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Microstructure and properties of VO_2 thin films deposited by MOCVD from vanadyl acetylacetonate

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Thin films of vanadium dioxide have been deposited on glass by low pressure metal-organic chemical vapour deposition using the β-diketonate complex, vanadyl acetylacetonate, as the precursor. It is found that nearly monophasic, monoclinic VO_2(M) films are formed in the narrow temperature range 475–520 °C, films formed outside this range comprising significant proportions of other vanadium oxide phases beside VO_2(M). The microstructure of these well-crystallized films varies significantly with temperature in this range. Films grown at 475 °C are dense and have a very strong (200) orientation. At 520 °C, films are somewhat porous, and display little preferred orientation. Film microstructure influences the semiconductor–metal transition noticeably. Films deposited at 475 °C have a large change in resistance at 66 °C, and display a small temperature hysteresis in the transition. The transition temperature in films grown at 520 °C is higher (72 °C), whereas the change in resistance is smaller and the hysteresis larger. An attempt has been made to understand the unusual microstructure of VO_2 films grown on glass substrates. The variation in the phase transition characteristics is interpreted in terms of the observed film microstructure. The thermal properties of the CVD precursor are also reported.

Introduction

Vanadium dioxide undergoes a well known, reversible, semiconductor-to-metal (S–M) transition[1] at 68 °C, accompanied by a crystallographic transformation from a monoclinic structure, VO_2(M), to the tetragonal rutile structure, VO_2(R). This first order phase transition is accompanied by large changes in electrical resistivity and infrared transmission, thus making VO_2 a candidate material for applications involving electrical or optical switching elements (memory devices).[2] The S–M transition temperature in VO_2, already quite close to room temperature, can be lowered further by doping it with aliovalent ions such as tungsten, molybdenum or niobium, and by subjecting thin films of VO_2 to ion bombardment.[3–5] The phase transition can therefore be used for VO_2-coated "smart windows" for buildings, so that efficient use can be made of the incident solar radiation.[2] Such an application would require coatings on large areas of glass.

Many thin film deposition techniques including sputtering,[6,7] evaporation,[4,8] pulsed laser deposition,[9] and chemical methods[10,11] have been used to prepare thin films of VO_2 on different substrates. It has been reported that highly oriented VO_2 thin films deposited on single crystal substrates by different techniques display excellent characteristics such as a large change in resistivity at the phase transition (by a factor of $\sim 2 \times 10^4$) and a small hysteresis in the transition temperature (~ 2 °C).[6,11] However, films deposited on glass substrates have not displayed similarly sharp changes at the S–M phase transition.[12–14]

Chemical vapour deposition (CVD) is a suitable technique for achieving uniform coatings over large areas. However, the existence of a large number of distinct vanadium oxide phases with different crystal structures,[15] including polymorphs of VO_2 and the Magnéli phases (V_nO_{2n-1} for $n = 3$–9), imply that CVD conditions within a narrow range might be needed to stabilize the monoclinic VO_2(M) phase. Specifically, with a given precursor, substrate temperature and the oxygen partial pressure may be expected to influence the V : O stoichiometry in the films, which in turn, affects their phase purity and their physical properties.

In this study, we have deposited VO_2 thin films on glass substrates by metal-organic CVD (MOCVD) using bis(penta-2,4-dionato)oxovanadium(IV), referred to as vanadyl acetylacetonate and denoted by $VO(acac)_2$, as the precursor. The role of deposition temperature on the degree of crystallinity and microstructure of the films and, hence on the ratio of resistance before and after the S–M phase transition and on the size of the temperature hysteresis, are discussed. It is found that VO_2 films deposited on ordinary glass by MOCVD at about 475 °C display a large change in resistance due to the transition and a small hysteresis in the transition temperature; the change in resistance at the S–M transition is less pronounced for films deposited at higher temperatures.

Experimental

Vanadium dioxide thin films were grown in a hot wall, horizontal, low pressure MOCVD system built in house. A schematic diagram of the system is shown in Fig. 1. The deposition chamber is made of a fused quartz tube (35 mm dia.). A resistive heating arrangement located outside the quartz tube allowed substrate temperatures up to 1000 °C to be attained and maintained. The metal-organic precursor employed, *viz.*, the β-diketonate complex vanadyl acetylacetonate, [$VO(acac)_2$], is a crystalline solid at room temperature

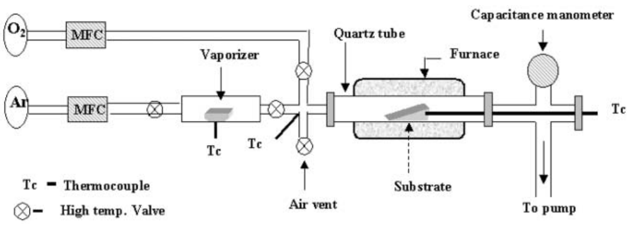

Fig. 1 Schematic diagram of the hot-wall, low pressure CVD reactor.

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that sublimes in the temperature range ~140–275 °C. The precursor was synthesized in our laboratory using standard procedures,[16] the formation of the complex being confirmed by a combination of techniques, namely, IR and mass spectroscopy, NMR spectroscopy and powder X-ray diffraction. The precursor was purified by repeated recrystallization, and the synthesis procedure scaled up to obtain ~10 g of the (dark green) crystalline complex per batch.

To determine the volatility of the precursor and hence to optimize the temperature at which the precursor vapouriser has to be maintained during the CVD process, thermal analysis of VO(acac)$_2$ was performed in flowing argon in a simultaneous thermogravimetric/differential thermal analyzer (Model STA 1500, made by Polymer Laboratories), at a heating rate of 10 °C min^{-1}. It can be seen from Fig. 2 that the vanadium complex begins to lose weight at ~140 °C, the weight loss amounting to about 4% of the initial sample weight when the temperature rises to ~175 °C. The differential thermal analysis data show an endothermic peak at 255 °C, corresponding to the melting point of the precursor, in good agreement with the data in the literature. The precursor weight loss is ~70% when the temperature reaches 275 °C. These thermal analysis data suggest that, in a CVD process, the precursor VO(acac)$_2$ may be vapourized in the temperature range 150–175 °C for, in this temperature range, the precursor is volatile enough. Yet, the temperatures are not too high to make it inconvenient to heat the precursor transport lines to prevent condensation of precursor vapour *en route* to the reaction chamber.

High purity (99.999%) argon gas was used to carry the precursor vapour to the reaction zone, while high purity (99.995%) oxygen gas, which acts as the oxidant, was fed into the reactor through a separate gas line. Electronic mass flow controllers were used to regulate the flow of both the gases. The total pressure in the reactor was measured by a capacitance manometer. The CVD process was conducted at a total reactor pressure of 2000 Pa. Thin films were deposited on glass (microscope) slides measuring 25 mm × 10 mm.

The substrates were cleaned successively in petroleum ether (bp 60–80 °C), 10% hydrochloric acid, distilled water, acetone and trichloroethylene, using ultrasonic agitation. The deposition conditions employed are given in Table 1. Detailed investigations, as reported below, were carried out on VO$_2$ thin films deposited at three different temperatures. Average film thickness was calculated from the weight gain due to the film measured on a semi-microbalance, assuming that the VO$_2$ film has bulk density (4.67 g cm^{-3}), and is of uniform thickness. The weight gain in a typical deposition run was about 200 µg, and the error in the average film thickness deduced is estimated to be ~10%. A part of this error is due to the presence of small and unknown amounts VO$_2$(B), a lower density polymorph of vanadium dioxide.[17] Identification of the phase(s) present in the films was performed using powder X-ray diffraction data (Scintag 2000 powder diffractometer, Cu-K$_\alpha$ radiation). The microstructure of the films was examined by optical microscopy, and by scanning electron microscopy (using the JEOL Model JSM–5600LV microscope). The S–M transition in the VO$_2$ films was studied by making four-probe measurements of resistance from room temperature to 90 °C. To determine the temperature hysteresis in the S–M transition accurately, sample resistance was measured after equilibrium was attained at each temperature, during both the heating and the cooling cycles.

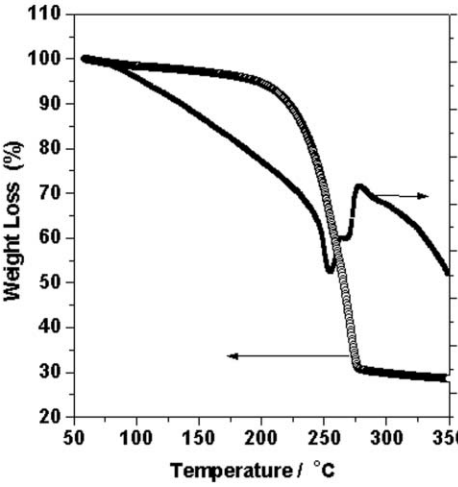

Fig. 2 Simultaneous thermogravimetric/differential thermal analysis of the precursor VO(acac)$_2$.

Table 1 Range of conditions used for the deposition of vanadium oxide thin films

Precursor	VO(acac)$_2$
Evaporator temperature/°C	150–175
Reactor pressure/Pa	1500–2000
Argon flow/sccm	50–100
Oxygen flow/sccm	20–60
Substrate	Glass
Deposition time/min	30–90

Results and discussion

Films deposited at various temperatures in the range 425–600 °C were all found to be well-crystallized and generally uniform in thickness and appearance over the area of the substrate. Though the deposition temperatures are rather low, the VO$_2$ films adhere strongly to the substrate (as determined by the adhesive-tape peel test) even when film thickness is as high as ~1000 nm. The XRD patterns of the thin films deposited at different temperatures, but of comparable thickness, are shown in Fig. 3, together with the standard powder pattern for polycrystalline, monoclinic VO$_2$ (JCPDS card no. 43-1051). In the discussion to follow, films deposited at temperatures of 475, 500 and 520 °C are designated VO$_2$(I), VO$_2$(II), and VO$_2$(III), respectively. It is to be noted in Fig. 3 that the relative intensities of the (200) reflection, for example, corresponding to $d = 0.2422$ nm, may be numerically

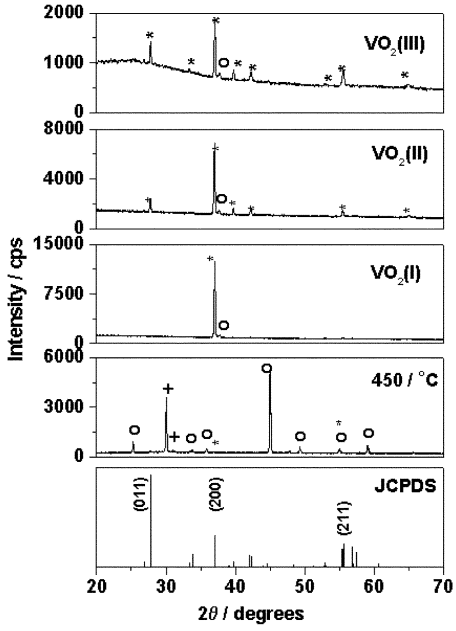

Fig. 3 XRD patterns of the vanadium oxide films of similar thickness, together with the standard pattern for polycrystalline VO$_2$(M). The intensities of reflections are directly comparable among VO$_2$(I), VO$_2$(II) and VO$_2$(III); (*) VO$_2$(M), (○) VO$_2$(B), (+) VO$_2$(A).

compared among the three samples, *i.e.*, the (200) reflection in $VO_2(I)$ is about 1000 stronger than in $VO_2(III)$. The XRD patterns show that the predominant component in films deposited in the temperature range 475–520 °C is the monoclinic $VO_2(M)$ phase. The weak reflection at $d = 0.236$ nm is due to the metastable $VO_2(B)$ phase of monoclinic symmetry,[18] whose intensity relative to $VO_2(M)$ reflections decreases as the deposition temperature is lowered. The high intensity of the (200) peak, compared to the others, suggests that the film $VO_2(III)$ shows a slight preference for the (200) orientation. The relative intensity of the (200) peak is higher in the film $VO_2(II)$ than in $VO_2(III)$, indicating that preference for growth with this orientation is greater when the deposition temperature is lower. The (200) peak intensity in the film $VO_2(I)$ is very high compared to the same in $VO_2(II)$ and $VO_2(III)$, showing strongly oriented growth of the film along the (200) plane, even though the substrate material is ordinary glass and the growth temperature is even lower than it is for $VO_2(II)$ and $VO_2(III)$. This tendency for preferred orientation at 475 °C has been confirmed through repeated growth runs. Table 2 gives a quantitative indication of the extent of preference for the (200) orientation in these films, compared to polycrystalline (ceramic) $VO_2(M)$ samples, as a function of the deposition temperature.

In general, the degree of preferred crystallographic orientation in thin films is greater when the growth temperature is higher, due to the greater mobility of the growth species. This trend is contradicted here by the high degree of preferred orientation in the VO_2 film grown at 475 °C, while films grown at 500 and 520 °C display hardly any preferred orientation. We speculate that such a tendency for stronger preferred orientation at lower growth temperature is due to the nature of the chemical reactions involved. In particular, it is surmised that the higher mobility that the growth species must possess to achieve a highly preferred orientation at a (nominally) low temperature is possibly provided by the enthalpies of the chemical processes occurring on the substrate surface.[19]

It is to be noted from the X-ray diffraction data (Fig. 3) that, when the deposition temperature is lower than 475 °C, the resulting film is a mixture of the $VO_2(A)$, $VO_2(B)$ and $VO_2(M)$ phases. We have also observed that, when the growth temperature is higher than 520 °C, the films deposited comprise other vanadium oxide phases beside $VO_2(M)$. X-Ray diffraction data indicate that one or more of the Magnéli phases may be formed at these higher temperatures. Thus, the phase composition and the microstructure of vanadium dioxide films prepared by MOCVD are sensitively dependent on temperature because the associated chemical reactions probably are temperature dependent.

The temperature dependence of the growth rate of the vanadium oxide films is shown in Fig. 4. Films deposited at temperatures below 475 °C and above 520 °C comprise a mixture of different vanadium oxide phases. Nearly monophasic films (as determined by XRD data) were obtained only in the narrow temperature range of 475–520 °C, comprising the monoclinic phase, $VO_2(M)$. Growth rates of 11, 19 and 31 nm min^{-1} were obtained for $VO_2(III)$, $VO_2(II)$ and $VO_2(I)$, respectively. It is seen that the growth rate of VO_2 increases when the deposition temperature is reduced. In a typical CVD process, film growth rate increases exponentially with temperature in accordance with the Arrhenius rule, up to a temperature characteristic of the specific chemical reactions involved. This is the so-called kinetically controlled CVD growth regime for which E_a, the activation energy for growth, can be deduced from the Arrhenius plot. At higher temperatures, growth rate decreases with increasing temperature because, at these temperatures, the rate of desorption of the adatoms from the substrate increases, and also because reactions in the gas phase and on the walls of the hot-wall reactor begin to dominate.[20] However, such an explanation cannot be applied readily to the CVD growth of the oxide(s) of a metal with multiple oxidation states wherein, under given deposition conditions, more than one phase may be formed simultaneously on a given substrate. It is thus possible that, due to the complexity of the V–O phase diagram, the kinetically controlled CVD growth regime of a specific vanadium oxide phase is very narrow. The occurrence of several polymorphs of vanadium dioxide, *viz.*, $VO_2(M)$, $VO_2(R)$, $VO_2(A)$ and $VO_2(B)$, further complicates any analysis of the CVD growth of VO_2. Films deposited at temperatures below 475 °C are found to consist of the phases $VO_2(A)$ and $VO_2(B)$, besides $VO_2(M)$, as noted already.

Table 2 Tendency for preferred (200) orientation in VO_2 films on glass; (011) is the strongest reflection in polycrystalline $VO_2(M)$

Sample	$I_{(200)}/I_{(011)}$
JCPDS Card No. 43-1051	0.3
$VO_2(I)$	>12000
$VO_2(II)$	2.80
$VO_2(III)$	1.24

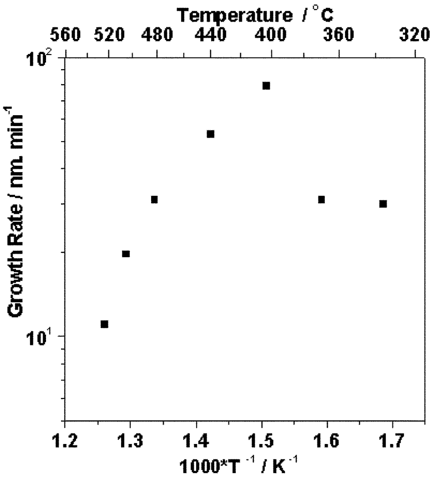

Fig. 4 Arrhenius plot of the growth rates of vanadium oxide films from $VO(acac)_2$.

SEM micrographs of the films, $VO_2(I)$, $VO_2(II)$ and $VO_2(III)$, shown in Fig. 5, indicate that crystallites are well formed in each case. From these micrographs, the distribution of grain sizes in the three VO_2 films deposited has been measured, the corresponding histograms being shown in Fig. 6. Histograms have been plotted by measuring the largest dimension of all the grains in a given a micrograph, numbering about eight hundred. Grain size distribution in the three films is summarized in Table 3. It is clear that crystallite size distribution varies noticeably with deposition temperature, even within the rather narrow temperature span from 475 to 520 °C. The range of grain sizes is the widest at 475 °C and the narrowest at 520 °C. As seen in Fig. 5, the presence of irregularly-shaped crystallites of many sizes at 475 °C leads to low porosity, with the smaller grains packing the intergranular space between the larger ones. The grain size distribution at 500 °C is very similar to that at 475 °C, though it can be discerned from the micrographs that grain orientation at 500 °C is more random than at 475 °C. As the deposition temperature is raised to 520 °C, film porosity increases, while the grains are more uniform in size and morphology. A narrower grain size distribution at a higher deposition temperature is contrary to the usual trend in the development of thin film microstructure, and may be attributed to the chemical nature of the processes at work. However, the connectivity between the grains is quite good, irrespective of the film deposition temperature.

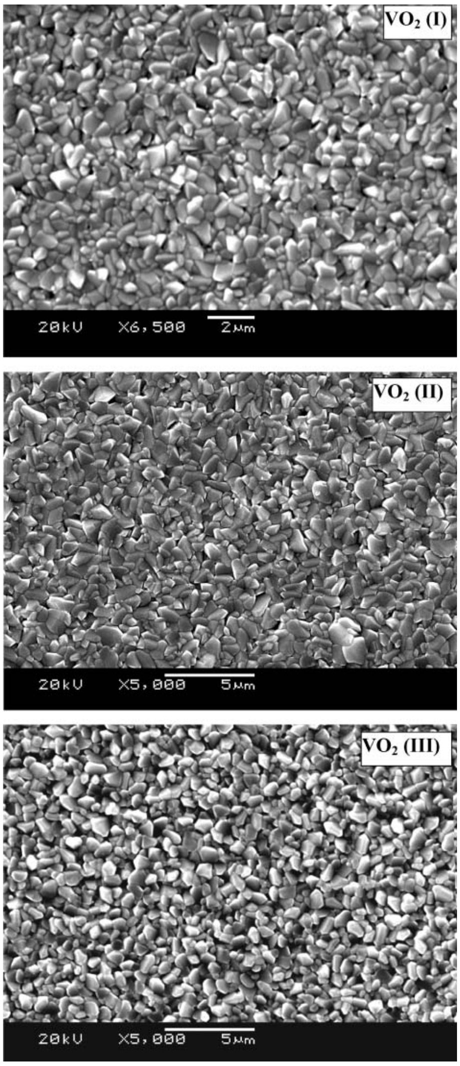

Fig. 5 SEM micrographs of VO_2(I), VO_2(II) and VO_2(III).

The evolution of microstructure observed here may be contrasted with that observed in copper thin films grown by MOCVD from Cu(II) dipivaloylmethanate[21] wherein, as a result of some grains developing at the expense of the others, film porosity increases with growth temperature. Such a growth process leads to a wider distribution of grain sizes at higher growth temperatures than at lower ones. It has been shown through Monte Carlo simulations that a higher deposition temperature leads to greater porosity, because the deposition of Cu by MOCVD from the aforementioned precursor is akin to a physical vapour deposition process.[21] In the case of VO_2, the grains are more uniform in size at 520 °C than at 475 °C, and the porosity is greater at 520 °C. We note here again that the film grown at 475 °C has a strong (200) orientation. We surmise, therefore, that the chemical reactions and growth processes involved in the MOCVD of VO_2 from VO(acac)$_2$ are more complex than those involved in the deposition of elemental Cu by MOCVD. As such, in the present process for the MOCVD of the monoclinic phase of vanadium dioxide, a straightforward interpretation of the observed microstructure evolution may not be possible. Nonetheless, it may be inferred that the greater porosity observed in the film grown at the higher temperature (520 °C) is due in part to the higher mobility of the growth species on the substrate surface.

Table 3 Grain size distribution in VO_2(I), VO_2(II) and VO_2(III)

Sample	Average grain size/μm	Grain size at peaks of distribution/μm		Range of grain size distribution/μm
VO_2(III)	0.6	0.6	—	0.3–0.9
VO_2(II)	0.7	0.4	0.6	0.1–1.3
VO_2(I)	0.8	0.6	0.9	0.2–1.4

The variation in the electrical resistance of the three films as a function of temperature is shown as Arrhenius plots in Fig. 7. Each plot displays a sharp change in resistance, characteristic of the semiconductor-to-metal phase transition in VO_2 that occurs at about 68 °C. The transition temperature, T_c, is defined as follows. Using the R *vs.* $1/T$ data, a plot of $dR/d(1/T)$ *vs.* T is obtained, yielding a fairly symmetrical curve with a well-defined maximum. The temperature corresponding to this maximum defines T_c (Fig. 7, inset). The temperature width of the transition is defined by the quantity ΔT_c, which is taken to be the FWHM of the peak that is used to define T_c. The discontinuity in resistance at T_c is defined as the ratio ΔR of the measured sample resistance just above and just below T_c. (At these two temperatures, $dR/d(1/T)$ is 10% of its maximum value, by our definition.) In all the three films, prior to the transition to the metallic phase, the resistance decreases exponentially with increasing temperature in the semi-conducting low temperature (monoclinic) phase, reflecting an

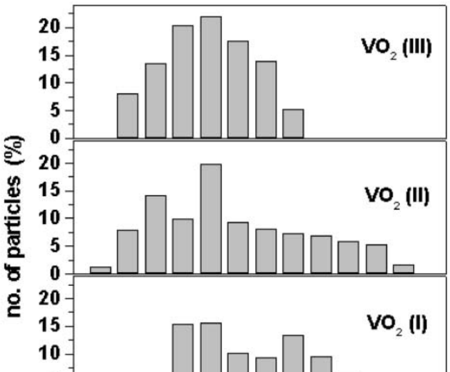

Fig. 6 Histograms showing the particle size distribution in VO_2(I), VO_2(II) and VO_2(III).

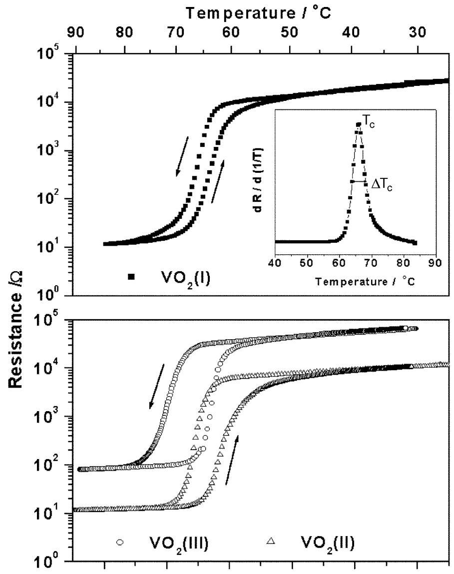

Fig. 7 Arrhenius plot of electrical resistance of VO_2(I), VO_2(II) and VO_2(III). The inset illustrates the definition of the transition temperature T_c.

Table 4 Characteristics of the S–M phase transition in $VO_2(I)$, $VO_2(II)$ and $VO_2(III)$

Sample	Transition temperature, T_c/°C		ΔR	Hysteresis width, ΔT_h/°C	Transition width, ΔT_c/°C	
	Heating	Cooling			Heating	Cooling
$VO_2(III)$	72	63	$10^{2.5}$	9	4	5
$VO_2(II)$	67	62	$10^{2.75}$	5	3.5	4.5
$VO_2(I)$	66	64	10^{3}	2	5	3

activation energy for conduction (E_a) of 0.18, 0.21 and 0.26 eV for the films $VO_2(III)$, $VO_2(II)$ and $VO_2(I)$, respectively. The activation energies are calculated from the measured resistance values between room temperature to T_c, before transition to metallic state occurs. The change in resistance, while reversible, is accompanied by a temperature hysteresis, ΔT_h, which is defined as the difference between the T_c values measured during the heating and cooling cycles; the size of ΔT_h varies from sample to sample. Upon heating above room temperature, a rather sharp S–M transition occurs at 68 °C, while an equally sharp M–S transition occurs upon cooling at ~60 °C. Such hysteretic behaviour is characteristic of first order phase transitions and thus, for example, is also observed in the well-known metal–insulator transition in V_2O_3.

A range of values for ΔR, ΔT_c and ΔT_h has been reported in the literature and they appear to depend on the method of sample preparation, its composition (*i.e.*, oxygen stoichiometry), and the state of its aggregation (*i.e.*, whether single crystal, polycrystal, epitaxial film or polycrystalline film). The change in resistivity at the S–M transition can be more than four orders of magnitude in single crystals[22] of VO_2, whereas ΔT_c is less than 1 °C. Reports from different investigators indicate that, in thin VO_2 films, ΔR depends on the deposition temperature. In polycrystalline films, the reported values for ΔR lie in the range 5–500, whereas ΔT_h lies in the range 8 to 20 °C. Among the polycrystalline films we have grown, $VO_2(I)$ has the largest ΔR, *ca.* 10^3, while the resistivity jump is somewhat smaller in the other two films. These are considerably larger than ΔR values reported for polycrystalline VO_2 films prepared by any technique, and compare well with the ΔR reported in the literature for epitaxial films.[4] The electrical behaviour of the three films at the S–M transition is summarized in Table 4.

The phase transition temperature, the temperature width of the transition, and the hysteresis in a thin film undergoing first-order phase transformations are controlled by the propagation of shear due to the transformation through grain boundaries in the film. The electrical behaviour of thin films of VO_2 at the S–M transition may, therefore, be expected to depend strongly on the microstructure (the grain orientation, in particular), and on the residual stress caused by the deposition process and the interaction of the film with the substrate. Two fundamental types of stress are involved. Extrinsic stress is introduced by a mismatch between thermal expansion coefficients of the film and the substrate. On the other hand, intrinsic stress is due to voids and grain boundaries. (A shift in the transition temperature with applied pressure is observed[23] in bulk VO_2.) Accordingly, variation in the transition temperature in films grown at different temperatures and on different substrate materials may be attributed to the variation in the stress arising from the mismatch in thermal expansion between the film and the substrate.[4] This is consistent with our experimental observation that in thin film VO_2, the deviation of T_c from its bulk value is the small when the deposition temperature is low.

Our measurements show that the electrical properties of VO_2 films, as indicated by ΔR, ΔT_c and ΔT_h, improve when the deposition temperature is lowered. Such improvement may be attributed to the details of the microstructure of the films. The largest ΔR observed is in the film $VO_2(I)$ that exhibits growth strongly oriented in the (200) direction, *i.e.*, parallel to the *c*-axis of monoclinic VO_2. The S–M transition in VO_2 is due to the structural change from monoclinic to rutile, which involves distortion along the c-axis. Since temperature hysteresis in phase transitions is due to nucleation barriers such as grain boundaries and voids, the microstructure of the film affects the width of the hysteresis. Thus, ΔT_h is very small (~1–2 °C) in epitaxial thin films of VO_2 grown on single crystal sapphire.[3] The observed smaller hysteresis width in $VO_2(I)$ may therefore be attributed to the high degree of the (200) orientation in the film. The superior electrical properties of $VO_2(I)$ are perhaps also due to the larger average grain size and the higher density of the film.

It is well known that, in vanadium oxides, the characteristics of phase transitions are a sensitive function of the chemical composition of the film, *i.e.*, metal–oxygen stoichiometry. Thus, it has been reported[22] that, in single crystals of VO_2 with carefully controlled oxygen stoichiometry, ΔT_h varies considerably with oxygen stoichiometry, and is the smallest when the V : O ratio deviates the most from 1 : 2.00. By contrast, it has been reported that in thin films of VO_2, small deviations from the 1 : 2.00 stoichiometry destroy the sharpness of the transition and increase the hysteresis width.[7] It has also been reported[8] that the magnitude of ΔR and the narrowness of the hysteresis are indicators of how close the stoichiometry is to $VO_{2.00}$. The large value of ΔR and the narrowness of hysteresis seem to imply that $VO_2(I)$ has a stoichiometry close to $VO_{2.00}$. A careful and accurate determination of V : O stoichiometry in the three films would be required to draw a firm conclusion.

Conclusions

Thin films of monoclinic vanadium dioxide of high quality, as evidenced by a sharp S–M transition and a large discontinuity in resistance at the transition, can be deposited on ordinary glass at relatively low temperatures by low pressure MOCVD, using a stable vanadium β-diketonate complex as precursor. Film microstructure depends sensitively on growth temperature—a very strong (200) orientation is present in films grown at 475 °C, whereas grain orientation is nearly random at 520 °C. Such unusual tendency for preferred orientation at a low (rather than a high) growth temperature may be understood qualitatively in terms of the chemical nature of the growth process. The strong grain orientation in films grown at 475 °C leads to a large drop in resistance at the semiconductor–metal transition, with minimal temperature hysteresis, just as in epitaxial VO_2 films grown on single crystal substrates. Films grown at higher temperatures show poorer transition characteristics, *i.e.*, smaller ΔR and larger ΔT_h. The capability to control the microstructure and properties of VO_2 films grown on ordinary glass by altering the process parameters in MOCVD can be significant for practical applications, including "smart windows".

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