) and H₀.₈₉VO₂ for the insulating H-VO₂ (I). Nevertheless, it is difficult to determine the exact H-atom concentration because of possible intermediate phases during experimental measurements.

The evolution of electronic structures can be inferred from measuring optical band gap. In-situ UV-Vis spectra in Fig.2 (b) indicated the enhancement of visible transparency along with increasing H-concentration in VO₂, suggesting the gradual decreasing/filling of empty d//sates at conduction band edge [24, 25]. Meanwhile, synchrotron-based X-ray diffraction (XRD) spectra in Fig. 2 (c) showed that diffraction peaks of hydrogenated VO₂ shifted towards low angles, indicating the presence of slightly enlarged lattice parameters and expanded cell volumes.

Synchrotron based XANES spectra suggested that H atoms intercalation actually caused electron doping effect. The V L-edge curves continuously shifted to lower energies as the H concentration increases (Fig.S3 in Ref. [19]), implying charge transfer to V atoms that caused valence state reduction from V⁴⁺ to V⁴⁺(4- δ), or even to the V⁺³ state [12]. The O K-edge mapping in Fig.2 (d) presented the transitions from O1s to O2p states, in which two distinct features of the t₂g and e₉g peaks reflected the unoccupied states [26, 27]. The intensity ratio of t₂g/e₉g decreased substantially with increasing H concentration, meaning that t₂g levels including the d//s and π* orbitals were gradually filled by electron doping. Considering the valence band structures shown in Fig.1 (b), the doped electrons will occupy the lower t₂g levels, resulting in an up-shift of the Fermi level. As the t₂g levels were gradually filled by electron doping, the intensity of t₂g peak decreased gradually, while the higher-energy e₉g peak increased simultaneously.

The above characterizations thus provide structural details for a thorough theoretical investigation on the microscopic kinetics of phase transitions. First-principles simulations at the density function theory (DFT) level were applied to
examine the H-doping induced geometric and electronic structure variations [19].

Fig.3 shows VO₂ models with corresponding calculation results. Compared to the pure monoclinic VO₂ (1×1×1) unit cell (V₄O₈), the optimized structures of both lightly H-doped cells (HV₄O₈ or H₂V₄O₈) and saturated doping cells (H₄V₄O₈) are quite stable with negative formation energies and H-O bonds of ~1.00 Å [19]. H-doping induces only subtle geometric variations including slightly enhanced lattice parameters and expanded cell volumes, consistent with above characterizations and previous reports [10]. In contrast, the electronic structures were heavily affected by H-doping. All hydrogen atoms hold strong positive charges (> 0.64 e⁻), inducing polarized electrons in V-O bonds. The energy distribution of polarized electrons can be inferred from the simulated density of states (DOS). For the pure V₄O₈ cell, valence band edge states are well separated from the conduction band in Fig.3 (d), accounting for the insulating properties of a typical semi-conductor band structure (Fig. 3(g)). With one or two H introduced into V₄O₈, the HV₄O₈ (Fig.S4 in Ref [19]) or H₂V₄O₈ cells exhibit partially occupied conduction band-edge states. The newly occupied states are mostly d/* orbitals of V atoms, suggesting that H-doping induce more d-electrons. The calculated charge densities clearly show the electron distributions and the charge transfer for the H-doped system (Fig.S5 in Ref. [19]). The polarized d-electrons then shift up the Fermi level, and consequently cause the conduction band edge in V₄O₈ (Fig.3 (g)) to become partially occupied (Fig.3h) for H₂V₄O₈, naturally leading to an insulator-to-metal transition. The evolution of electronic structures becomes more interesting when we add 4 H atoms into a V₄O₈ cell. The computed DOS in Fig.3 (f) shows that the polarized electrons fully occupy the original conduction band edge states in V₄O₈. These states with lowered energies become the new valence band maximum (Fig. 3i), leading to an insulating ground state. The effect of varying different interstitial H sites was tested, giving similar electronic structures (Fig.S6 in Ref. [19]).

In order to unravel the actual microscopic mechanism, the gradual filling of V-3d orbitals with increasing H-concentration were simulated. A larger (1×2×1) cell of V₈O₁₆ was constructed. These together with the above H-doped V₄O₈ models
enabled us to examine the effect of varying doping concentration (H_xV_8O_16 with x=0~8). The DOS features in Fig. 4(a) and Fig. S7 show that increasing H-doping gradually shifted up the Fermi level to exceeding the conduction band edge state of the V-3d orbitals [19]. The V-3d occupancy was computed by integrating the corresponding DOS below the Fermi level (Fig. 4(a)). Surprisingly, the V-3d occupancy increases linearly with H-doping concentration (Fig. 4(b)). This clear relationship thus explains the phase transitions, from the insulating state (VO_2) with empty V-3d/\text{*} orbitals, to the metallic states (H_xV_8O_16, x=1~7) with un-saturated H-doping and partially-occupied conduction band edge states, and eventually to the new insulating state (H_8V_8O_16) with saturated H-doping and fully-occupied V-3d/\text{*} orbitals which already became the new valence band edge. It should be noticed that the electron correlations in VO_2 system need to be accounted by many-body techniques. To test the consistency, both PBE+U and advanced HSE06 computations were conducted and exhibited nearly the same linear filling of V-3d/\text{*} orbitals by H-doping (Fig.S8-9 in Ref. [19]), providing key insights for mechanism investigation.

In conclusion, the present experimental and theoretical work provides a comprehensive description of the whole dynamic process of hydrogen-induced consecutive phase transitions in VO_2 crystal. We accomplished direct detection of gradual electron occupation of the e_g/t_2g orbitals along with increasing H-concentration, when the formation of O–H bonds is accompanied by electrons donating from H to V and O atoms. These polarized electrons cause the partial filling of the conduction band edge, leading to metallic behavior. With saturated O–H bonds, the additional polarized electrons eventually occupy all d/\text{/} orbitals at the previous conduction band edge, creating new valence band edge states and producing a new insulating gap. A linear relationship describing the dependence of d/\text{/} orbital occupancy on H-doping concentration was revealed. These data and analysis provide fundamental physical insights into the H-doping-induced electronic band/orbital occupancy variations and reveal the underlying mechanism of the reversible doping controlled insulator-metal-insulator phase transition. This approach should lead to the accurate control of electronic properties of this and other oxide materials in a
continuously adjustable manner.

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Figure Captions

FIG. 1 (a) Scheme for the phase transitions induced by temperature and electron doping. For the hydrogenation effect, two hydrogen-doped VO$_2$ phases exist, which show insulating (H-VO$_2$ (I)) and metallic (H-VO$_2$ (M)) states, respectively; (b) Molecular orbitals and band diagrams for monoclinic VO$_2$ insulator and H-doped VO$_2$ in its metallic/insulating phase; (c) R-T curves for metallic H-VO$_2$ (M) and insulating H-VO$_2$ (I) film samples. During a series of 20 heating/cooling cycles in vacuum over the range of 35 °C to 90 °C at a constant ramp rate of 0.4K/s, the R-T curve for the H-VO$_2$ (I) insulator film shows a gradual transformation to the metallic H-VO$_2$ (M) state. (d) The metallic H-VO$_2$ (M) reverts to the monoclinic insulator state after baking in air at 180°C. After the 30min treatment, recovery to the initial M-VO$_2$ state is nearly complete.

FIG. 2 (a) XPS spectra for VO$_2$ films: the as-prepared M-VO$_2$ film, hydrogenated metallic (M) and insulator (I) films, and dehydrogenated film, showing clear differences between the V2p and O1s peaks. (b) The UV-Vis spectra for hydrogenated samples during phase transitions. (c) The crystal lattice variations during the hydrogenation process. (d) The synchrotron based O K-edge XANES spectra mapping for the electron occupancy of the t$_{2g}$ and e$_g$ orbitals during the hydrogenation process.

FIG. 3 Optimized atomic structures (top panel), density of states (DOS: middle panel), band structures (bottom panel) of the pure monoclinic VO$_2$ unit cell (V$_4$O$_8$) and
H-doped cells (H_xV_4O_8 with x=2, 4). (a), (b), (c) are the crystal structures of V_4O_8, H_2V_4O_8, and H_4V_4O_8, respectively. The red, grey, and blue balls represent O, V and H atoms, respectively. (d), (e), (f) are the DOS of V_4O_8, H_2V_4O_8 and H_4V_4O_8, respectively, where the Fermi level E_F is marked with dashed lines. (g), (h), (i) are the band structures of V_4O_8, H_2V_4O_8 and H_4V_4O_8, respectively.

FIG. 4 (a) The DOS of H_3V_4O_8, in which the shaded areas represent occupancy of the conduction band edge state, corresponding to DOS below the Fermi level E_F. (b) The electron occupancy of the total and V-3d DOS (computed by integrating the shaded areas) as a function of H-doping concentration.
Figure-1

(a) M-VO₂ (Insulator) → H-VO₂ (Metal) → R-VO₂ (Metal)

(b) M-VO₂ (Insulator) → H-VO₂ (Metal) → H-VO₂ (Insulator)

(c) Resistance (Ω) vs Temperature (°C) for M-VO₂ (M) and H-VO₂ (I) with cycle No.

(d) Resistance (Ω) vs Temperature (°C) for M1-VO₂ with different hydrogenation times (5 min, 10 min, 15 min, 20 min, 30 min, pure M1-VO₂).
Figure-2
Figure-3
Figure-4