# Pulsed laser deposition of $VO_2$ thin films

D. H. Kim and H. S. Kwok[a)]
*Department of Electrical and Computer Engineering, State University of New York at Buffalo, Amherst, New York 14260*

(Received 22 April 1994; accepted for publication 19 October 1994)

High quality vanadium dioxide ($VO_2$) thin films have been successfully deposited by pulsed laser deposition without postannealing on (0001) and ($10\bar{1}0$) sapphire substrates. X-ray diffraction reveals that the films are highly oriented with (010) planes parallel to the surface of the substrate. $VO_2$ thin films on (0001) and ($10\bar{1}0$) substrates show semiconductor to metal transistions with electrical resistance changes as large as $4\times10^4$, $10^5$, respectively. Thin films on ($10\bar{1}0$) substrate have a transition at as low as 55 °C with a hysteresis less than 1 °C. These transition properties are comparable with single crystal $VO_2$. © *1994 American Institute of Physics.*

Since the early work of Morin,[1] there has been a lot of interest in vanadium oxide because of their metal-to-semiconductor transitions and the abrupt changes in their optical and electrical properties which accompany these transitions. Of all the different types of vanadium oxides, $VO_2$ has been studied the most because its transition temperature is near room temperature. It exhibits a change in electrical resistivity in the order of $10^5$ over a temperature change of 0.1 °C at 68 °C in a single crystal.[2] Its infrared transmission characteristics also change dramatically over the phase transition. These features make $VO_2$ films suitable for applications in thermal sensing and switching. Thin films of $VO_2$ have been prepared by various methods including metalorganic chemical vapor deposition,[3] evaporation,[4,5] sputtering,[6–8] and sol-gel dip coating.[9] Most $VO_2$ thin films demonstrate a transition of electrical resistance by as much as $10^3$–$10^4$ at 68 °C with a thermal hysteresis of 2–5 °C upon heating up and cooling down. Since the magnitude of the resistivity change and the narrowness of the hysteresis are very sensitive to the stoichiometry and the crystalline structure of the $VO_2$ thin film, these parameters are good indicators of its quality. Generally the characteristics of the thin films are inferior to those of single crystals. Additionally, there have been a considerable amount of research performed in an attempt to reduce the transition temperature by using dopants,[10,11] deposition by ion-assisted reactive evaporation followed by thermal annealing,[5] and relaxing tensile stress by ion bombardment.[12] Unfortunately, while the transition temperature is reduced, the desired electrical and optical properties are somewhat degraded as well.

Pulsed laser deposition (PLD) has been employed for many materials successfully, i.e., semiconductors, superconductors, insulator, dielectric materials, and etc.[13–17] Since PLD can be performed under considerably high background pressure, it has proven to be an excellent method specially in depositing oxide thin films. For the case of $VO_2$, reasonably good results have been obtained on $R$-cut sapphire substrates with post annealing by PLD.[18] Here, we would like to report the successful deposition of *in situ* $VO_2$ by PLD on (0001), and ($10\bar{1}0$) sapphire substrates with excellent electrical transition properties. It was found that the substrate orientation has a profound effect on the quality of the $VO_2$ films. Typically the electrical resistance of our samples changes by 4–5 orders of magnitude over the semiconductor–metal transition.

Our PLD system has been described previously.[19] Briefly, an ArF excimer laser at a wavelength of 193 nm was focused onto a target with a fluence of 2–3 J/cm$^2$. The target was made of pressed 99% pure $V_2O_3$ powder. No heat treatment was applied to the pressed powder target. Films were grown on (0001), and ($10\bar{1}0$) sapphire substrates. The distance between the target and the substrate was typically 5 cm. The deposition chamber was pumped to $<10^{-5}$ Torr before oxygen gas was introduced into the chamber. The depositions were performed in an ambient of 20–30 mTorr oxygen. The substrate temperature was maintained at 630 °C during the deposition. After the deposition, the samples were cooled down at the deposition oxygen pressure to room temperature. No postannealing was performed on the samples.

The crystalline structure of the as-deposited vanadium oxide thin films was determined by x-ray diffraction (XRD) measurements. The result of $\theta$–$2\theta$ x-ray scan of vanadium oxide thin films on a (0001) sapphire substrate is shown at Fig. 1. The film shows two peaks corresponding to (020) and (040) of monoclinic $VO_2$.[7] No other peak is observed indicating highly oriented crystalline structure. For the $VO_2$ (020) peak, the full width at half-maximum (FWHM) of the rocking curve is found to be $\sim$0.5°. Figure 2 shows $\theta$–$2\theta$ x-ray scan of the film on ($10\bar{1}0$) sapphire substrate. The peak at $2\theta$=64.7° corresponds to the (040) of the M2 phase of $VO_2$.[20] The FWHM of this peak is also $\sim$0.5°. The only other peak observed in our scanning range 20°–70° is at 21.7°, which has an intensity 20 times less than the peak at 64.7°. This peak does not correspond to any known phases of vanadium oxides. XRD patterns from JCPDS Powder Diffraction File[20] for various vanadium oxides, including $V_6O_{11}$, $V_7O_{13}$, $V_8O_{15}$, $V_3O_7$, $V_4O_9$, $V_6O_{13}$, and various other phases of $VO_2$, were examined, but the peak at 21.7° cannot be assigned to any of those.

A standard four probe method was used for the electrical characterization of the film. As the sample was heated in air from room temperature to a temperature of 100 °C and cooled back to room temperature, the resistance was mea-

[a)]Also at Hong Kong University of Science and Technology, Clearwater Bay, Hong Kong.

 0003-6951/94/65(25)/3188/3/$6.00 © 1994 American Institute of Physics

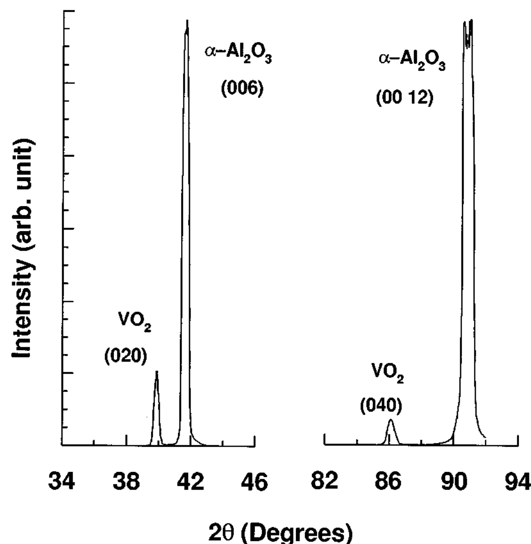


FIG. 1. $\theta$–$2\theta$ x-ray scan for a $VO_2$ thin film on (0001) sapphire substrate.

sured to find the dependence of the electrical resistance of the sample on temperature. Figure 3 shows the electrical resistances of the samples on (0001) and $(10\bar{1}0)$ sapphire substrates as a function of temperature. The optimum oxygen pressures for the depositions were 20 and 30 mTorr for (0001) and $(10\bar{1}0)$ substrates, respectively. The films qualities were very sensitive to the oxygen pressures. Semiconductor-to-metal phase transitions are clearly seen for both samples. The samples show a typical semiconductor characteristic of a decreasing electrical resistance with increasing temperature below the transition temperature. On the other hand, electrical resistance increases with increasing temperature above the transition temperature indicating metallic behavior. The transition temperatures for films on the (0001) and $(10\bar{1}0)$ substrates are 65 and 55 °C, respectively, and are in agreement with the transition temperature of $VO_2$.[5,10–12] It should be pointed out that even small variations in the oxygen content in vanadium oxides result in a

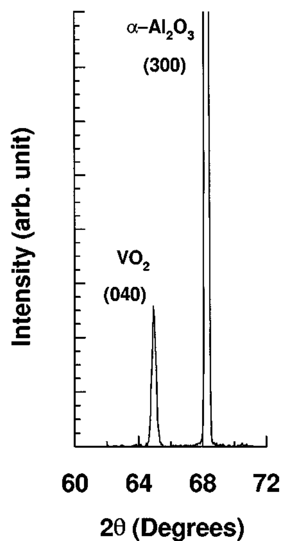


FIG. 2. $\theta$–$2\theta$ x-ray scan for a $VO_2$ thin film on $(10\bar{1}0)$ sapphire substrate.

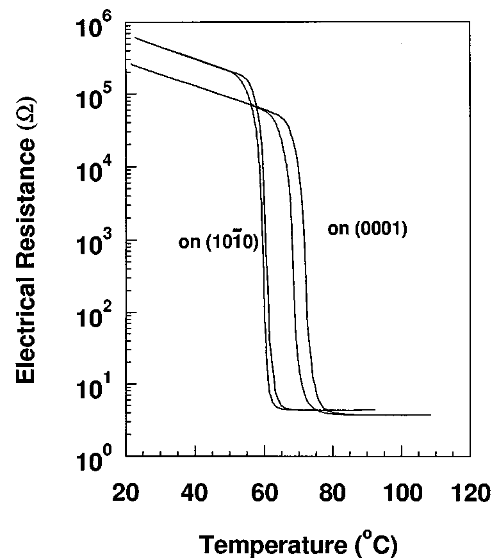


FIG. 3. Electrical resistance as a function of temperature for $VO_2$ thin films. Thermally induced semiconductor to metal transitions are clearly seen with $4\times10^5$, $10^5$ changes in electrical resistance for the films on (0001), $(10\bar{1}0)$ sapphire substrates, respectively.

large shift in transition temperature ($T_t$), e.g., $T_t(V_5O_9)=135$ K,[6] $T_t(V_6O_{13})=145$ K.[21] This confirms that both films are $VO_2$, consistent with XRD data. Hysteresis on electrical resistance is observed upon the heating and the cooling of the samples. The width of the hysteresis is found to be narrower for the film on $(10\bar{1}0)$ substrate compare with the film on (0001) substrate. This width is typically less than 1 °C for the film on $(10\bar{1}0)$ substrate while that of the film on (0001) substrate is 3 °C. The film on $(10\bar{1}0)$ substrate also has a lower transition temperature than the films on (0001) substrate. The ratios of the electrical resistance at 35 and 90 °C are as large as $4\times10^4$ and $1\times10^5$ for the films on (0001) and $(10\bar{1}0)$ sapphire substrates, respectively. These values are as good as or better than $VO_2$ thin films made by other methods. Other efforts to reduce the transition temperature for $VO_2$ films have resulted in degradation of the transition properties.[5,10–12] However, our $VO_2$ film on $(10\bar{1}0)$ substrate has a lower transition temperature with the enhanced transition properties. The large resistance change and the narrowness of hysteresis indicate that our films have a very close stoichiometry to bulk crystalline $VO_2$. The eletrical properties of our thin films on the $(10\bar{1}0)$ substrate are comparable with those of a single crystal.

While we have used pressed $V_2O_3$ powder target, the as-deposited thin films have a very close stoichiometry to $VO_2$. The particles ablated from the target react with the oxygen in the chamber while they are traveling to the substrate, resulting in the increased oxygen content. This explains also why the oxygen pressure is one of the critical parameters for the optimization of the growth process. The exact nature of the mechanisms involved will be the topic of another study. We also have preliminary results showing that $V_2O_5$ films can be obtained at higher deposition pressures. The ability to control the oxygen content of the deposited film easily is one of the major advantages of PLD which can

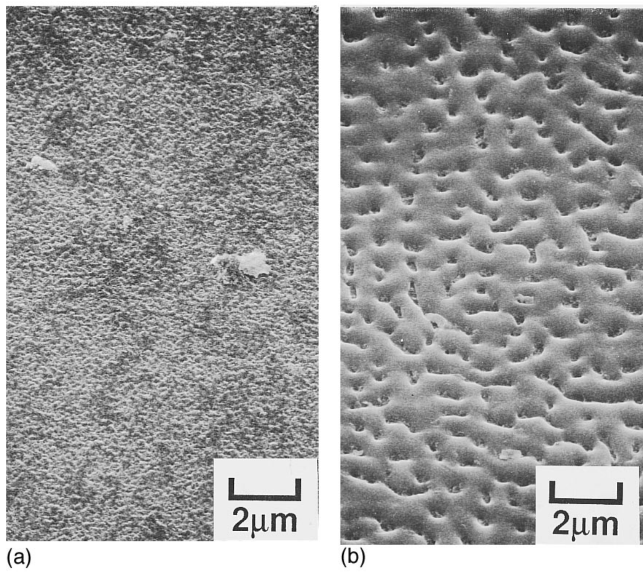


FIG. 4. SEM images of $VO_2$ thin films on (a) (0001) and (b) $(10\bar{1}0)$ sapphire substrates.

be performed under considerable background gas pressure.

The surface morphology of the deposited vanadium oxides thin films was examined by scanning electron microscope (SEM). A SEM image of the films on (0001) substrate is shown at Fig. 4(a). The grains are very densely packed with a size typically around 0.1 $\mu$m. We can see from Fig. 4(b) that grain size of the film on a $(10\bar{1}0)$ substrate is much larger than that of the film on a (0001) substrate. This is a possible explanation of the superior transition properties of the film on a $(10\bar{1}0)$ substrate. Since the resistance change is strongly dependent on the nature of the grain boundary structure and percolation effect,[7] it is most likely that the film with larger grain has a better chance to have superior electrical properties. Unfortunately, the film on $(10\bar{1}0)$ substrate comes with a porous surface structure under visual examination. The color of this film appears purple–blue in reflected room light. This is similar to the so-called anomalous blue $VO_2$ film[22] in terms of the size of the grains and the color.

The dependence of the transition temperature on different types of substrates in $VO_2$ thin films has been observed by other group.[12] This has been attributed to extrinsic stress developed in the film on cooling from the process temperature to room temperature due to the mismatch in thermal expansion coefficients between the film and the substrate. Since the difference between the thermal coefficients of sapphire substrate along $c$ axis and perpendicular to $c$ axis is very small, the large reduction in transition temperature in the thin film on $(10\bar{1}0)$ substrate cannot be explained in terms of extrinsic stress. However, it is also possible that the porous structure of the film on $(10\bar{1}0)$ substrate helps in releasing the intrinsic stresses resulting in lowering the transition temperature. In fact, it was observed that Ar ions bombardment on $VO_2$ thin films reduced the transition temperature and the hysteresis width which can be explained by intrinsic stress releases.[12]

In conclusion, we have deposited oriented $VO_2$ thin films having (020) planes in parallel with the substrates surface with PLD on (0001) and $(10\bar{1}0)$ single crystal sapphire substrates. No post annealing process was needed to obtain high quality thin films with large resistance changes over the semiconductor–metal transition. In particular, $VO_2$ thin films on $(10\bar{1}0)$ substrate have outstanding electrical properties comparable to a single crystal with a transition temperature as low as 55 °C.


[1] F. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[2] D. Kucharczyk and T. Niklewski, J. Appl. Crystallogr. **12**, 370 (1079).
[3] H. K. Kim, H. You, R. P. Chiarello, H. L. M. Chang, T. J. Zhang, and D. J. Lam, Phys. Rev. B **47**, 12 900 (1993).
[4] F. C. Case, Appl. Opt. **30**, 4119 (1991).
[5] F. C. Case, J. Vac. Sci. Technol. A **5**, 1762 (1987).
[6] K. D. Rogers, J. A. Coath, and M. C. Lovell, J. Appl. Phys. **70**, 1412 (1991).
[7] J. F. De Natale, P. J. Hood, and A. B. Harker, J. Appl. Phys. **66**, 5844 (l989).
[8] E. E. Chain, J. Vac. Sci. Technol. A **4**, 432 (1986).
[9] S. Lu, L. Hou, and F. Gan, J. Mater. Sci. **28**, 2169 (1993).
[10] H. Futaki and M. Aoki, Jpn. J. Appl. Phys. **8**, 1008 (1969).
[11] C. N. R. Rao, M. Natarajan, G. V. Subba Rao, and R. E. Loehman, J. Phys. Chem. Solids **32**, 1147 (1971).
[12] F. C. Case, J. Vac. Sci. Technol. A **2**, 1509 (1984).
[13] J. T. Cheung and H. Sankur, Crit. Rev. Solid State Mater. Sci. **15**, 63 (1988).
[14] H. S. Kwok, J. P. Zheng, S. Witanachi, P. Mattocks, L. Shi, Q. Y. Ying, X. W. Wang, and D. T. Shaw, Appl. Phys. Lett. **52**, 1095 (1988).
[15] H. S. Kwok, J. P. Zheng, S. Witanachi, L. Shi, and D. T. Shaw, Appl. Phys. Lett. **52**, 1815 (1988).
[16] L. Shi, Y. Hashishin, S. Y. Dong, J. P. Zheng, and H. S. Kwok, Appl. Phys. Lett. **59**, 1377 (1991).
[17] J. P. Zheng and H. S. Kwok, Appl. Phys. Lett. **63**, 1 (1993).
[18] M. Borek, F. Qian, V. Nagabushnam, and R. K Singh, Appl. Phys. Lett. **63**, 3288 (1993).
[19] H. S. Kwok, J. P. Zheng, S. Watanachi, Z. Q. Huang, P. Mattock, L. Shi, Q. Y. Ying, X. W. Wang, and D. T. Shaw, Appl. Phys. Lett. **52**, 1095 (1988).
[20] JCPDS Powder Diffraction File, JCPDS International Centre for Diffraction Data, 1992 (unpublished).
[21] S. Shin, S. Suga, M. Taniguchi, M. Fujisawa, H. Kanzaki, A. Fujimori, H. Daimon, Y. Veda, K. Kosuge, and S. Kachi, Phys. Rev. B **41**, 4993 (1990).
[22] F. C. Case, Appl. Opt. **27**, 1803 (1988).