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Optical properties for the Mott transition in VO_2

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The relationship between the first-order metal-insulator transition (MIT) and the structural phase transition (SPT) in VO_2 film is analyzed by dielectric function, optical conductivity, plasma energy, and electrical conductivity. The MIT and SPT temperatures in VO_2 films were approximately 68 and 75 °C, respectively, with an intermediate phase existing between 68 and 75 °C. The optical and electrical results indicate that the first-order MIT in VO_2 films is not driven by the SPT. [http://dx.doi.org/10.1063/1.3696031]

Several vanadium oxides undergo a reversible metal-insulator transition (MIT) involving drastic changes in electrical and optical properties.[1] Of all the vanadium oxides, the transition temperature (T_c=68 °C) of VO_2 is closest to room temperature and undergoes an MIT from a high temperature metallic rutile (R) phase to a low temperature insulating monoclinic (M_1) one.[2] Owing to its outstanding characteristic, VO_2 has been intensely investigated to be applying for electronic or optical devices.[3–5]

For describing the MIT in VO_2, two major mechanisms have been argued: the electron-phonon mechanism (the Peierls mechanism[6,7]) and the electron correlation mechanism (the Mott mechanism[8,9]). There is much experimental evidence of a strong electronic correlation in VO_2. For example, Kim *et al.*[10] reported time-resolved pump-probe measurements for VO_2 and demonstrated causality between the MIT and the SPT via analyzing coherent phonon oscillations. They suggested that the appearance of coherent phonon oscillations at 4.5 and 6.0 THz indicating the rutile metal phase of VO_2 does not occur simultaneously with the first-order MIT near 68 °C. Moreover, Qazilbash *et al.*[11] investigated the MIT and unconventional metallic transport in VO_2 with a combination of spectroscopic ellipsometry (SE)[12] and reflectance measurements. Their study of the temperature dependence of the optical conductivity showed that MIT involves a redistribution of spectral weight within a broad energy range below 5.5 eV. This optical data supports an electronic correlation in VO_2.

In present study, we report the temperature dependence of dielectric function and optical conductivity characterized by measurements of SE as evidence of an electron correlation mechanism in VO_2 film. Measurement of the resistance is also carried out to identify the MIT in the film. Finally, the relationship between the first-order MIT and the SPT in VO_2 films is discussed by analyzing the dielectric function, optical conductivity, plasma energy, and electrical conductivity.

VO_2 film with a thickness of ∼115 nm was prepared on a both-side polished Al_2O_3 (0001) substrate by RF sputtering using a V_2O_5 target and post-annealed under an ambient O_2. Temperature dependence of Raman spectra was measured by using a Raman/PL spectrometer (Horiba Jobin-Yvon, LabRAM HR). The spectra of the ellipsometric constants (Ψ and Δ) were measured using a spectroscopic ellipsometer (Jobin-Yvon, Uvisel UV/NIR) with a photon energy range of 0.75 eV to 4.0 eV. SE data for the VO_2 film were analyzed via an optical model based on the Bruggeman effective medium approximation (BEMA).[13] The triple new amorphous (TNA) formula, combined

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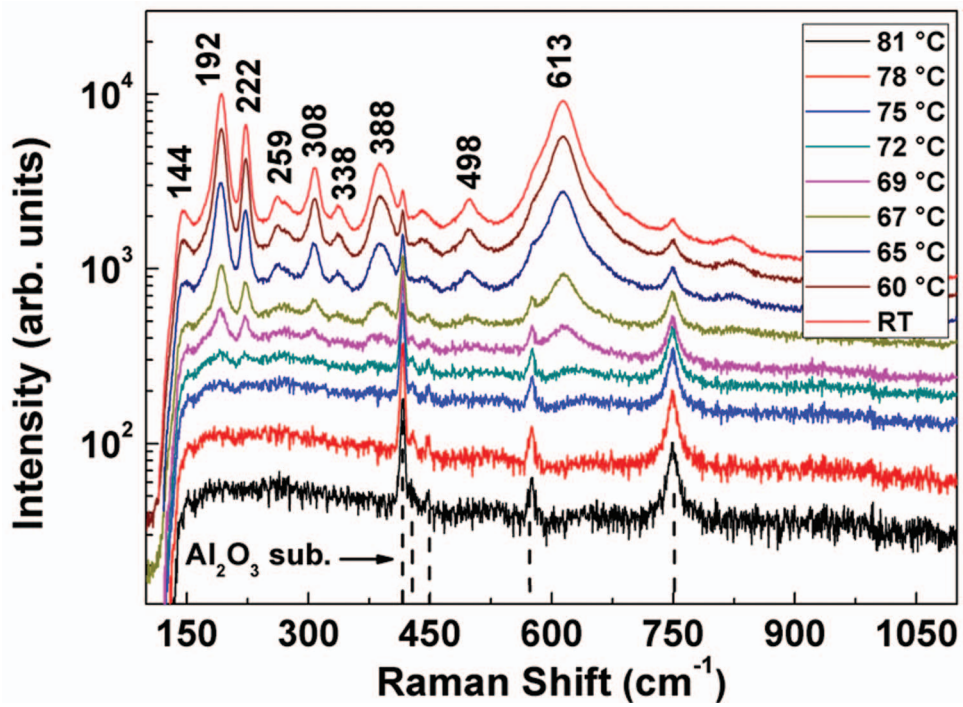

FIG. 1. Temperature dependence of Raman peaks: the typical Raman-active modes for the monoclinic phase disappear near 75 °C.

with three oscillators, was utilized to describe the dispersion in the dielectric function of the VO_2 film.[12] Details of modeling and analysis were reported previously.[12,14] The temperature dependence of the resistance of the VO_2 film was measured to confirm the optical results using an electrometer (Keithley, 237).

The temperature dependence of Raman spectra for the VO_2 film is shown in Fig. 1. At room temperature, seven peaks regarding as the phonon modes of the monoclinic phase for VO_2 are observed.[15–17] The modes observed at 192, 222, 259, 308, 338, 388, and 498 cm^{-1} are confirmed as A_g symmetry of the phonons.[16,17] The peaks at 142 and 613 cm^{-1} are also assigned to the B_{1g} and A_{1g} symmetric modes, respectively.[17] In the temperature range from room temperature to 72 °C, all peaks of the typical Raman-active modes for the monoclinic phase significantly weaken and broaden. The peaks disappear at 75 °C. In our measurements, although the tetragonal A_{1g} peak indicating the SPT from the monoclinic to the rutile tetragonal structure[17,18] is not observed, the disappearance of the typical Raman-active modes for the monoclinic phase above 75 °C points out a variation of crystalline structure in VO_2.

Figures 2(a) and 2(b) present the real (ε_1) and imaginary (ε_2) parts of the dielectric function for the VO_2 film below and above T_c. As the temperature increases from room temperature to 80 °C, both the ε_1 and ε_2 spectra significantly vary over the entire photon energy range. In the ε_1 spectra shown in Fig. 2(a), the spectra change dramatically as the temperature increases from 40 °C to 65 °C, and above 65 °C, the ε_1 spectra show gradual change with increasing temperature. As shown in Fig. 2(b), the ε_2 spectra reveal a weak Drude absorption feature below 0.8 eV due to an increase in free charge carriers above 65 °C. However, the monoclinic phase still exists from 65 °C to 72 °C even though the intensity considerably decreases the temperature region [see Fig. 1.]. This indicates that a first-order MIT in the VO_2 film occurs without SPT and a structural inhomogeneity[18] is induced in the temperature region. The structural inhomogeneity can be generated by external excitations such as temperature, pressure, doping, and light. This structural inhomogeneity causes a monoclinic metal (MM) phase regarding as an intermediate state which exists in a region between the MIT and the SPT temperatures.

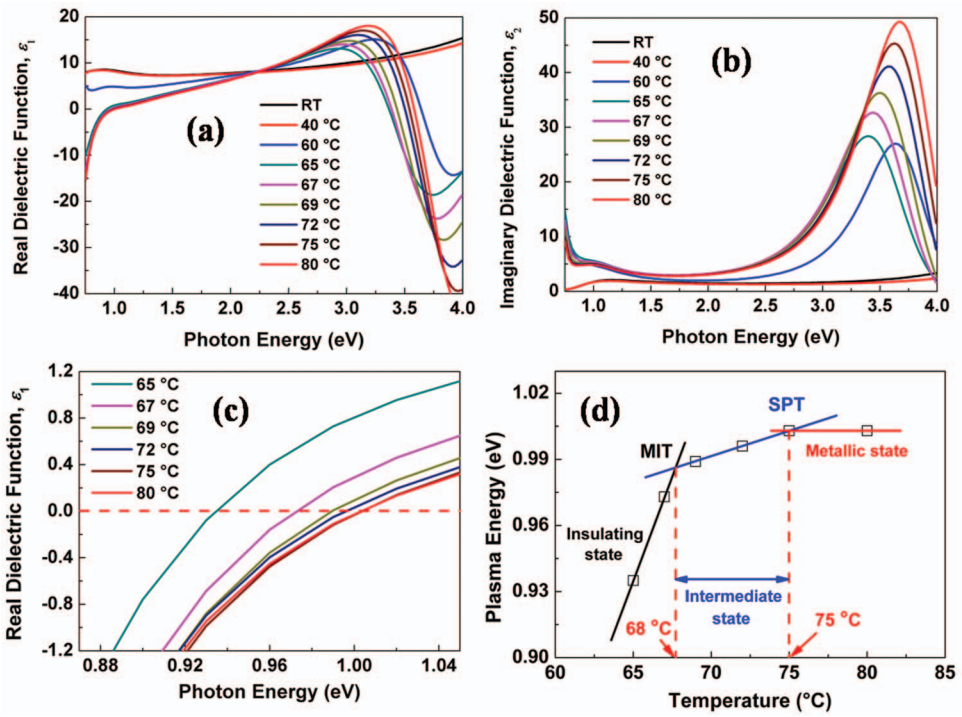

FIG. 2. Temperature dependence of the (a) real (ε_1) and (b) imaginary (ε_2) parts of dielectric function for VO_2 film: (c) show enlarged ε_1 in the 0.80-1.08 eV range. (d) Temperature dependence of the plasma energy: the plasma energy is obtained by extrapolating of the ε_1 spectra.

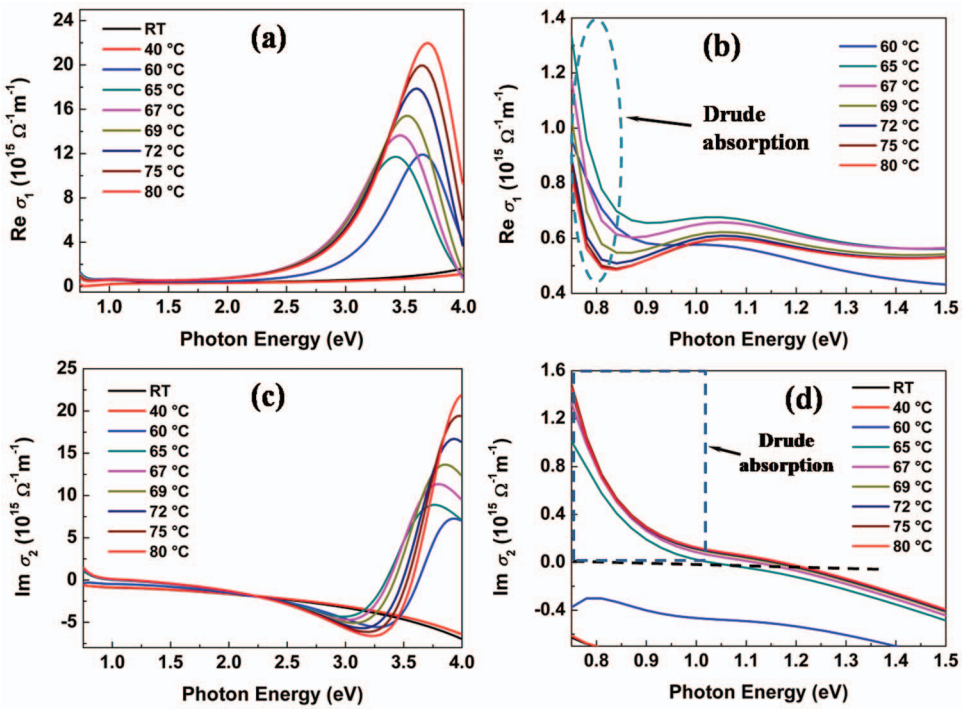

FIG. 3. Temperature dependence of the (a) real (σ_1) and (c) imaginary (σ_2) optical conductivities of VO_2 films: (b) and (d) show enlarged σ_1 and σ_2 in the 0.75-1.50 eV range.

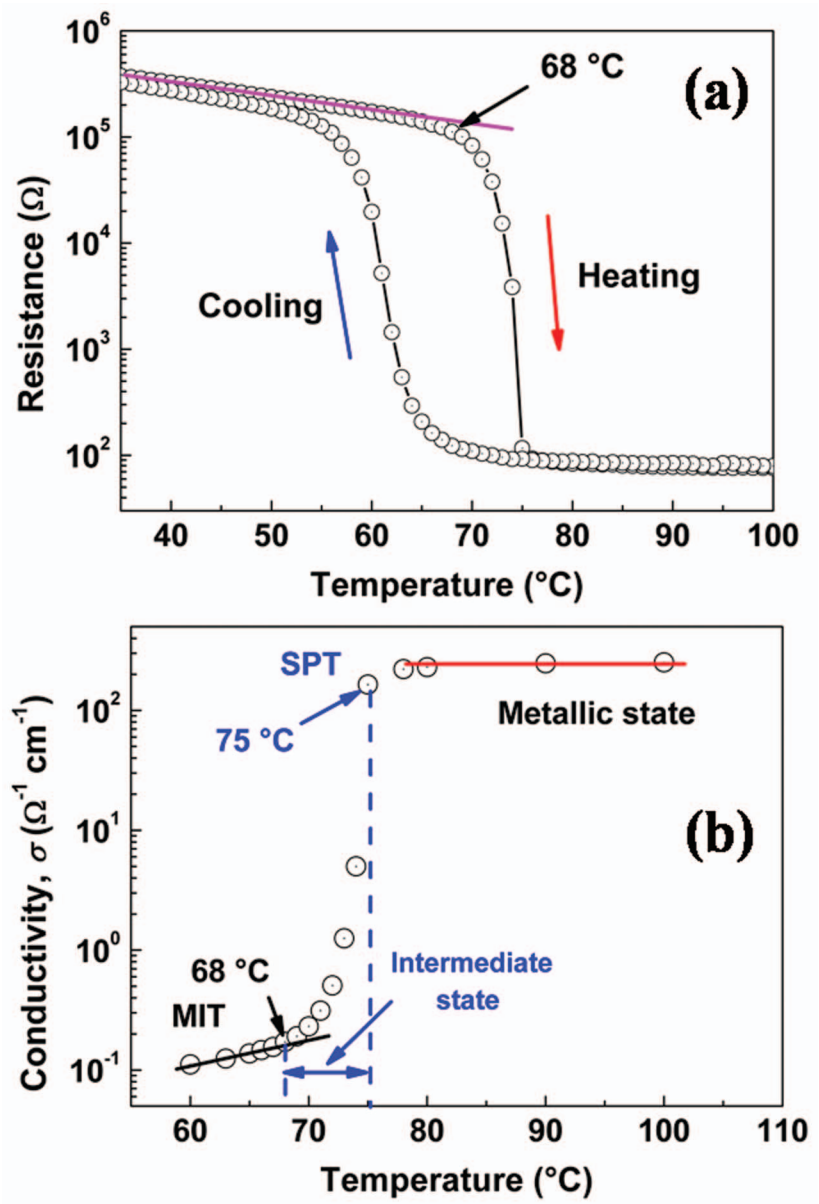

FIG. 4. (a) Temperature dependence of the resistance for VO_2 film and (b) temperature dependence of electrical conductivity (σ) calculated from the resistance.

Figure 2(c) shows an enlarged ε_1 in the 0.80-1.08 eV range and the temperature dependence of the plasma energy is displayed in Fig. 2(d). Plasma energies above 65 °C are obtained by extrapolating of the ε_1 spectra and the values are found to be 0.935, 0.973, 0.989, 0.996, 1.003, and 1.003 eV, respectively. According to the Drude-Lorentz model,[12,19] ε_1 becomes zero at $\omega = \omega_p$. As shown in Fig. 2(d), the rate of increase ($\Delta E/\Delta T$) of the plasma energy differs below and above 68 °C. Below 68 °C, $\Delta E/\Delta T$ is $\sim 1.9 \times 10^{-2}$ eV/°C, while between 68 °C and 75 °C, it is $\sim 2.3 \times 10^{-3}$ eV/°C. The region between 68 °C and 75 °C may be considered an intermediate regime between the first-order MIT and the SPT.[15] Existence of the intermediate regime implies that the first-order MIT is not driven by the SPT and the MIT and the SPT do not occur simultaneously. Kim *et al.*[10] defined a monoclinic and correlated metal (MCM) phases between the MIT and the SPT. They classified a monoclinic T phase instead of monoclinic M_2 in VO_2 as a correlated paramagnetic

Mott insulator before the MIT occurs. They also defined the MCM phase existing between the MIT and the SPT as an intermediate state which may be regarded a nonequilibrium state.

The SPT in VO_2 is well known from micro-Raman measurements.[17,20] In accordance with past results, the rutile tetragonal phase is observed near 70 °C after the MIT occurs. In our Raman measurements, although the rutile tetragonal phase indicating the SPT is not observed, a significant change of crystalline structure is shown above 75 °C. Thus, the SPT temperature may be regarded as 75 °C and it may be considered that a first-order MIT in VO_2 is not a structure-driven MIT.

Figures from 3(a) to 3(d) show the real (σ_1) and imaginary (σ_2) parts of the optical conductivity for the VO_2 film calculated from the complex dielectric function. An enlarged σ_1 in the 0.75-1.50 eV range is shown in Fig. 3(b). The spectra reveal a weak Drude absorption feature below 0.8 eV due to an increase in free charge carriers at 65 °C. As the temperature increases from 65 °C to 80 °C, the absorption feature becomes clear. The presence of the Drude absorption at 65 °C strongly indicates that VO_2 has a monoclinic metallic state[10] distinguished from tetragonal metallic state[2] because the temperature is lower than $T_c = 68$ °C. The result shown in Figs. 3(a) and 3(b) implies that the change in the electronic structure does not depend on change in atomic structure.

Figure 3(c) and 3(d) provide the σ_2 spectra and the enlarged σ_2 in the 0.75-1.50 eV range. Above 65 °C, the σ_2 spectra show a gradual change with increasing temperature and become positive below about 1.0 eV. The positive σ_2 means that the extinction coefficient k is larger than refractive index n. This also indicates that the medium absorbs lights with photon energies below 1.0 eV region. In general, the presence of free carriers leads to the absorption of light in a semiconductor or an insulator. This effect can be observed in the near-infrared spectral region below the fundamental absorption edge at the band gap.[19] The results shown in Figs. 3(c) and 3(d) imply that the Drude absorption due to the free carriers in VO_2 film occurs above 65 °C.

The reversible temperature dependence of the resistance in VO_2 film is measured to confirm the optical results. As shown in Fig. 4(a), the resistance begins to deviate from the linear trend at 68 °C. Therefore, T_c may be taken as 68 °C. Figure 4(b) shows the temperature dependence of σ calculated from the resistance with temperature. A significant σ jump is observed between 68 °C and 75 °C, and above 75 °C, σ is nearly saturated. This is in good agreement with the optical results, and suggests that an intermediate phase[10] exists between 68 °C and 75 °C. These results may be regarded as optical evidence of the Mott MIT in VO_2.

In conclusion, the Mott MIT in VO_2 film was investigated by analysis of complex dielectric function, complex optical conductivity, and plasma energy using SE measurements. The optical results were confirmed by the temperature dependence of electrical conductivity deduced from resistance measurements. The MIT and SPT temperatures in VO_2 films were as 68 °C and 75 °C, respectively, and it is suggested that an intermediate phase exists between 68 °C and 75 °C. Our optical and electrical results showed that the first-order MIT in VO_2 film is not driven by the SPT.

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[1] F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[2] J. P. Pouget *et al.*, Phys. Rev. Lett. **35**, 873 (1975).
[3] M. Soltani, M. Chaker, E. Haddad, and R. Kruzelesky, Meas. Sci. Technol. **17**, 1052 (2006).
[4] M.-J. Lee, Y. Park, D. S. Suh, E. H. Lee, S. Seo, D. C. Kim, R. Jung, B. S. Kang, S. E. Ahn, C. B. Lee, D. H. Seo, Y. K. Cha, I. K. Yoo, J. S. Lim, and B. H. Park, Adv. Mater. Weinheim, Ger. **19**, 3919 (2007).
[5] T. Driscoll, H. T. Kim, B. G. Chae, M. Di Ventra, and D. N. Basov, Appl. Phys. Lett. **95**, 043503 (2009).
[6] T. M. Rice, H. Launois, and J. P. Pouget, Phys. Rev. Lett. **73**, 3042 (1994).
[7] R. M. Wentzcovitch, W. W. Schulz, and P. B. Allen, Phys. Rev. Lett. **73**, 3043 (1994).
[8] H. T. Kim, B. G. Chae, D. H. Youn, S. L. Maeng, G. Kim, K. Y. Kang, and Y. S. Lim, New J. Phys. **6**, 52 (2004).
[9] M. M. Qazilbash, M. Brehm, B. G. Chae, P. C. Ho, G. O. Andreev, B. J. Kim, S. J. Yun, A. V. Balatsky, M. B. Maple, F. Keilmann, H. T. Kim, and D. N. Bosov, Science **318**, 1750 (2007).
[10] H. T. Kim, Y. W Lee, B. J. Kim, B. G. Chae, S. J. Yun, K. Y. Kang, K. J. Han, K. J. Yee, and Y. S. Lim, Phys. Rev. Lett. **97**, 266401 (2006).

[11] M. M. Qazilbash, K. S. Burch, D. Whisler, D. Shrekenhamer, B. G. Chae, H. T. Kim, and D. N. Basov, Phys. Rev. B **74**, 205118 (2006).
[12] H. Fujiwara, *Spectroscopic Ellipsometry : Principles and Applications* (Wiley, New York, 2007).
[13] D. A. G. Bruggemann, Ann. Phys. (Leipzig) **24**, 636 (1935).
[14] M. Losurdo and G. Bruno, Appl. Phys. Lett. **77**, 1129 (2000).
[15] S. P. S. Porto, P. A. Fleury, and T. C. Damen, Phys. Rev. **154**, 522 (1967).
[16] J. C. Parker, Phys. Rev. B **42**, 3164 (1990).
[17] C. Chen, R. Wang, L. Shang, and C. Guo, Appl. Phys. Lett. **93**, 171101 (2008).
[18] B. J. Kim, Y. W. Lee, S. Y. Choi, J. W. Lim, S. J. Yun, H. T. Kim, T. J. Shin, and H. S. Yun, Phys. Rev. B **77**, 235401 (2008).
[19] M. Fox, *Optical Properties of Solids* (Oxford University Press, Sheffield, 2011).
[20] E. Arcangeletti, L. Baldassarre, D. Di Castro, S. Lupi, L. Malavasi, C. Marini, A. Perucchi, and P. Postorino, Phys. Rev. Lett. **98**, 196406 (2007).