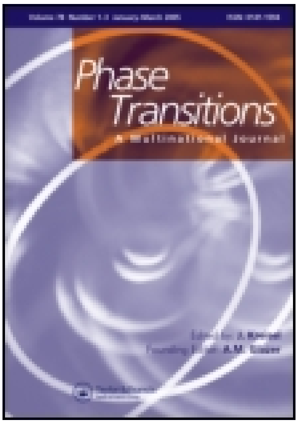

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The metal insulator transition (MIT) characteristics of macro-size single-domain VO_2 crystal were investigated. At the MIT, the VO_2 crystal exhibited a rectangular shape hysteresis curve, a large change in resistance between the insulating and the metallic phases, in the order of $\sim 10^5$, and a small transition width (i.e. temperature difference before and after MIT) as small as 10^{-3}°C. These MIT characteristics of the VO_2 crystals are discussed in terms of phase boundary motion and the possibility of controlling the speed of the phase boundary, with change in size of crystal, is suggested.

Keywords: metal insulator transition; VO_2; optical microscopy; phase boundary

Vanadium dioxide (VO_2) is insulating (metallic) below (above) a critical transition temperature, $T_c \sim 67$°C, and exhibits a dramatic first-order metal-insulator transition (MIT) at the T_c [1]. Since the MIT in VO_2 can be triggered by several distinct stimuli, such as temperature [2], electric field [3], and photo-excitation [4], VO_2 has been highly regarded as a potential material for diverse advanced techonolgies, including ultrafast sensors, extreme switching devices [4], and ultradense optical storage [5]. Typically, the applications to those functional devices require a sharp and rapid phase transition, a high electrical resistance ratio (R_I/R_M) between the insulating (R_I) and the metallic phases (R_M), and a rectangular-shape hysteresis loop [6,7].

Although the VO_2 thin films and nano crystals with large resistance ratio (R_I/R_M), up to 10^5, have been fabricated by a few research groups [7,8], the other desired qualities, i.e.

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clear and rapid phase transition with rectangular-shape hysteresis have not been realized either thin films or in nano crystals. Multi-domain structures and the percolative nature of MIT in these materials are preventing the realization of those extreme properties. On the other hand, it has been recently reported that macro-size single-domain VO_2 crystal was fabricated, showing the onset of MIT through the propagation of the phase boundary along the rutile *c*-axis [9]. This non-percolative nature of the transition in single domain crystal contains the ideal characteristics of MIT for the realization of advanced applications of VO_2, i.e. high functional industrial devices.

In this report, we investigate the MIT characteristics of VO_2 macro single-domain crystal. With optical microscopy, the MIT is shown to occur with the appearance of metallic phase at one end and proceed with the sharp phase boundary at the speed of $\sim$0.4 mm s^{-1}. The VO_2 crystal shows a $\sim 10^5$ fold resistance change at MIT with the transition width of as sharp as 10^{-3}°C. In addition, the temperature-resistance curve displays a rectangular shape hysteresis. The MIT characteristics of the VO_2 crystals can be explained by the analysis of phase boundary motion. Our results suggest that single domain macro size VO_2 crystals can be of practical use for ultrafast switching and ultradense optical storage.

VO_2 single crystals are synthesized with a self-flux method the details of which are reported elsewhere [10]. The temperature-resistance measurements of VO_2 single crystals are carried out using a dc two-contact four-probe method. Indium metal is used as the contact material between the VO_2 crystal and the gold wire. In both of the optical and the electrical measurements, the samples are mounted on a single-side polished sapphire wafer on the heating stage on which the temperature is controlled.

Optical microscope is applied to visualize the dynamics of MIT near the critical temperature. Due to the significant difference in the optical reflectivity between the metallic and insulating phases of VO_2, it is possible to monitor simultaneously both the metallic and insulating phases and the motion of the phase boundary during the MIT. Optical microscope images of VO_2 crystals are recorded during heating at a rate of 1.0°C min^{-1}. Figure 1 shows the optical images of VO_2 single crystal during MIT. The time interval between two consecutive images was $\sim$400 ms. Thus transition time T_t, i.e. time

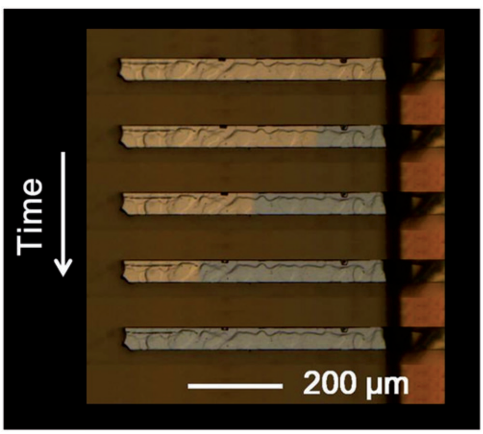

Figure 1. Optical microscope images of VO_2 crystal with a single phase boundary during the onset of MIT at fixed temperature ramp up rate of 1°C min^{-1}. The boundary of metal and insulator phases propagates along the rutile *c* axis (horizontal length direction) of a VO_2 crystal.

required to complete the MIT, was 1.6 s. The phase boundary speed is measured to be $0.3 \sim 0.4\,\mathrm{mm\,s^{-1}}$. Due to the significant movement of the crystal during MIT, originated from the structural phase change of VO_2, one end of the crystals was maintained with a thermally conducting tape. The dark and bright areas along the crystal rod represent the metallic rutile R and insulating monoclinic M1 phases of VO_2, respectively [9]. The propagation angle between the phase boundary and the rutile **c**-axis was either 90 degree or ~60 degree. In contrast to a recent report [11] showing that the metallic phase (R) domains always nucleate around the insulating phase (M1) twin walls in nano-crystalline VO_2, and is randomly distributed, our results in Figure 1 show a completely different phase domain behavior. Figure 1 shows that the single-domain metallic phase nucleates at one end of the crystal and that the phase boundary thus propagates towards the other end. The MIT proceeds with the continuously increasing metallic phase volume via a sharp phase boundary motion at a speed of $\sim 0.4\,\mathrm{mm\,s^{-1}}$ along the rutile c-axis. This shows that the MIT in VO_2 crystal occurs via a heterogeneous nucleation process [12], in which the new phase appears at particular sites where the nucleation energy barrier is considerably reduced. It is generally believed that nucleation sites are bulk point defects, dislocations, and grain boundaries etc. From the result of Figure 1, it is found that the nucleation sites are limited to the end plane normal to rutile c–axis, along which vanadium atoms in monoclinic M1 phase are dimerized in zigzag type [13]. A clear change in the crystal length before and after MIT can be noticed. The structural phase transition from monoclinic M1 to rutile R phase is accompanied by a change in atomic volume and thus a change in crystal length. From the optical images in Figure 1, we can estimate that the rutile **c**-axis effectively shrinks (expands) by ~1.5%. Compared to previously reported value from VO_2 nanocrystals, i.e. ~1.0% spontaneous shrinkage along c axis during MIT, our crystal results shows higher change [11,13].

The electrical properties of VO_2 single crystal are also investigated. Figure 2 shows the resistance-temperature curve of VO_2 single crystal with the optical image of the measured sample in inset. There are two structural transitions, one low temperature between two insulating phases (M2 and M1), at ~50°C and one at high temperature, the MIT at ~66°C. In the following we will mainly focus on the MIT. The low temperature transitions has been discussed in elsewhere [10]. In Figure 2, it can be clearly seen that an extremely sharp transition occured at the MIT with a high resistivity ratio (R_I/R_M), in the

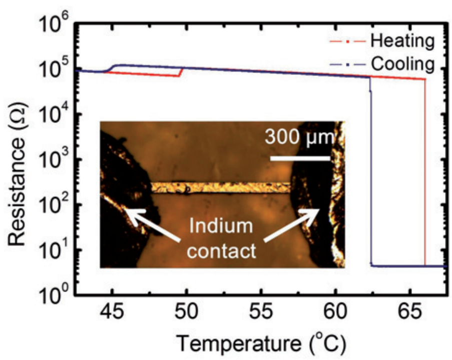

Figure 2. (Colour version available online). Resistance-temperature curve of single domain VO_2 crystal. The red (blue) line denotes increasing (decreasing) temperature. Inset: A measurement set up of VO_2 single crystal used for the resistance measurements.

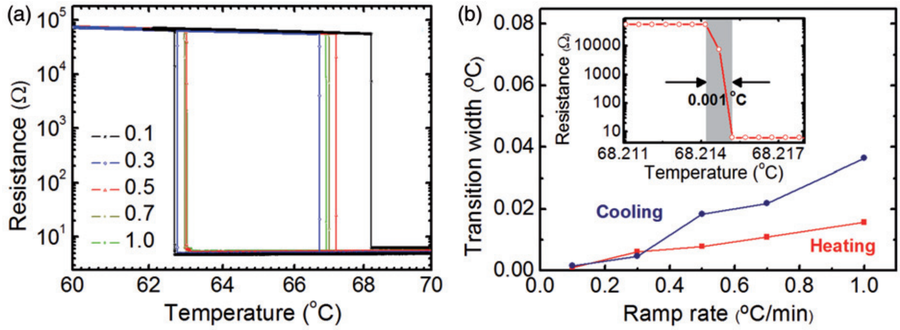

Figure 3. (Colour version available online). (a) Temperature ramp rate dependence of temperature-resistance curve temperature rates in the range $0.1 \sim 1°C\,min^{-1}$. Measurement rate was 3 Hz. (b) Dependence of transition width (W_T) on temperature ramp rate. Inset in Figure 3(b): a close-up view of metal insulator transition width at temperature rate of $0.1°C\,min^{-1}$.

order of $\sim 10^5$. Also, the rectangular shape of the hysteresis curve of resistance in Figure 2 is significantly different from those of thin film and nano crystalline VO_2, which normally shows the slanted-shape with long tails and lesser changes in resistance. Figure 3(a) shows the temperature-resistance curves of VO_2 crystal at varying temperature ramp rates of $0.1 \sim 1°C\,min^{-1}$ while Figure 3(b) presents the dependence of the transition width (i.e. temperature difference before and after MIT) with the temperature ramp rates. The inset of Figure 3(b) shows a close up view of the MIT transition width, at temperature rate of $0.1°C\,min^{-1}$. The MIT temperature shows sporadic variations owing to super-cooling and super-heating effects [10,14]. During temperature ramp up, the transition width is $2 \times 10^{-2}°C$ at ramp rate of $1°C\,min^{-1}$, and decreases with reducing temperature ramp rate. At the ramp rate of $0.1°C\,min^{-1}$, it reaches a value as small as $1 \times 10^{-3}°C$. The transition width of the VO_2 crystal under the present study is much narrower by two orders of magnitude than what is previously reported for high quality VO_2 single crystals in the literature, $\sim 0.1°C$ [15]. Although at a fixed ramp rate, the transition width during the heating process is much narrower than the one observed during the cooling process, this difference in transition width is getting smaller as temperature ramp rate is decreased. From the temperature-resistance curves, the phase boundary speed shows a weak dependence with the ramp rate and is estimated to be between $0.3\,mm\,s^{-1}$ and $\sim 0.5\,mm\,s^{-1}$, in good agreement with the optical measurements.

Now, we will discuss the above MIT characteristics of VO_2 in the light of phase boundary motion. During the rectangular shape MIT of single-domain VO_2 crystal, the resistance, R, is the sum of two contributions:

$$R = \rho_I L_I / A + \rho_M (L - L_I)/A,$$

where ρ_I and ρ_M are respectively the resistivity of the insulating M1 phase and of the metallic R phase, L_I and L are respectively the lengths of insulating region and of the whole sample, A is the cross section of the sample. The contact resistance between the gold wire and the VO_2 crystal is neglected. Since ρ_M is much smaller than ρ_I, the resistances of just before, during, and just after the MIT can be written as $\rho_I\, L/A\ (= R_I)$, $\rho_I\, L_I/A$, and $\rho_M\, L/A\ (= R_M)$, respectively. Thus the resistance ratio R_I/R_M becomes equal to the ratio of ρ_I/ρ_M. Therefore, the observed large resistance ratio, R_I/R_M of approximately $\sim 10^5$, and linear dependence of the resistance on L_I can be understood.

Next, the narrow transition width, W_T, i.e. the temperature variation during the transition time, is given by T_{ramp} (L/v), where v and T_{ramp} are phase boundary speed and temperature ramp rate, respectively. As expected, W_T is observed to linearly decrease with lower T_{ramp} when v is assumed constant. In fact, the speed of the phase boundary, v, can become a critical parameter in time-sensitive device applications, i.e. ultrafast sensor or memory switch in which the high frequency operation is desirable. Even though the origin of v is not clearly understood, it is expected that v is greatly dependent on the size of sample and the latent heat $d\mathrm{H_L}$ should play a role in the determination of v. Latent heat is given by $d\mathrm{H_L} = \rho c A v\, dt$, where ρ, c, and dt are the density, specific heat capacity, and given time, respectively. During the MIT, the latent heat must be conducted via heat transfer along the sample and should be supplied (released) via thermal conduction process during heating (cooling). Therefore, the higher velocity is expected on the smaller sample that has larger surface areas. That is, v can be controlled with the ratio of surface area to volume (surface/volume).

In summary, we have shown that VO_2 single domain crystals can exhibit a transition width of as narrow as 10^{-3}°C, and generate rectangular shape hysteresis curve ideal for applications in functional devices. It is shown that the transition width is a function of the temperature ramp rate. The possibility of increasing the phase boundary speed by adjusting the size of the crystal is also discussed. Understanding of single domain properties of VO_2 is useful for not only comprehending the underlying physical mechanism behind the MIT but also fully exploiting the material properties for industrial applications.

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References

[1] J. Morin, *Oxides which show a metal-to-insulator transition at the Neel temperature*, Phys. Rev. Lett. 3 (1959), pp. 34–36.

[2] A. Zylbersztejn and N.F. Mott, *Metal-insulator transition in vanadium dioxide*, Phys. Rev. B 11 (1975), pp. 4383–4395.

[3] H.-T. Kim, B.-G. Chae, D.-H. Youn, G. Kim, K.-Y. Kang, S.-J. Lee, K. Kim, and Y.-S. Lim, *Raman study of electric-field-induced first-order metal-insulator transition in VO_2-based devices*, Appl. Phys. Lett. 86 (2005), p. 242101.

[4] A. Cavalleri, Cs. Tóth, C.W. Siders, J.A. Squier, F. Ráksi, P. Forget, and J.C. Kieffer, *Femtosecond structural dynamics in VO_2 during an ultrafast solid-solid phase transition*, Phys. Rev. Lett. 87 (2001), p. 237401.

[5] A.A. Bugayev and M.C. Gupta, *Femtosecond holographic interferometry for studies of semiconductor ablation using vanadium dioxide film*, Opt. Lett. 28 (2003), pp. 1463–1465.

[6] Joyeeta Nag, E. Andrew Payzant, K.L. More, and R.F. Haglund Jr, *Enhanced performance of room-temperature-grown epitaxial thin films of vanadium dioxide*, Appl. Phys. Lett. 98 (2011), p. 251916.

[7] D.H. Kim and H.S. Kwok, *Pulsed laser deposition of VO_2 thin films*, Appl. Phys. Lett. 65 (1994), pp. 3188–3190.

[8] B.-G. Chae, H.-T. Kim, S.-J. Yun, B.-J. Kim, Y.-W. Lee, D.-H. Youn, and K.-Y. Kang, *Highly oriented VO_2 thin films prepared by sol-gel deposition*, Electrochem. Solid-State Lett. 9 (2006), pp. C12–C14.

[9] B.S. Mun, K. Chen, J. Yoon, C. Dejoie, N. Tamura, M. Kunz, Z. Liu, M.E. Grass, S.-K. Mo, C. Park, Y.Y. Lee, and H. Ju, *Nonpercolative metal-insulator transition in VO_2 single crystals*, Phys. Rev. B 84 (2011), p. 113109.

[10] B.S. Mun, K. Chen, Y. Leem, C. Dejoie, N. Tamura, M. Kunz, Z. Liu, M.E. Grass, C. Park, J. Yoon, Y.Y. Lee, and H. Ju, *Observation of insulating–insulating monoclinic structural transition in macro-sized VO_2 single crystals*, Phys. Status Solidi RRL 5 (2011), pp. 107–109.

[11] W. Fan, J. Cao, J. Seidel, Y. Gu, J.W. Yim, C. Barrett, K.M. Yu, J. Ji, R. Ramesh, L.Q. Chen, and J. Wu, *Large kinetic asymmetry in the metal-insulator transition nucleated at localized and extended defects*, Phys. Rev. B 83 (2011), p. 235102.

[12] D.A. Porter, K.E. Easterling, and M.Y. Sherif, *Phase Transformations in Metals and Alloys*, 3rd ed., CRC Press, Boca Raton, FL, 2009.

[13] V. Eyert, *The metal-insulator transitions of VO_2: A band theoretical approach*, Ann. Phys. (Leipzig) 11 (2002), pp. 650–702.

[14] J. Wei, Z. Wang, W. Chen, and D.H. Cohen, *New aspects of the metal–insulator transition in single-domain vanadium dioxide nanobeams*, Nature Nanotechnol. 4 (2009), pp. 420–424.

[15] D. Kucharczyk and T. Niklewski, *Accurate X-ray determination of the lattice parameters and the thermal expansion coefficients of VO_2 near the transition temperature*, J. Appl. Crystallogr. 12 (1979), pp. 370–373.