LETTER TO THE EDITOR

Single-crystalline epitaxy and twinned structure of vanadium dioxide thin film on (0001) sapphire

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Abstract. VO_2 thin films prepared by pulsed-laser ablation have been investigated by high-resolution x-ray diffraction, x-ray pole-figure, Rutherford backscattering/channelling and electrical measurements. The results show that VO_2 films deposited on (0001) sapphire substrates grow with well determined orientations in the plane: VO_2 [100] ∥ sapphire [11$\bar{2}$0] and out of the plane: (010) VO_2 ∥ (0001) sapphire. The aligned-to-random ratio of backscattered yield of the spectra (χ_{min}) can be as low as 5%, and the electrical resistivity changes by a factor of 6×10^4 during the phase transformation with a hysteresis loop width of 0.9 °C, which implies that both the structure and the properties of the film are very close to those of bulk single-crystal VO_2. The (010)-oriented VO_2 film 'prefers' to form twinned structure with 120° domain walls. Molybdenum substitutional doping up to the level of 1.5 at.% does not degrade the crystal quality.

Vanadium dioxide (VO_2) thin film has been extensively investigated not only because of the scientific research interest in the first-order phase transformation from the high-temperature metallic phase to the low-temperature semiconductor phase (MST) [1, 2], but also because of the attraction of its considerable potential for applications [3–5]. Although a lot of achievements and progress have been made during past few decades, it has also been found that both bulk and thin-film single-crystal VO_2 are difficult to grow, which frustrates attempts to achieve a deep understanding of the mechanism of the MST and related phenomena. In addition, some attempts [6, 7] have been made to reduce the phase transition temperature (T_t) by incorporating dopants, but T_t can only be decreased at the expense of a degradation of the film properties; the explanation of the release of stress is far from satisfactory, and much more insight from further study is needed, which relies on the growth of high-quality thin films of VO_2.

   Much effort has been devoted to the preparation of high-quality VO_2 film by different preparation methods [8–10]. It has been reported that highly oriented VO_2 thin film prepared by pulsed-laser ablation [11, 12] exhibits good properties with a high ratio of the resistivity before the phase transformation to that after (RR) and a small hysteresis width (HW) (2×10^4 and 2 °C, respectively). Recently, single-crystalline films of VO_2 have been

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successfully grown in our laboratory; the RR reaches 6×10^4 and the HW is less than 1.0 °C, much closer to the data for bulk single-crystal VO_2 (10^5 and 0.1 °C–0.2 °C [13], respectively). The doping proceeded without any discernible deterioration of the crystal quality.

In this study, the samples were deposited on (0001) single-crystal sapphire substrates by pulsed-laser ablation (YAG; wavelength: 1064 nm; pulse frequency: 10 Hz; duration: 145 μs). The substrates were annealed at a temperature of 1450 °C for 12 h in open air. Vanadium atoms were ablated from a rotating vanadium target (>99.99%) and reacted with the oxygen to form oxide film. The target–substrate distance and laser power were kept at 50 mm and 1.0 W, respectively. Before deposition, the chamber was pumped to a vacuum of less than 1×10^{-5} Torr. The oxygen partial pressure (P_{O_2}) and substrate temperature (T_s) were optimized to the values of 50 mTorr and 500 °C respectively. Molybdenum doping was realized by direct heating of a Mo plate to form Mo oxide vapour which was deposited simultaneously with vanadium oxide. The structure of the VO_2 films was characterized by high-resolution XRD (monochromated Cu Kα irradiation), x-ray pole-figure measurement (Philips X'pert) and Rutherford backscattering/channelling analysis. The phase transition properties were measured in a computer-controlled system with two thermocouples for temperature control and measurement respectively; its accuracy is 0.1 °C. The sample thickness was estimated from the RBS spectrum by RUMP program simulation. The deposition rate was about 3 nm min^{-1}.

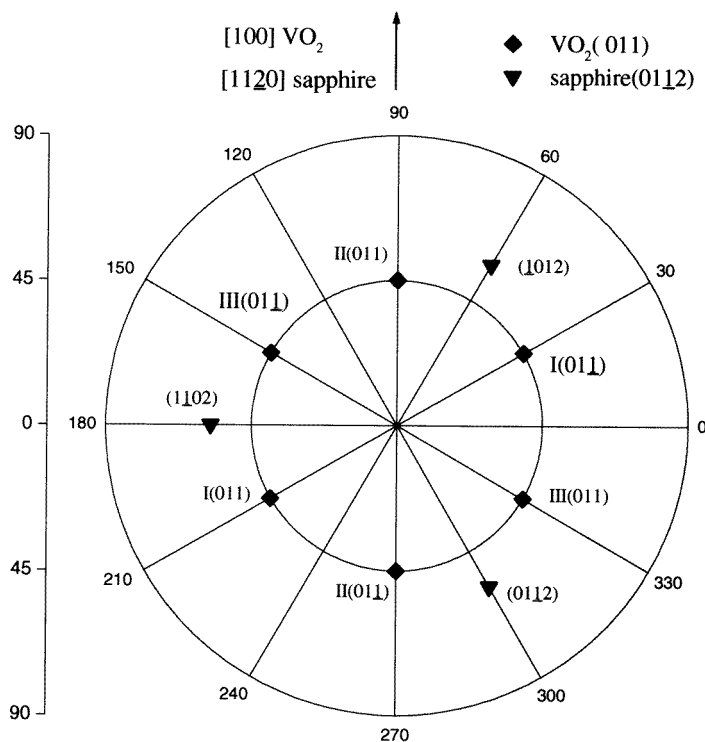**Figure 1.** Combined sets of pole figures of (011) VO_2 and ($01\bar{1}2$) sapphire reflections. The Miller and Miller–Bravais indices mark VO_2 and sapphire peaks, respectively. I, II and III represent three different twinned crystals with 120° domain walls.

The high-resolution x-ray diffraction measurement was carried out for all of the samples. The results show that only the (0006) sapphire peak, and the (020) and (040) VO_2 peaks are observed in the 2θ scan range of $20°$–$90°$, indicating oriented growth along the [010] direction. The pole figures were measured to get an idea of the degree of epitaxy of the VO_2 film and the relative orientations of the film and the sapphire substrate. The texture was determined by scanning the tilt angle (Ψ) from 0 to $88°$ in steps of $2°$ and scanning the azimuthal angle (Φ) from 0 to $360°$ in steps of $5°$ for different fixed values of 2θ. The results show that almost all of the planes (Miller index < 4) have well defined reflection peaks compared with those from (020) monoclinic crystallography after excluding the possible interference from the substrate. Figure 1 presents combined pole figures obtained for the (011) VO_2 and (01$\bar{1}$2) sapphire. The epitaxial growth was determined as being in-plane growth, VO_2 [100] ∥ sapphire [11$\bar{2}$0], and parallel to the normal of the substrate, (010) VO_2 ∥ (0001) sapphire.
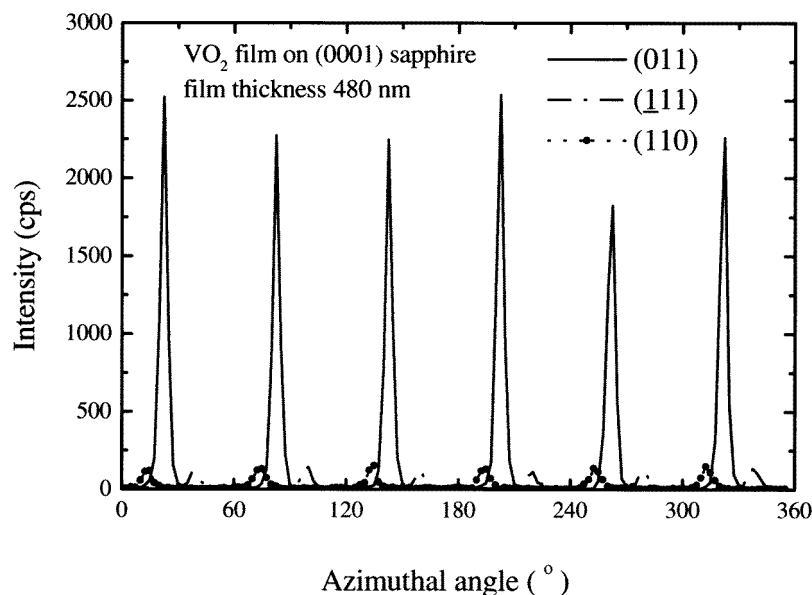

Figure 2. Azimuthal scans for the planes of (010) oriented VO_2 (a) (011), at $2\theta = 27.82°$ and $\Psi = 45°$, (b) ($\underline{1}$11), at $2\theta = 26.86°$ and $\Psi = 43°$, (c) (110), at $2\theta = 26.92°$ and $\Psi = 43.1°$. The intensities from the (110) and ($\bar{1}$11) planes are less than 10% of that from the (011) plane; their influence on the reflection peaks from the (011) plane can be neglected.

As is well known, monoclinic crystal has twofold symmetry. For the (011) plane of VO_2, two poles should appear at $\Psi = 45°$. But in figure 1 there are clearly six poles; the possibility of reflection from other planes near (011) can be excluded. Although the (110) and ($\bar{1}$11) planes have almost the same values of 2θ and Ψ as the (011) plane, the latter has the strongest reflection intensity in monoclinic VO_2 crystal; the azimuthal scans from 0 to $360°$ with 2θ and Ψ set at the reflection maximum for each plane show that the intensity of the six poles arising from the (011) plane is much higher than that arising from the (110) or ($\bar{1}$11) planes; the results are shown in figure 2. The reflection intensity from the (110) and ($\bar{1}$11) planes is less than 10% of that from the (011) plane. The interference from the sapphire substrate was also checked by means of Ψ and Φ scans for

pure sapphire substrate; no peak was found as compared with the background of (011) VO_2. Therefore, we assume that these six poles arise from three different symmetry-equivalent twinned crystals; each twinned crystal contains single-domain, (010)-oriented VO_2 in an alternating sequence, separated by 120° domain walls as the pole figure shows (figure 1). What interested us was that this kind of microstructure does not change even when the film thickness is decreased to 30 nm. It seems that it is a stable and preferred micro-defect in VO_2 film deposited on (0001) sapphire (here we call such kinds of micro-defect 'triplets', to distinguish them from single twinned structures). The main driving force for forming triplets can be ascribed to the large misfit [14] (21% and 13% for lattice parameters a and c, respectively) between the interface of (010) VO_2 and the (0001) sapphire substrate ($a_{VO_2} = 0.575$ nm, $c_{VO_2} = 0.538$ nm, $a_{sapphire} = 0.476$ nm). The reason that the film prefers to form triplets rather than single twins needs further explanation, both theoretically and experimentally.
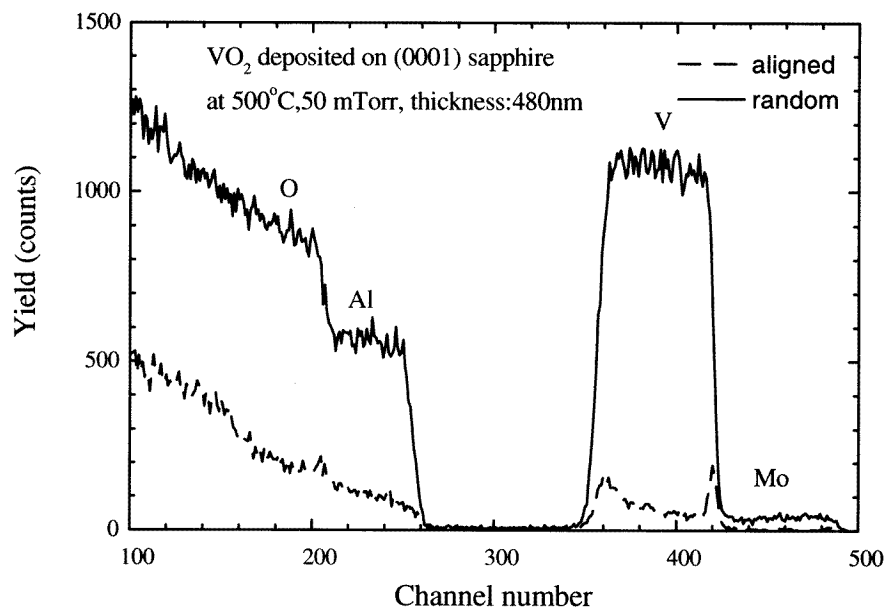

Figure 3. RBS/channelling spectra of 1.5 at.% molybdenum-doped VO_2 film along the [010] axis for 2 MeV $^4He^+$-ion incidence.

The crystal quality was examined by means of ion channelling with 2 MeV $^4He^+$ ions along the [010] direction. Channelling can be detected for all of the samples deposited under optimized conditions in this study. A typical result is shown in figure 3 (here we provide the curve for doped VO_2, because the shape is almost the same as that for the pure VO_2 sample, except as regards the existence of a Mo shoulder). The ratio of the backscattered yield of aligned spectrum (dashed line) to that of random spectrum (solid line) (χ_{min}) can be as low as 5%; such a low χ_{min}-value reflects that the fact that the quality of the film is comparable to that of single crystal, which is further confirmed by the rocking curve of this sample. The measurement was carried out in a Philips X'pert diffractometer with angular resolution of 0.0001°. A sharp peak for (020) VO_2 at $\omega = 19.78°$ has been observed; the full width at half-maximum (FWHM) can be as low as 0.0072°, comparable to that of (0001) single-crystal sapphire substrate, i.e. 0.0029° in this study.

The phase transition properties of VO_2 films were measured under temperature cycling from 25 °C to 95 °C; the values of the RR and HW are 6×10^4 and ~ 0.9 °C, respectively. This is further evidence of high crystal quality, because these two parameters are often taken as indicators of the film quality of VO_2.
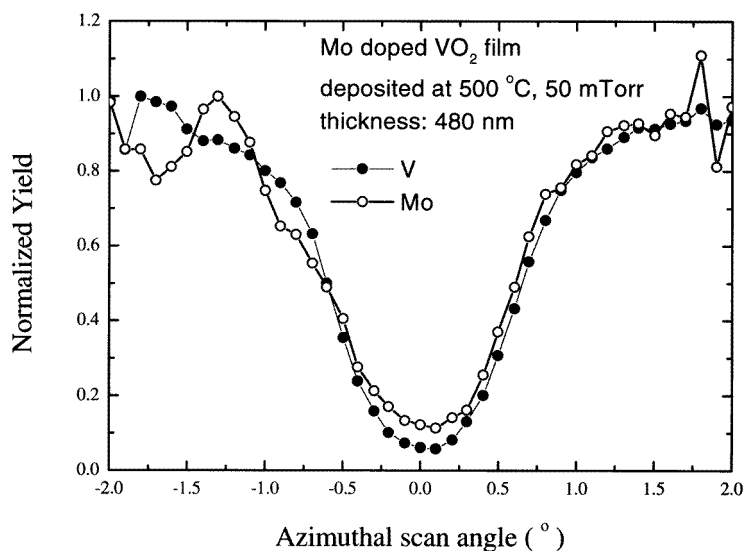

Figure 4. Angular scans of aligned vanadium and molybdenum atomic channelling in (010)-oriented VO_2.

It is important to study the effect of doping on the film structure, because it is hard to account for the effects of doping on the change of properties if no information on the structure is given. Therefore, the same analysis procedures were carried out for the films doped with molybdenum. The XRD and pole-figure results indicate that there are no detectable changes; the crystal structure of VO_2 film is almost unaffected by the incorporation of dopant up to a level of 1.5 at.%. Doping is confirmed by a pronounced shoulder of Mo in the RBS spectra (figure 3). In the figure, one can see clearly that the Mo atoms are homogeneously distributed through the whole film thickness; this can be ascribed to the simultaneous deposition of molybdenum oxide species together with the vanadium oxide species. It is worth noting that Mo atoms are aligned together with the vanadium atoms. Further ion-channelling analysis was carried out for both V and Mo sublattices. Figure 4 presents normalized curves of the tilt-angle scans. The good agreement between the results for the V and Mo sublattices suggests that the Mo atoms successfully occupy the sites of the V sublattice as a substitutional dopant, which might open the way for us to study further the effects of doping of VO_2—for example, exploring the origins of the MST and the shift of T_t.

As is well known, the structure of vanadium oxide is very sensitive to the deposition conditions, especially the substrate temperature (T_s) and oxygen partial pressure (P_{O_2}) [15]. Therefore in our study, we first kept $T_s = 400$ °C constant and adjusted P_{O_2} to ensure that the deposited film was VO_2, and then changed T_s with optimized P_{O_2} to investigate the effect of T_s on the film quality. The results show that the film deposited at 500 °C exhibits the best crystal quality. Although the same value of T_s was used by Borek *et al* [11], the lack of single-crystalline epitaxy can be ascribed to the ($01\bar{1}2$) sapphire substrate used in
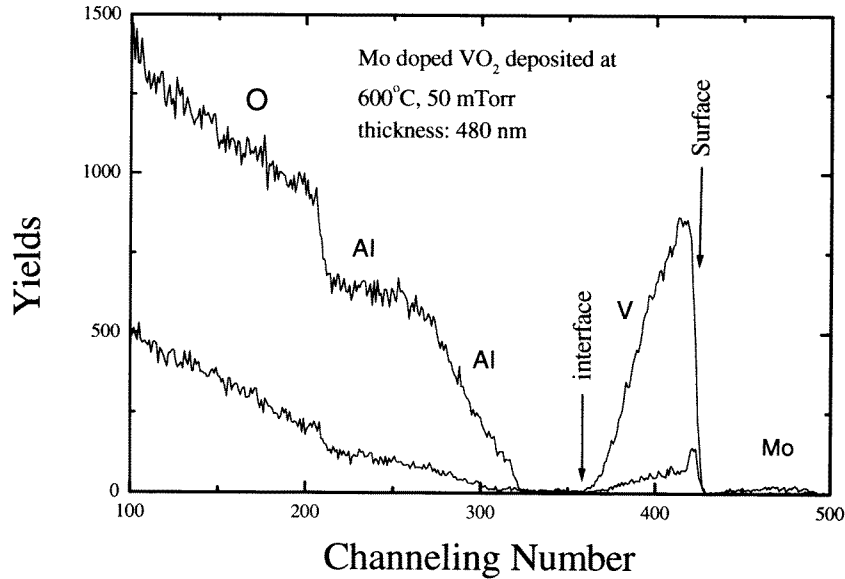
Figure 5. RBS/channelling spectra of Mo-doped VO_2 film deposited at $T_s = 600$ °C along the [010] axis for 2 MeV $^4He^+$-ion incidence. The inter-diffusion of V or Al is clearly seen from the decrease in the yield of V or the increase in the yield of Al from the film surface to the interface.

their study; from our results, single-crystalline thin film is difficult to grow on sapphire substrates with other orientations, because of their larger misfits compared with that of the (0001) orientation. $T_s = 500$ °C is higher than the previously reported substrate temperature of 400 °C, but lower than that reported by Kim and Kwok in [12], where $T_s = 630$ °C was used. Increasing T_s obviously benefits the crystal growth, because of the increased surface mobility of the growing species. The results of RBS analysis show that the value of χ_{min} decreases with the increase of T_s, but if T_s exceeds 550 °C there will be inter-diffusion of V or Al between the film and the substrate. Figure 5 presents the RBS result for the 600 °C deposited sample; as the figure shows, the inter-diffusion of Al or V in the interface becomes so extreme that the Al and V atoms almost coexist in the film, which will substantially degrade the crystal quality of the film. The effect of substrate surface morphology on the film quality was also checked by annealing the substrates. The XRD rocking curve shows that after annealing, the FWHM for (0001) sapphire decreases from (unannealed) 0.0064° to 0.0029°; as a result, the surface roughness of the substrates and, consequently, the film quality have been improved.

   In conclusion, the single-crystalline epitaxy of VO_2 film has been characterized by measurements of the high-resolution and pole-figure XRD, RBS/channelling and electrical resistivity. The epitaxial relationship is determined to be as follows: in the plane: VO_2 [100] ∥ sapphire [11$\bar{2}$0]; normal to the substrate surface: (010) VO_2 ∥ (0001) sapphire. RBS/channelling and XRD rocking curve results have proven that the film is of single-crystal quality, which is almost unaffected by the incorporation of dopant up to a level of 1.5 at.%. The XRD pole-figure analysis reveals that the growth of VO_2 on sapphire (0001) 'prefers' to form triplets rather than single twinned structures.

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