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Intrinsic evolutions of optical functions, band gap, and higher-energy electronic transitions in VO_2 film near the metal-insulator transition region

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Transmittance spectra of (011) vanadium dioxide (VO_2) film have been studied in the temperature range of 45–80 °C. Owing to increasing carrier concentration, the near-infrared extinction coefficient and optical conductivity around metal-insulator transition (MIT) rapidly increase with the temperature. Moreover, three electronic transitions can be uniquely assigned and show the hysteresis behavior near the MIT region. It was found that the optical band gap decreases from 0.457 to 0.042 eV before the MIT, then reduces to zero for the metal state. This confirms the fact that the a_{1g} and e_g^{π} bands are moved close and finally overlap with the temperature. © *2011 American Institute of Physics*. [doi:10.1063/1.3665626]

Vanadium dioxide (VO_2) has attracted considerable attention owing to the metal-insulator transition (MIT) at the critical temperature (T_c).[1–3] The MIT is accompanied by a dramatic changes in electrical and optical properties.[4,5] Much effort has been made on the physical origin of the MIT and there have been many explanations describing the phase transition. However, the underlying physical picture of the MIT process is still far from the clarification.

How do the intrinsic physical phenomena evolve from the insulator state to the metal state in VO_2? One of the effective methods is to investigate the related parameters in the vicinity of the phase transition temperature. As we know, the electronic transitions, optical constants, and optical band gap (OBG) undergo a considerable change when the MIT occurs. Fortunately, single crystalline VO_2 sample contains a low level of defects and impurities, allowing us to probe the intrinsic optical properties of individual phase in the vicinity of transition.[6] Note that the low-temperature dependence of electronic transitions and dielectric function in VO_2 film have been studied.[7] However, the ultraviolet optical constants and higher-order interband transitions at the temperature around T_c are scarce.

The VO_2 film was prepared on sapphire substrate using direct-current magnetron sputtering at room temperature (RT).[8] The normal-incident transmittance spectra were recorded at 45–80 °C using a ultraviolet-infrared spectrophotometer. The VO_2 film and sapphire substrate were mounted into a heating stage for high temperature experiments, respectively. The crystalline structure of the VO_2 film was analyzed by x-ray diffraction at RT. From the inset of Fig. 1, the film presents only (011) orientation, which indicates that the VO_2 sample is of the single monoclinic phase at RT. The resistances in Fig. 1 show a hysteresis behavior and about four orders of magnitude change can be observed. Moreover, the delay of MIT temperature is estimated to about 9 °C. In the high-temperature metal state, the free-carriers are electrons while the carriers are holes in the insulating monoclinic state.[9] Based on the results of Hall experiment in the heating process,[9,10] it can be deduced that the transfer temperature of carriers in the cooling process is lower than that of the heating process. Therefore, the holes cannot be immediately generated when the temperature is decreased back down, resulting in the transition delay.

The near-infrared (NIR) region below 1.5 eV (825 nm) is assigned to a strong Drude response [Fig. 2]. The isosbestic point at 1.5 eV, which is defined as the location of invariant transmittance, is one of several spectroscopic fingerprints in doped Mott insulators. The location of the isosbestic point is similar to that observed in other VO_2 films.[1,11] In the heating process, the transmittance in the NIR region slightly decreases until the temperature is up to 67 °C, which suggests that the MIT occurs. This is because the free carriers increase with the temperature, which can weaken the electronic transitions and result in strong reflectance. On the contrary, the MIT appears at about 58 °C for the cooling process.

The optical constants of the VO_2 film can be derived by fitting the transmittance spectra using the Drude-Lorentz (DL) oscillator dispersion relation:[12] $\tilde{\varepsilon}(E) = \varepsilon_r + i\varepsilon_i = \varepsilon_\infty - [A_D/(E^2 + iEB_D)] + \sum_{j=1}^{3}[A_j/(E_j^2 - E^2 - iEB_j)]$; $\tilde{n} = n + ik = \sqrt{\tilde{\varepsilon}}$, where ε_∞ is the high-frequency dielectric constant, A_j, E_j, B_j, and E are the amplitude, center energy, broadening of the jth oscillator, and the incident photon energy, respectively. A_D is the square of the plasma frequency and B_D is the electron collision or damping frequency. The transmittance of a single film on the transparent substrate can be calculated by Snell's law considering the film to be isotropic. The optical component of each layer and the propagation matrix for the film can be expressed by the 2×2 matrix. The resultant matrix, which is the product of all separate matrix, is applied to

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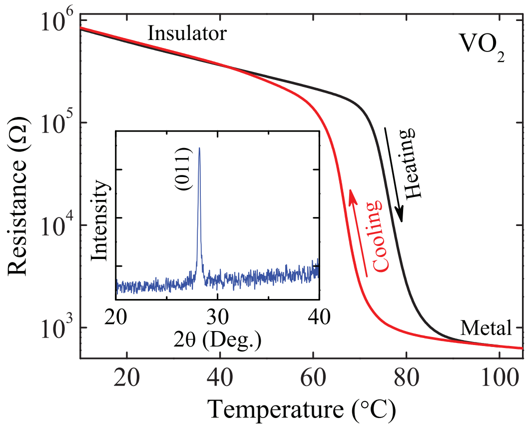

FIG. 1. (Color online) Temperature dependence of the resistance in the VO_2 film. The inset shows the x-ray diffraction pattern of the film.

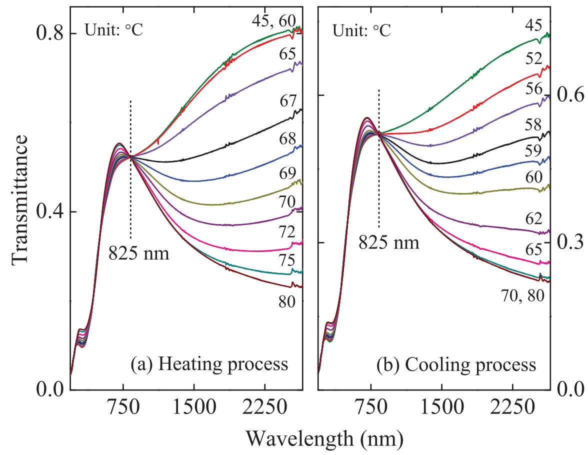

FIG. 2. (Color online) The transmittance spectra for the (a) heating and (b) cooling processes, respectively. The dashed lines at 825 nm denote the isosbestic (equal transmittance) points.

readily calculate the transmittance.[13] Although the optical constants can be directly derived by both transmittance and reflection due to more optical parameters,[14] the application of only spectral transmittance technique is accurate enough to obtain the optical constants of the film on transparent substrate because the light reflection from the substrate is small and a reference mirror is normally necessary in the measurement. The A_D and B_D parameters nearly approach zero at the low temperature, suggesting an insulator behavior. When the temperature increases to 67 °C, the contributions from the Drude response become more prominent, which indicates that the film is well-conductive. The similar phenomena can be also observed at 58 °C from the cooling process.

The extinction coefficient k at the NIR region rapidly increases with the temperature, especially near the MIT region [Fig. 3]. The extinction coefficient of the metals and conductive metallic oxide is associated with the electrical properties such as conductivity or the carrier concentration. The carrier concentration is proportional to the square of the plasma frequency A_D and the carrier mobility is inversely proportional to the electron collision or damping frequency B_D.[15,16] The A_D value increases with the temperature, suggesting that the carrier concentration increases with the temperature [Fig. 4(a)]. The fact that the B_D value in Fig. 4(b) decreases with increasing the temperature indicates that the carrier mobility increases with the temperature. Moreover, the electron concentration of VO_2 film increases about four orders of magnitude from RT to T_c, which has been observed by Hall measurement.[17] Therefore, the variation of k value at the NIR region can be ascribed to increasing carrier concentration and mobility with the temperature. The Lorentz oscillators can correspond to different interband electronic transitions. Three features can be also clearly identified from the k curves and are labeled with E_1, E_2, and E_3, respectively.

Several singularities denote the corresponding electronic transition between the filled and empty bands [Figs. 4(c) and (d)]. The σ_r value evidently increases with the temperature. The Drude-like metallic response can be attributed to the transitions between narrow vanadium (V) 3d excitations near the Fermi level. Note that a hump appears when the film heating to 67 °C and becomes more evident with increasing the temperature. It indicates that the metallic regions have been percolated (connected) forming a macroscopic conducting path for charge carriers.[3] From the inset of Fig. 4(c), the σ_r value at 0.5 eV rapidly changes at the temperatures near the MIT and shows a typical hysteresis loop. Note that the MIT information shows a slight difference from the resistance and optical experiments, which can be caused by the temperature error in the two systems. On the other hand, the changing trend from spectral transmittance becomes more consistent with increasing the temperature, especially for the cooling process [Fig. 2(b)].

The fitting results reveal that the optical transition peaks at 45 °C are located at about 1.34 (E_1), 3.61 (E_2), and 6.34 (E_3) eV, which can be readily distinguished from the k and σ_r spectra. The three center energies can be assigned to the following electronic transitions:[18–20] (1) lower V 3d filled a_{1g} bands to empty e_g^π bands; (2) the filled O_{2p} bands to the empty e_g^π bands; and (3) lower V 3 d filled a_{1g} bands to empty e_g^σ bands. The center transition energies of E_1 and E_2 show the hysteresis behavior [Fig. 4(e)]. This is because the change of the transition energies is directly related to the variation of band gap. In the high-temperature metal phase, the a_{1g} bands overlap the e_g^π bands and the two bands are both partially occupied.[21] Therefore, the band gap of the VO_2 film is reduced to zero. The close of the band gap will result in the dramatic decrement of transition energies when the transition occurs. Nevertheless, the highest-order transition E_3 does not follow a regular relationship with the temperature.

Fig. 4(f) presents the evolution of the indirect OBG estimated using the power law. The OBG of insulating VO_2 can be assigned to the indirect transition from the top of filled a_{1g} bands to the bottom of empty e_g^π bands. It can be found that the OBG decreases from 0.457 to 0.042 eV with increasing the temperature to 67 °C. Then the band gap becomes close to zero with further increasing the temperature. On the contrary, the gap open at 58 °C with the value of 0.006 eV for the cooling process and further increases to 0.275 eV at 45 °C. Note that the switch temperature of OBG is the same to that of the Drude parameters A_D and B_D. Note further that the indirect OBG at 45 °C is similar to that from previous reports by theoretical calculation (0.32 eV)[22] and experimental measurements (0.31 and 0.30 eV).[23,24]

When raising the temperature up to T_c, the a_{1g} and e_g^π bands overlap and the Fermi level crosses partially filled the two bands. One can deduce that both the a_{1g} and e_g^π bands are

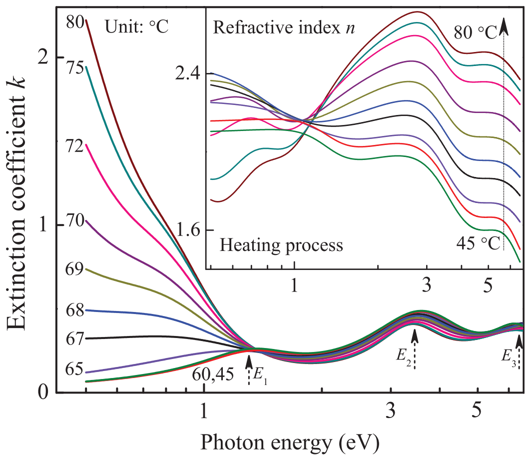

FIG. 3. (Color online) The extinction coefficient k of the VO_2 film with increasing the temperature from 45 to 80 °C. The arrows indicate the positions of the electronic transitions and the inset shows the refractive index n.

gradually moved close and finally overlap, resulting in the fact that the band gap gradually closes toward zero.[19] It should be emphasized that the metal-insulator transition in VO_2 is a percolation process with the coexistence of metallic and insulating phases. Owing to the temperature sensitivity, the selected model and the fitting method can only describe the major transition steps for this inhomogeneous system. Thus, the fitting results are definitely the averaged data of two phases near the MIT process. Moreover, the present work ideally shows the evolution trend from the experimental temperature point selected. On the other hand, the gradual closing of band gap when raising the temperature also comes from an averaged effect of two phases, which can be ascribed to different crystallinity and defects. For the cooling process, the monoclinic lattice distortion removes the overlap, which is presented within the V 3*d* bands at the Fermi level in the rutile state, opening an energy gap. In addition, the charge transfer from the center V atom to the six oxygen ligand, the increased symmetry in the V atom chains, and the increased *p-d* overlap coming with the antiferroelectric distortion of the VO_6 octahedra can also induce the dramatic change of the OBG.[2,5,22] Nevertheless, the carrier-lattice and carrier-carrier interactions, which include both the exchange and correlation energies, could also contribute to the VO_2 band gap variation.[6]

To summarize, the intrinsic mechanisms derived from the hysteresis behaviors of the electronic transitions and band gap have been presented during the MIT process.

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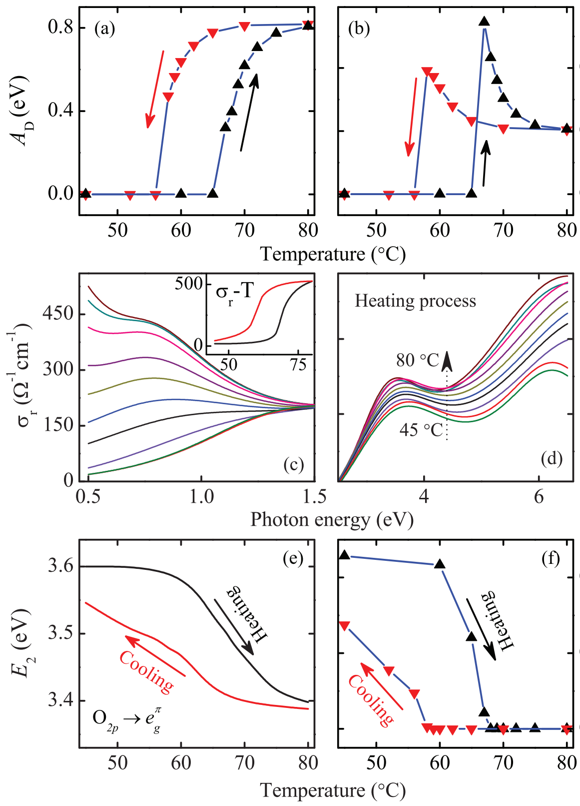

FIG. 4. (Color online) Temperature dependence of the Drude oscillator parameters (a) A_D and (b) B_D. The real part of the optical conductivity σ_r for the heating process in the photon energy region of (c) 0.5-1.5 eV and (d) 2.5-6.5 eV. The inset of (c) shows the σ_r value at the photon energy of 0.5 eV as a function of temperature. (e) The hysteresis loop of the electronic transition E_2. (f) The evolution of the optical band gap.

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