

Metalorganic chemical vapor deposition of highly oriented thin film composites of V_2O_5 and V_6O_{13} : Suppression of the metal–semiconductor transition in V_6O_{13}

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Thin films of vanadium oxides were grown on fused quartz by metalorganic chemical vapor deposition using vanadyl acetylacetonate as the precursor. Growth at temperatures ≥ 560 °C results in composites of strongly (00 l)-oriented V_2O_5 and V_6O_{13} . The dominant phase of the film changes from V_2O_5 to V_6O_{13} , and back to V_2O_5 , as the growth temperature is raised from 560 to 570 °C, then to 580 °C, as evidenced by x-ray diffraction and Rutherford backscattering analyses. This reentrant-type growth trend was interpreted on the basis of the small difference in the free energy of formation of V_2O_5 and V_6O_{13} and the presence of metal–oxygen bonds in the precursor. In contrast with single-crystalline V_6O_{13} , the film predominantly composed of highly oriented single-crystalline platelets of V_6O_{13} did not undergo the semiconductor–metal transition at -123 ° K, despite the connectivity being well above the percolation threshold. Instead, a semiconductor-to-semiconductor transition was observed in this film, which is explained in terms of the observed relaxation of the edges of all the platelets of metallic V_6O_{13} to semiconducting V_2O_5 .

I. INTRODUCTION

The vanadium oxide system is rich and interesting because of the diversity of physical properties observed in apparently similar phases. For example, while vanadium pentoxide is a wide band gap semiconductor,¹ V_6O_{13} , which has a very similar structure, is a metal at room temperature. V_6O_{13} undergoes a metal–semiconductor (M-S) transition at -123 ° C, with a jump in resistivity by a factor of 10^5 , though this is observed only in single-crystalline specimen.² Sintered polycrystalline V_6O_{13} , by contrast, is reported to be a semiconductor at room temperature³ with activation energy for conduction E_a of 0.42 eV. It exhibits a semiconductor-to-semiconductor (S-S) transition³ at approximately 150 K, where the resistivity jumps by about an order of magnitude, the E_a at low temperatures being 0.21 eV. The M-S transition is accompanied by a crystallographic distortion.⁴ Furthermore, an antiferromagnetic ordering⁵ takes place in V_6O_{13} at 50 K. While V_2O_5 is thermodynamically stable, the V_6O_{13} phase, being an ordered defect structure closely related to V_2O_5 , is metastable. Although accurate thermodynamic data (ΔG , the Gibbs free energy of formation) are not available for

V_6O_{13} , it may be expected from the V–O binary phase diagram⁶ that the free energy of V_6O_{13} is likely to be close to that of V_2O_5 . This is substantiated by the present study and is understandable given the intimate relationship between the crystal structures of V_2O_5 and V_6O_{13} . The V_2O_5 lattice in the c direction can be considered as stacking of alternately pure vanadyl oxygen (O) and mixed vanadium oxygen (V–O) layers [Fig. 1(a)]. Along the c axis, each vanadyl oxygen is bonded to two vanadium atoms, in one direction by a double bond and in the opposite direction by a van der Waals bond. The successive O and V–O layers are kept together by an equal number of weak van der Waals bonds and much stronger double bonds.⁷ The crystal structure of V_6O_{13} can be deduced from the V_2O_5 stacking by removing each third O layer and successive shear over $1/6[10\bar{3}]$. The resulting stacking sequence⁸ is of the form . . . O, V–O, O, V–O, O, V–O, V–O . . . [Fig. 1(b)]. It should be noted that in V_6O_{13} the bonding between the pure O layers and V–O layers is of neither the vanadyl nor the van der Waals type. However, V_2O_5 and V_6O_{13} have similar polyhedral connectivity and a similar two-dimensional repeat unit along the a - b plane [Figs. 1(c) and 1(d)]; the unit cell of the $V_2O_5(001)$ surface is 11.52×3.56 Å, and that of $V_6O_{13}(001)$ surface is 11.92×3.68 Å. The a - b planes of both V_2O_5 and V_6O_{13} are made up of a network of corner sharing zig-zag strings consisting of edge-shared polyhedra, forming closely packed dense planes.⁶

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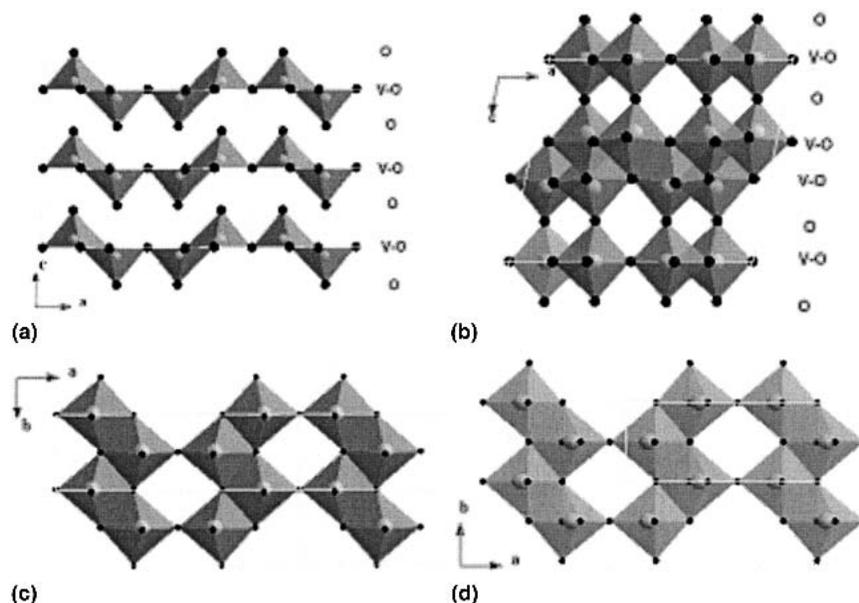


FIG. 1. The arrangement of oxygen polyhedra in the (ac) plane, depicting the stacking sequences of O and V-O layers in (a) V_2O_5 , (b) V_6O_{13} , and in the (ab) plane in (c) V_2O_5 and (d) V_6O_{13} .

Moreover, both V_2O_5 and V_6O_{13} are technologically important. V_2O_5 has been widely studied as a promising material for a variety of applications: as a catalyst,^{9,10} a gas sensor,¹¹ a window material for solar cells, in electrochemical devices,¹² as a cathode material for solid-state batteries.¹³ Theoretical studies predict that the orientation of V_2O_5 has a great influence on Li-ion transport across the electrolyte/cathode interface in solid-state thin film batteries or electrochromic devices (cyclic stability and reversibility).¹⁴ Fang et al. have reported that the $(00l)$ orientation of V_2O_5 improves cycle stability of Li-ion intercalation and de-intercalation and its reversibility.¹⁵ For this reason, different deposition techniques such as pulsed laser deposition,^{15,16} plasma-enhanced chemical vapor deposition (PECVD),¹⁷ atmospheric pressure chemical vapor deposition (CVD),¹⁸ and vacuum evaporation,^{19,20} have been explored to grow oriented V_2O_5 films. Similarly, V_6O_{13} has also been studied extensively as a candidate cathode material in solid-state lithium-ion batteries.^{21,22} As V_6O_{13} has a structure similar to that of V_2O_5 , it appears that $(00l)$ -orientated V_6O_{13} films would also be interesting as intercalation hosts for Li ions in rechargeable batteries and electrochromic devices, just as $(00l)$ -oriented V_2O_5 . However, there are very few reports on thin films of V_6O_{13} and, in particular, on oriented V_6O_{13} thin films.^{23,24} To exploit the potential of these two materials fully, a further understanding of the dependence of phase formation, crystallinity, and orientation of the film on deposition parameters is required, because of the close relationship between the structures of the two oxides. In our recent effort to investigate the metalorganic CVD

(MOCVD) of vanadium oxide thin films using vanadyl acetylacetonate, $VO(acac)_2$, as the precursor, we have observed that highly oriented films of different phases such as $VO_2(B)$, $VO_2(M)$, and $\beta-Na_xV_2O_5$ can be obtained by varying process parameters.²⁵⁻²⁷ It is also found that the phase formed, microstructure, orientation, and the crystallinity of the film change significantly, even within a narrow range of growth temperatures.²⁵⁻²⁷

In this study, we have therefore grown thin films of vanadium oxides on fused quartz by MOCVD using $VO(acac)_2$ as the precursor, at various temperatures from 550 to 610 °C. The phase formed and the microstructure of the films were examined as a function of deposition temperature. It is observed that, as the temperature is varied from 560 to 580 °C in steps of 10 °C, the films deposited comprise a mixture of strongly oriented V_2O_5 and V_6O_{13} phases, with the x-ray diffraction (XRD) patterns being alternately dominated by either V_6O_{13} or V_2O_5 . Indeed, films grown at various temperatures >550 °C have a strong tendency for the $(00l)$ texture, irrespective of the dominant phase. Such reentrant-type behavior in phase formation has not been reported to date and is interpreted here through suitably designed experiments. Further, it is found that the film predominantly comprised of highly oriented V_6O_{13} does not undergo the S-M transition at 150 K. This is explained on the basis of the observed relaxation of the edges of V_6O_{13} crystallites into the thermodynamically more stable V_2O_5 phase. This argument is further extended to explain the reported absence of S-M transition in the polycrystalline samples of V_6O_{13} .

II. EXPERIMENTAL

Thin films of composites of V_2O_5 and V_6O_{13} were grown on polished fused quartz substrates (measuring approximately $10\text{ mm} \times 10\text{ mm}$) by low pressure MOCVD in a hot-wall, horizontal reactor built in house, using vanadyl acetylacetonate $[VO(acac)_2]$ as the precursor. This precursor, a crystalline solid that sublimates beginning at approximately $150\text{ }^\circ\text{C}$, was synthesized in our laboratory and purified by repeated recrystallization. A detailed description of the CVD system and the thermal analysis of $VO(acac)_2$ are given elsewhere.²⁵ The precursor was vaporized at $175\text{ }^\circ\text{C}$, while high-purity argon was used as the carrier gas, and high purity oxygen as the oxidant gas. Gas flow was regulated using electronic mass flow controllers. A relatively high flow rate of oxygen (350 sccm) was used, compared to that of argon (60 sccm), in the expectation that vanadium oxide films might be formed, in which at least some of the vanadium would be in the 5+ state. A capacitance manometer was used to measure the total reactor pressure, which was maintained at 100 Torr. The films were deposited for 2 h, at different temperatures in the range 550 to $610\text{ }^\circ\text{C}$. The exact temperature of the substrate was measured using a K-type thermocouple inserted into the susceptor, on which the substrate was placed. At the end of each deposition, power supply to the reactor was turned off, thus allowing the samples to cool to room temperature in an ambient of flowing oxygen (350 sccm). Some of the samples were subjected to post-deposition annealing for various durations in flowing oxygen, at the temperature of deposition of the given sample.

Identification of the phases present in the films was carried out using powder XRD (Scintag 2000 diffractometer, $\text{Cu K}\alpha$ radiation). To determine film composition, some of the samples were analyzed by Rutherford backscattering spectrometry (RBS), employing 2.4 MeV alpha particles in a 3 MV tandem accelerator (HVEE, Europa, Amsterdam, Holland). A well-collimated beam (spot size $<0.5\text{ mm}$) of alpha particles was incident normal to the specimens, and the backscattered particles were detected by a silicon surface barrier detector positioned at 170° with respect to the direction of the incident beam.

The microstructure of the films was examined by scanning electron microscopy (SEM; JEOL Model JSM-5600LV, Tokyo, Japan) and transmission electron microscopy (TEM; JEOL model JEM 200CX, Tokyo, Japan). Film thickness was measured using cross-sectional SEM micrographs. TEM samples were prepared by scraping the film out of the substrate and dripping it using acetone onto a carbon-coated copper grid. The resistance of the film mainly comprising V_6O_{13} was measured by the linear four-probe method from 20 – 300 K in a closed-cycle cryostat, during both the cooling and heating cycles. The optical properties of the films grown at different temperatures were studied by recording their

transmittance in the ultraviolet-visible (UV-vis) region in a scanning spectrophotometer (Shimadzu, double beam, resolution 0.1 nm).

III. RESULTS

Films deposited on fused quartz at various temperatures in the range 550 to $610\text{ }^\circ\text{C}$ are designated as VT, where T gives the temperature in degrees celsius. XRD patterns of these films are given in Fig. 2 and are indexed according to the standard powder patterns for polycrystalline, orthorhombic V_2O_5 , tetragonal V_4O_9 , and monoclinic V_6O_{13} (JCPDS file Nos. 41-1426, 23-0720, and 43-1050, respectively).²⁸ The film V550 is a mixture of the phases V_2O_5 , V_6O_{13} , and V_4O_9 , with no tendency for preferred orientation. The peak intensities are very low, even though the film is quite thick (Table I) and well crystallized, as is evident from the SEM shown below [Fig. 3(a)]. The broad hump in the range $2\theta = 15^\circ$ to 30° is due to the underlying fused quartz substrate. By contrast, this hump is inconspicuous in the XRD pattern of the films grown at temperatures $>550\text{ }^\circ\text{C}$ because of the much higher intensities (by more than an order of magnitude) of the reflections arising from the pronounced (001) orientation of either or both of the phases, V_2O_5 and V_6O_{13} , present in these films. (The presence of V_4O_9 , if any, in the films grown at temperatures $>550\text{ }^\circ\text{C}$ is below the limit of detection of XRD.) For example, in the XRD

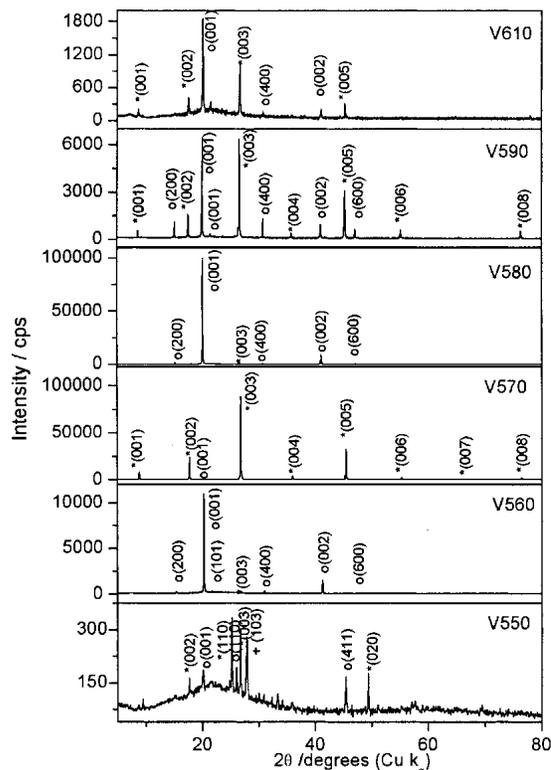


FIG. 2. XRD patterns of the films grown at various temperatures in the range 550 to $610\text{ }^\circ\text{C}$: (*) V_6O_{13} , (o) V_2O_5 , and (+) V_4O_9 .

TABLE I. Phase content, oxygen-to-vanadium ratio, color in transmission, and thickness of films grown at different temperatures for 2 h; bold font designates the phase dominating the XRD pattern

Sample designation	Phase content	Color in transmission	Film thickness (nm)	Oxygen to vanadium ratio from RBS data	$V_2O_5:V_6O_{13}$ (mol%) calculated from RBS data
V550	V_2O_5 , V_6O_{13} , V_4O_9	Opaque	1530		
V560	V_2O_5 , V_6O_{13}	Yellow	450	2.45	85:15
V570	V_2O_5 , V_6O_{13}	Brownish black	500	2.2	12:88
V580	V_2O_5 , V_6O_{13}	Pinkish yellow	1250	2.3	41:59
V590	V_2O_5 , V_6O_{13}	Brown + yellow	1200		
V610	V_2O_5 , V_6O_{13}	Sparse coating	300		

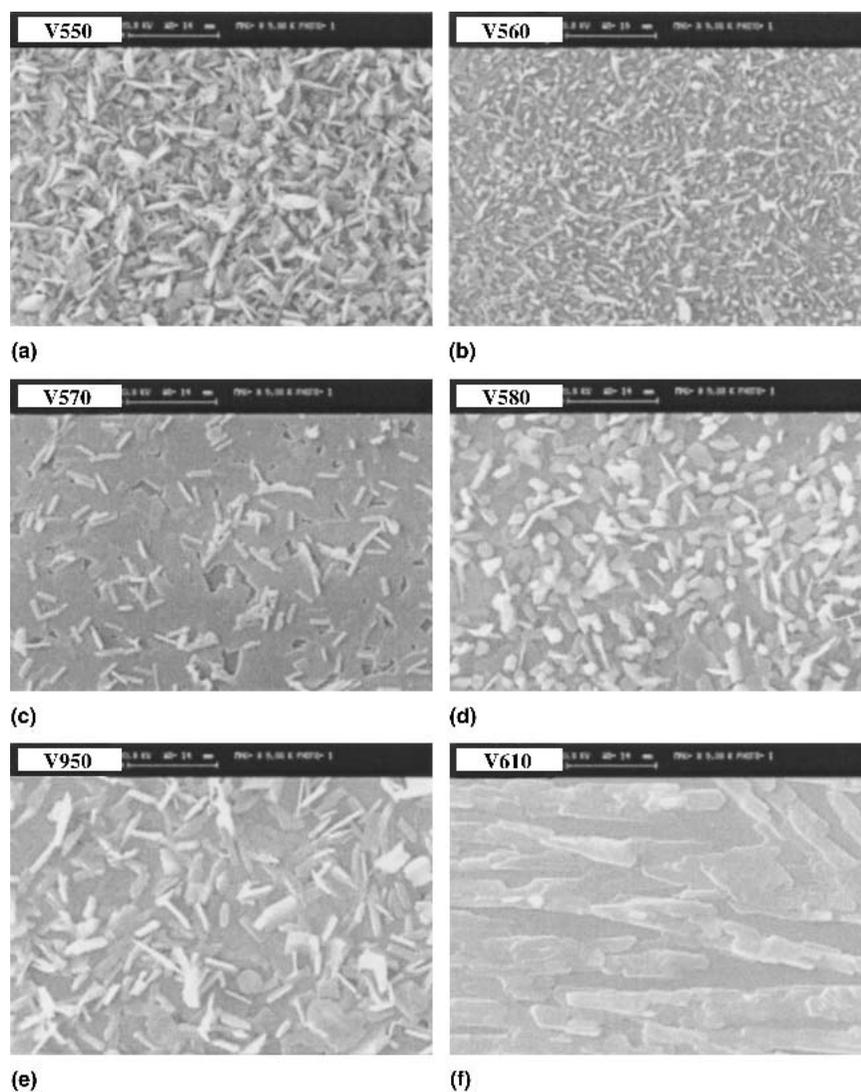


FIG. 3. SEM micrographs of the films grown at various temperatures: (a) 550 °C, (b) 560 °C, (c) 570 °C, (d) 580 °C, (e) 590 °C, and (f) 610 °C.

pattern of V560, the intensity of the (00 l) reflections of V_2O_5 , in comparison with that of the other peaks, is very high. Even though the (00 l) peak is the strongest reflection in the polycrystalline powder pattern of V_2O_5 , the intensity ratio ($I_{(001)}/I_{(hkl)}$) in V560 is much higher than it would be in polycrystalline V_2O_5 , indicating growth with a strong (00 l) texture. The simultaneous deposition of

V_6O_{13} in V560 is evidenced by the low intensity peak at $2\theta = 26.8^\circ$ seen in the XRD pattern. However, it must be noted that the preferred orientation of V_2O_5 in the film prevents an estimation (using XRD data) of the relative proportion of the two oxide phases in V560. When the deposition temperature is 570 °C, the XRD pattern of the resulting film is dominated by V_6O_{13} , with peak

intensities higher by an order of magnitude than in V560. The presence of only the (00 l) reflections indicates that V570 is a film of V_6O_{13} with a strong (00 l) texture. However, the (001) peak of V_2O_5 observed in V570 remains in the film V560, though its intensity is sharply reduced. When deposition is carried out at 580 °C, the dominant reflection is due to V_2O_5 , which has a strongly preferred (00 l) orientation, just as in V560, but with a further increase in the intensity of the (001) peak. It should be noted that the intensities of the XRD peaks due to V_6O_{13} and V_2O_5 from V570 and V580, respectively, are comparable to the intensities of the peaks observed from an epitaxial film grown on a single crystal substrate. The formation of films containing highly oriented grains of both V_2O_5 and V_6O_{13} , each phase dominating the other by turn when the deposition temperature is varied within the very narrow range from 560 to 580 °C, has been confirmed by repeated growth runs. When the growth temperature is increased again by 10 °C to 590 °C, the resulting film continues to be a mixture of V_2O_5 and V_6O_{13} , both with a pronounced (00 l) texture. However, in this film (V590), the intensities of the peaks due to V_2O_5 and V_6O_{13} are comparable, neither dominating the other, in contrast with films grown at lower temperatures. Furthermore, the intensity of the XRD peaks in V590 is lower by more than an order of magnitude than in V570 and V580. As the growth temperature is raised further to 610 °C, the resulting film is again comprised of (00 l)-oriented V_2O_5 and V_6O_{13} , with peak intensities comparable to each other. But, the intensity of the pattern is smaller still than that of V590. Thus, over a narrow range of deposition temperatures, strongly textured growth of a thin film composite of V_2O_5 and V_6O_{13} is observed. As a function of deposition temperature in the range 560–580 °C, each of the two oxide phases dominates the other alternately in the XRD patterns of these composite films. This may be termed as reentrant-type behavior in the growth of vanadium oxide films under the MOCVD conditions used here.

A measurement of the oxygen content of these films is, therefore, pertinent. The phase content, the oxygen-to-vanadium ratio, color in transmission, and the thickness of the films grown at different temperatures (for 2 h) are summarized in Table I. It is noteworthy that V560 and V570 have a similar thickness, but much smaller than that of V550, V580, or V590. As two or more phases are being deposited simultaneously, no Arrhenius-type dependence of growth rate on temperature, typical of CVD processes, may be expected.^{25,27} It is also to be noted that the oxygen content of the films V560, V570, and V580, as analyzed by RBS, has an accuracy of 5%. A reason for this (relatively) low accuracy is the absence of a sharp interface between the film and substrate. Given the limited accuracy of the RBS analysis, it is not possible to determine very reliably the relative proportions of the

two phases present in the film. Within these limitations, the percentages of V_2O_5 and V_6O_{13} present in V560, V570, and V580, as estimated from RBS data, are listed in Table I. It is to be noted that these values are quite sensitive to the O:V assumed in the estimations. For example, assuming that the error in RBS analysis is as low as 2%—i.e., when O:V = 2.45 ± 0.05 —the relative proportion of V_2O_5 and V_6O_{13} lies within a band of 100:0 (when O:V ratio is taken to be 2.50) to 70:30 (when O:V ratio is 2.40). This illustrates the difficulty in determining experimentally the proportions of two such compositionally close phases comprising a thin film sample. Nevertheless, the variation in the measured oxygen content of the films with the deposition temperature supports the inference from XRD data that reentrant-type growth occurs in the MOCVD of higher vanadium oxides.

Because of the observed curious progression in the XRD patterns of the films deposited over a narrow range of temperatures, the microstructure of the films was examined by scanning electron microscopy. It is found that the microstructure varies significantly with deposition temperature, as manifested in the SEM micrographs shown in Fig. 3. However, all the films except for V550 share a common feature; i.e., they consist of two types of crystallites with different levels of contrast, the relative proportion of the two types varying with the growth temperature. It is well known that semiconductors and insulators appear brighter in SEM micrographs than metals, because of the lower rates of charge leakage. Based on the XRD data presented, and the SEM micrographs [Figs. 3(b)–3(e)], it may be concluded that the films grown at temperatures between 560 and 590 °C consist of a non-conducting phase (V_2O_5) and a conducting phase (V_6O_{13}), whose relative proportion appears to vary with the growth temperature, as verified by RBS analysis (Table I).

It may be seen from Fig. 3(a) that the film V550 is well crystallized and the crystallites are large, measuring up to 2 μm in extension, with many of them being platelets of different shapes. We surmise that the observed microstructure is due to the simultaneous deposition of three different oxide phases. The film V560, by contrast, comprises only two phases, i.e., V_2O_5 (the bright crystallites), and V_6O_{13} (the darker crystallites). Nevertheless, crystallite size, as well as crystallite shape, covers a wide range, as can be readily noted from Fig. 3(b). Indeed, a thin “ribbon”—ostensibly of V_2O_5 , because of its brightness—near the center of the micrograph measures as much as 5 μm . On the other hand, V570 is made of large, dark platelets, presumably of V_6O_{13} , lying parallel to the substrate surface [Fig. 3(c)]. Given the high intensity of the XRD pattern, we infer that V560 is composed of single-crystalline platelets of V_6O_{13} , some measuring more than 25 μm across. On these dark platelets is seen a random and sparse “sprinkling” of bright crystallites.

Because the XRD pattern of V570 consists of a minute peak corresponding to V_2O_5 , we hypothesize that the small, bright crystallites dispersed over the large platelets are those of V_2O_5 . By contrast, the SEM of the film V580 [Fig. 3(d)] reveals it to be an intimate composite of bright and dark crystallites, which may be inferred as those of V_2O_5 and V_6O_{13} , respectively. The crystallites of V_2O_5 are highly faceted, suggesting that growth (of V_2O_5) occurs at this temperature under close-to-equilibrium conditions. It is also to be noted that the crystallites of V_6O_{13} are much smaller, and are no longer the large platelets that nearly cover the entire substrate as in V570. As evident from Fig. 3(e), V590 is also composed of two types of crystallites, i.e., V_2O_5 and V_6O_{13} , both with a preference for the (001) orientation, and in comparable proportion. The average size of the crystallites is larger than in V580, though they are faceted to a lesser degree. As the deposition temperature is raised to 610 °C, the rate of deposition falls sharply, resulting in a much thinner "film." Indeed, the coating is very sparse on the substrate and is made of branched, interconnected platelets parallel to the substrate, with a continuously changing contrast in the SEM [Fig. 3(f)], suggesting intergrowth of V_2O_5 and V_6O_{13} .

As the films grown at different temperatures are shown by XRD and SEM to be composites of V_2O_5 and V_6O_{13} , respectively a semiconductor and a metal, their optical transmittance was examined as a function of wavelength. The transmittance of V560, V570, and V590 are shown in Fig. 4. The transmittance of V560 is a very gradually increasing function of wavelength, reaching a maximum of approximately 35% at 1000 nm, whereas V570 has a peak transmittance of approximately 8% at 540 nm. The film V590 is poorly transmitting, reaching a maximum of only 5% at 1000 nm, but with an inflexion at 540 nm, presumably corresponding to the wavelength of maximum transmission in V570. The composite nature of the films renders the estimation of the respective band gap from a plot of α^2 versus $h\nu$ difficult. Nevertheless, a value of 2.0 eV may be estimated for the V_2O_5 component of V590, which is in good agreement with the reported band gap²⁹ of single crystals of V_2O_5 .

The selected-area diffraction (SAED) pattern of one of the large platelets of V_6O_{13} in V570, taken along (002) is shown in Fig. 5. Also shown in the figure is the SAED pattern of a well-faceted crystallite of V_2O_5 from V580, taken along (002). It is clear from the SAED patterns that V_6O_{13} and V_2O_5 have a very similar structure in the a - b plane. (That the latter pattern is due to V_2O_5 was verified by obtaining identical SAED patterns from a number of crystallites in V_2O_5 with different, strongly faceted morphologies, which constitute V580.)

As single crystals of V_6O_{13} have been shown to undergo (upon cooling) a M-S transition at 150 K, a temperature-dependent resistance measurement of the

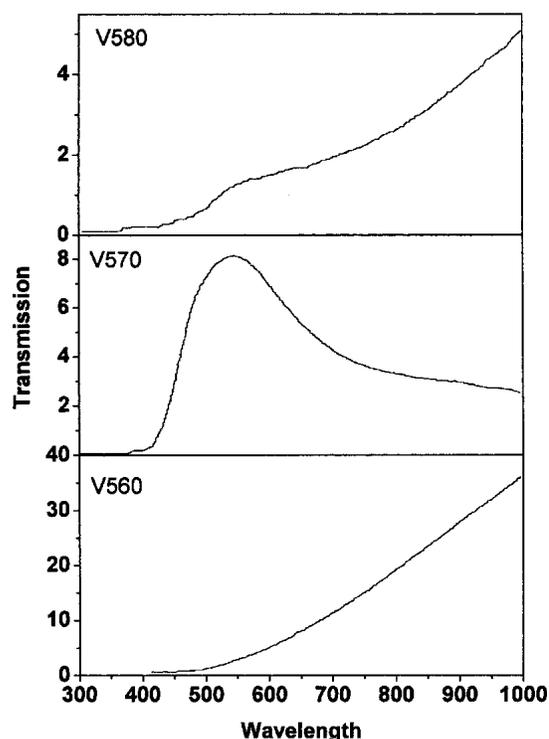


FIG. 4. Transmittance spectra of V560, V570, and V590.

film V570 consisting predominantly of V_6O_{13} , was carried out. The Arrhenius plot of resistance versus temperature is given in Fig. 6. Curiously, even though the film is composed of large, well connected, single-crystalline platelets of V_6O_{13} , no evidence of a S-M transition within the temperature range 20–300 K is observed. The film is found to be semiconducting throughout this temperature range, with a change in slope in the Arrhenius plot at about 125 K. While conduction from 300 to 125 K is characterized by an activation energy of 0.07 eV, conduction at lower temperatures has a complex dependence on temperature. Even though there is no report of electrical measurements on thin films of V_6O_{13} , the temperature dependence of the conductivity of polycrystalline V570 (though strongly oriented) may be expected to be similar to that of polycrystalline V_6O_{13} . However, unlike a sintered polycrystalline pellet of V_6O_{13} , the film V570 does not display any discontinuity in resistance at any temperature. The absence of a M-S transition at 150 K, i.e., a jump in conductivity at ~150 K in the film V570, is puzzling because it is composed of relatively large, single-crystalline platelets of V_6O_{13} , all of them aligned with the a - b plane parallel to the substrate surface, and apparently well connected; indeed, the connectivity, as observed through SEM, is well above the percolation threshold.

To unravel these intriguing features, a closer examination of the film V570 was undertaken. In particular,

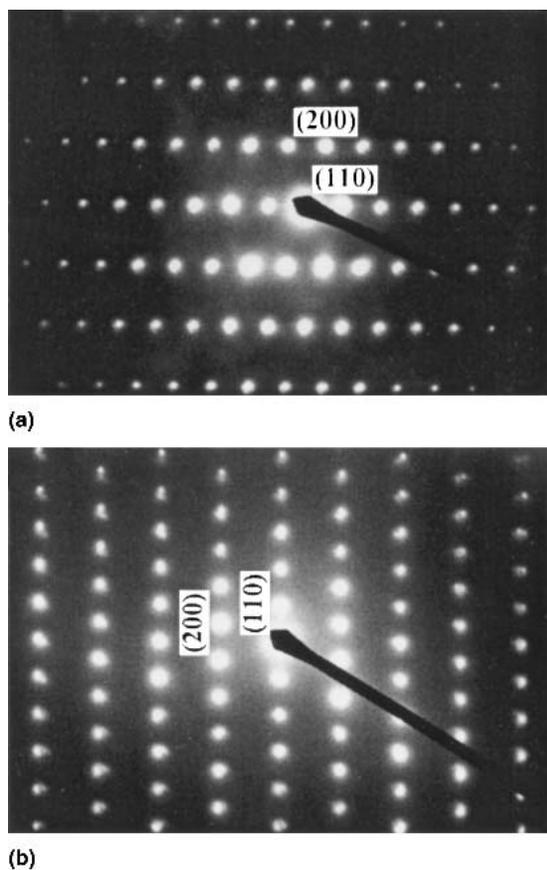


FIG. 5. SAED pattern of (a) V_6O_{13} and (b) V_2O_5 , taken along [002].

SEM analysis of the film was carried out at higher resolution. The SEM image of a segment of V570 is shown in Fig. 7. It may be seen that where two platelets of V_6O_{13} meet each other such that the edges of the platelets are “exposed,” the contrast of the image is very high: the edges are distinctly much brighter than the “inner” segments of the platelets. This suggests that the edges of the platelets might indeed be made of V_2O_5 , a large band gap semiconductor, accounting for the contrast in the SEM image. It was found by detailed SEM analysis that, at every location in V570 where platelets of V_6O_{13} meet, the edges of the platelets exhibit a sharp contrast in brightness with the “inner” portions of the platelets, suggesting the edges of all (single crystalline) platelets of V_6O_{13} had been transformed into V_2O_5 . (It was verified that the contrast in the SEM images was not an artifact of the orientation of the specimen relative to the electron beam.)

Prompted by this observation, transmission electron microscopy was used to examine the edges of the platelets in V570. Two TEM bright-field images of a large platelet of V_6O_{13} in V570, one taken at its center and the other at one edge, are given in Fig. 8, together with the corresponding SAED patterns taken along (002). Three boundaries and dislocation fringes are seen vividly at the

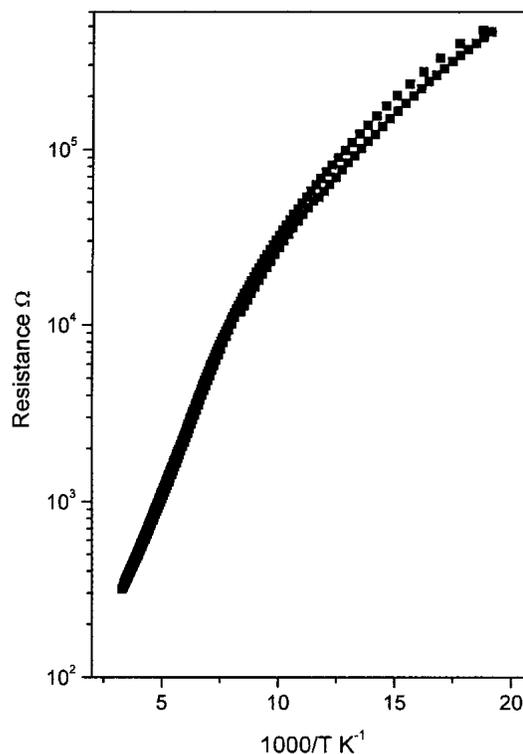


FIG. 6. Arrhenius plot of resistance of the film V570.

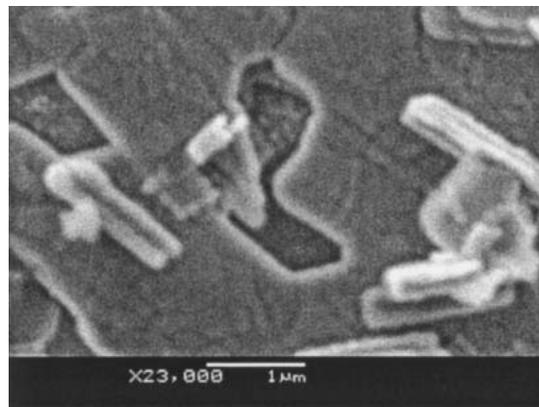


FIG. 7. SEM image of a segment of V570 at higher resolution, showing the brightness contrast between the edges and the interior of platelets.

edge [Fig. 8(c)], in contrast with the smooth interior of the platelet [Fig. 8(a)]. Further, the corresponding SAED patterns show large differences between the two regions of the platelet. The diffraction pattern of the center of the platelet is single crystalline [Fig. 8(b)]. Multiple reflections are observed at the edge [Fig. 8(d)], possibly from two or more phases present at the edge and from double diffraction (i.e., from diffraction in addition to that attributable to V_6O_{13}).

To investigate further the formation of the V_2O_5 phase at the edges of V_6O_{13} crystals, the films V560, V570, and V580 were annealed in flowing oxygen at the deposition

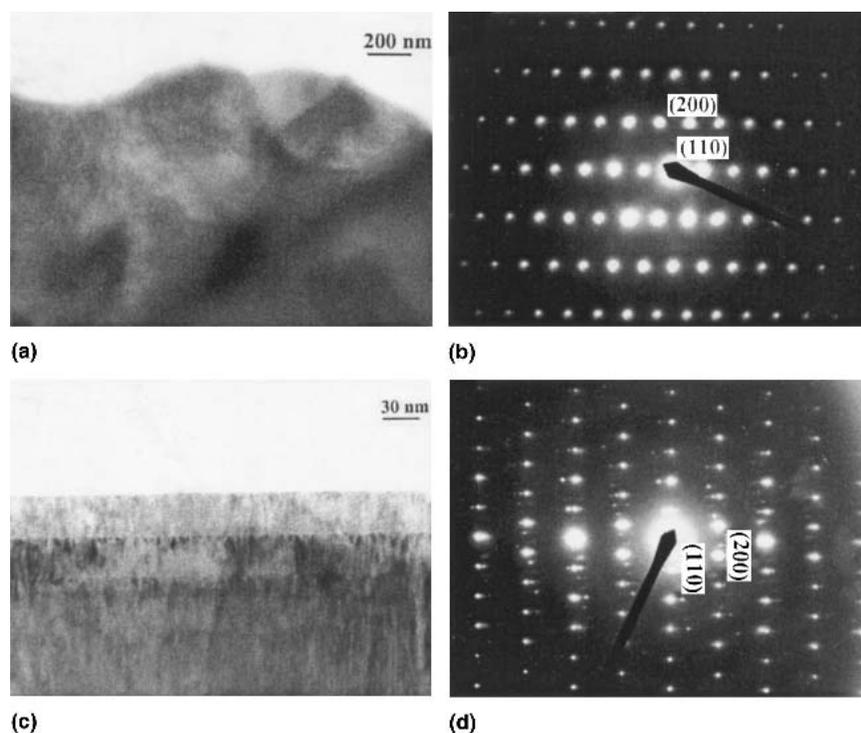


FIG. 8. TEM bright-field image and the corresponding SAED pattern taken along (002) of one of the larger platelets of V_6O_{13} in V570: (a,b) interior of the platelet, (c,d) edge of the platelet.

temperature. It is observed that the V_6O_{13} phase in the films V560 and V580, whose XRD patterns were dominated by V_2O_5 , converts completely to V_2O_5 after 20 min of annealing. However, in the sample, V570, which is dominated by V_6O_{13} , complete conversion to V_2O_5 occurs only after 90 min of annealing in oxygen ambient. However, annealing does not affect the strong (00 l) texture of the films. From this, it can be concluded that the conversion of V_6O_{13} to V_2O_5 is topotactic, consistent with the crystallographic similarities between the two phases.

IV. DISCUSSION

Preferred crystallographic orientation in thin films grown on smooth, amorphous substrates has been previously reported.³⁰ This has been explained to be a consequence of the tendency for minimization of the surface energy of the film.^{26,27} Growth occurs in such a way that the most densely packed crystallographic plane of the film material is parallel to the substrate. This reduces the surface energy, leading to strongly textured growth.^{30–32} As noted already, the a - b planes of both V_2O_5 and V_6O_{13} are made up of networks of corner-sharing octahedra, forming closely packed, dense planes. The strong (00 l) texture of the V_2O_5 and V_6O_{13} films deposited on the smooth surface of fused quartz, at temperatures in the range 560–610 °C, may be understood on the basis of

the similarly anisotropic crystal structures of the two oxides. In general, the presence of even a small percentage of a second phase can hinder the development of the microstructure (especially, texture) of the primary phase of a film. However, in the present case, the presence of V_2O_5 in V_6O_{13} (or vice versa) does not affect the oriented nature of the film because of the similar arrangement of the polyhedra in the two phases in the a - b plane. This is evident from the SAED patterns (Fig. 5) of V_2O_5 and V_6O_{13} crystallites taken along [002].

The changing phase content of the films deposited at 10 °C intervals in the range 550 to 590 °C may be represented as $(V_2O_5 + V_4O_9 + V_6O_{13}) \rightarrow (V_2O_5 + V_6O_{13}) \rightarrow (V_6O_{13} + V_2O_5) \rightarrow (V_2O_5 + V_6O_{13}) \rightarrow (V_2O_5 + V_6O_{13})$, where the bold font designates the phase dominating the XRD pattern. Between 560 and 580 °C, the phase content displays what may be termed a “reentrant-type” behavior, with V_2O_5 and V_6O_{13} being the dominant phase by turn, as illustrated schematically in Fig. 9. This may be understood from the close relationship between the crystal structures of V_2O_5 and V_6O_{13} . As noted in the introduction, the structural similarities between the two oxide phases imply that the difference between their free energies is likely to be small. This is manifest in the binary phase diagram of the V–O system, wherein the phases V_2O_5 and V_6O_{13} adjoin each other.⁶ The existence of vanadium in adjacent oxidation states (the V^{5+} state in V_2O_5 and both the V^{4+} and V^{5+} states in V_6O_{13}), and the

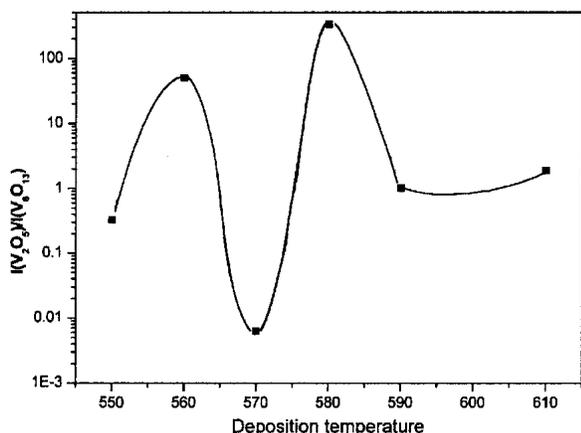


FIG. 9. Variation with growth temperature of the ratio of the intensity of the (001) peak of V_2O_5 to the intensity of the (003) peak of V_6O_{13} , the strongest of the respective XRD patterns. The solid line is as drawn as a guide to the eye, to illustrate the reentrant-type behavior in the growth of the dominant phase.

close resemblance between their crystal structures, suggests a rather facile interconvertibility between V_2O_5 and V_6O_{13} through oxidation/reduction. Indeed, such reversible conversion between V_2O_5 and V_6O_{13} in single-crystal samples has been demonstrated.⁶ This is also confirmed here, by the complete topotactic conversion of V_6O_{13} present in the films V560, V570, and V580 to V_2O_5 . Furthermore, as the metalorganic precursor used in this work, $VO(acac)_2$, contains direct V–O bonds in its molecular structure, the binary V–O phase diagram may only be useful as a rough guide to the formation of different oxides of vanadium in the MOCVD process. Given this and the complexity of the low-pressure CVD process, it may be expected that certain deposition conditions may lead to “straggling” across the “phase boundary” that demarcates regions of stability of the two vanadium oxide phases in the binary V–O phase diagram. This can account for the simultaneous deposition of vanadium oxide films deposited at different temperatures in the range 550 to 590 °C, wherein more than one oxide phase is present in each of the films. That the structures of the phases V_4O_9 , V_6O_{13} , and V_2O_5 have common features⁶ make simultaneous deposition more probable, because the free energies of these oxides may be expected to be close to one another. A similarly simultaneous deposition of two oxide phases of cobalt, CoO and Co_3O_4 , has been observed³³ in the MOCVD process employing a β -diketonate precursor of Co that contains direct Co–O bonds. Such a simultaneous deposition of two oxides of the same (transition) metal may be rationalized on the basis of thermodynamic modeling of the MOCVD process assuming that equilibrium conditions prevail during the deposition.³⁴

The reentrant-type behavior seen in the development of the XRD patterns of the films as a function of deposition temperature may be understood as follows. It is to

be recalled that the thickness of the films deposited at 560 and 570 °C is sharply lower than that of the film deposited at 550 °C. This reduction in thickness is accompanied by the development of a strong crystallographic texture in the films. At 560 °C, the XRD pattern is dominated by V_2O_5 , with a strong (001) texture whereas at 570 °C, the phase V_6O_{13} with the same (001) texture dominates. As described above [Fig. 3(c)], the film deposited at 570 °C essentially consists of large ($\sim 20 \mu\text{m}$) platelets of V_6O_{13} covering the entire fused quartz substrate, with much smaller needlelike crystallites with a bright contrast “sprinkled” on the platelets. It is therefore surmised that, at this growth temperature, the conditions are almost exactly those needed for the nucleation and growth of V_6O_{13} , to the near exclusion of V_2O_5 . Similarly, the growth conditions at 560 °C are close to those needed for the near-exclusive formation of V_2O_5 . As a result of the near exclusion of one of the two phases in the films deposited at 560 and 570 °C, the thickness of the films deposited at these two temperatures is substantially smaller than the thickness of films deposited at neighboring temperatures, either higher or lower (Table I). The films grown at 560 and 570 °C, therefore, represent the formation of nearly pure phases, with a strong (001) texture, attributable to growth on smooth amorphous (silica) substrates, and to the characteristically similar crystal structures of V_2O_5 and V_6O_{13} . That a difference of 10 °C in the growth temperature (i.e., a difference of 10 K at ~ 850 K) can lead to such a sharp change in the phase content and the microstructure of the films illustrates the closeness of the free energies of these two oxide phases of vanadium. Though striking, such “straggling” across phase boundaries, leading to unusual behavior of the type reported here, is a characteristic of the MOCVD process employing β -diketonate precursors that contain direct metal–oxygen bonds. This is especially so with a multi-valent 3d metal such as vanadium, which forms a rich variety of oxides, including those with ordered defect structures, as well as a number of oxide polymorphs (of VO_2) with the same nominal valence.²⁵

The domination of the XRD pattern of the film grown at 580 °C by (001)-oriented V_2O_5 probably has a different origin. It must be noted that, at this temperature, the film thickness is sharply higher than that at 560 and 570 °C, suggesting that significant proportions of both V_2O_5 and V_6O_{13} might have been deposited. However, a close examination of the SEM micrograph [Fig. 3(d)] of this film shows crystallites, which are much more strongly faceted than in other films. As these faceted crystallites have a bright contrast, and as the XRD pattern of this film is dominated by V_2O_5 , it is surmised that the high intensity of the (001) reflections of V_2O_5 arises from the very strong faceting of its crystallites, rather than from the exclusion of the V_6O_{13} phase altogether.

The absence of a strong (00 l) orientation in V550 is striking because the structure of V_4O_9 is also similar to those of V_2O_5 and V_6O_{13} in the a - b plane. However, a temperature lower by 10 °C may make a crucial difference in “placing” the deposition process in a regime less suitable to the formation of a dominant phase. Moreover, the lower temperature may also provide marginally lower mobility than required for the formation of a strong (00 l) texture.

At the end of the deposition process, the films were allowed cool down from the deposition temperature under the flow of oxygen (which was maintained). During this cooling, because of the oxygen available, the single crystalline platelets of V_6O_{13} relax into the thermodynamically more stable oxide, V_2O_5 . However, a complete transformation of the film (the platelets) does not occur, as the natural cooling of the CVD system rapidly brings the deposition chamber to temperatures too low for the oxidation of the edges into V_2O_5 to continue. This incomplete oxidation of V_6O_{13} accounts for the complex SAED pattern of the platelet edge (Fig. 8), which possibly consists of regions comprising V_4O_9 and V_3O_7 , in addition to V_2O_5 . It is very probable that the extreme edge is made of V_2O_5 . The anisotropy of the crystal structure of V_2O_5 [Fig. 1(c)], with relatively wide “channels” parallel to the a - b plane, leads to preferred diffusion of oxygen parallel to the a - b plane, i.e., parallel to the surface of the substrate. As such, oxidation of V_6O_{13} into V_2O_5 , initiated at the edges, proceeds inwards from the edges of the platelets in a direction parallel to the substrate surface. That is, once the edges of the V_6O_{13} platelets are oxidized to (or, relax into) V_2O_5 , these transformed edges of the platelets become preferred channels for the diffusion of oxygen, promoting the further oxidation of the “interior” of the platelets. Because of the low rate of oxygen diffusion perpendicular to the a - b plane of the V_6O_{13} platelets, the large flat faces of these platelets (parallel to the substrate) are not affected by the oxygen flow during the cool-down. This is evidenced not only by the dark contrast of the platelet faces, but also by the SAED pattern of the “interior” of a platelet, as shown in Fig. 8.

The hypothesis of the relaxation of the platelets of V_6O_{13} into V_2O_5 is supported by the occurrence of small crystallites “sprinkled” on the platelets of V570. It is observed that, while some of these small crystallites have a fully bright contrast, some are bright at the edges, with the relatively small “interior” region retaining the dark contrast (Fig. 7). As the perimeter-to-volume ratio is high for a small V_6O_{13} platelet, the diffusion of oxygen into it is greater, leading to the oxidation of a comparatively large proportion of it into V_2O_5 . Indeed, some platelets of V_6O_{13} relax fully into V_2O_5 . As these V_2O_5 crystallites, too, have the (00 l) orientation, the XRD pattern of V570 contains (00 l) reflections due to V_2O_5 , much weaker than

those due to V_6O_{13} . The proposed hypothesis is further supported by the differing durations of annealing required for the complete (topotactic) conversion of the samples V560, V570, and V580. While a 20-min anneal sufficed to convert V560 and V580 to V_2O_5 , an annealing duration of as much as 90 min was required to convert V570 completely into V_2O_5 . (Such conversion into V_2O_5 was confirmed by the determination of the optical bandgap at 2.0 eV, which corresponds closely to that of V_2O_5 . These converted films were too resistive for R versus T measurements.) This difference in the annealing times required is consistent with the higher proportion of V_6O_{13} present in V570, necessitating a longer annealing duration for complete oxidation. Furthermore, as noted above, the diffusion of oxygen occurs preferentially along the plane parallel to the substrate, in which direction the crystallite dimension is large (~20 μ m) compared to its dimension perpendicular to the substrate surface (~0.5 μ m, the film thickness).

It is likely that the sample V570, as deposited, comprised entirely of V_6O_{13} . To have retained the integrity of the monophasic sample, it would have been necessary to cool the sample down not in flowing oxygen, but in an appropriate buffering mixture of gases (such as H_2/H_2O). In such a mixture, the oxygen partial pressure varies as a function of temperature in such a way as to be consistent with the maintenance of the integrity of the desired phase.³⁵ However, a detailed, accurate binary V:O phase diagram would be needed to choose the correct buffering gas mixture, given the narrow range of stability of a phase such as V_6O_{13} .

The transformation of the edges of the single crystalline platelets of V_6O_{13} to semiconducting V_2O_5 , detailed above, can account for the observed electrical behavior of V570. Even though the film is made of well-connected platelets of V_6O_{13} , the connection takes place between adjacent platelets at their edges, which have relaxed into V_2O_5 . (The electrical behavior of V_3O_7 and V_4O_9 is not known. We assume that they are semiconducting, just as V_2O_5 .) Thus, the metallic behavior of V_6O_{13} observed in single crystals is suppressed in the film V570, even though it is made of highly oriented single crystalline platelets of V_6O_{13} . However, the M-S transition in V_6O_{13} is evidenced in the change in slope of the Arrhenius plot of the resistance of V570 (Fig. 6). The resistivity of V570 at low temperatures is complex, and may be attributed to the intricate composition of the edges of the platelets, as established by TEM.

Based on this understanding of the electrical behavior of the film V570 that is predominantly made of V_6O_{13} , we have attempted to interpret the reported³ electrical properties of sintered, polycrystalline V_6O_{13} . The semiconducting nature of this specimen at room temperature is likely to have been due to the relaxation of the surface of the pellet (during cool-down) to V_2O_5 , to which

electrical contacts are effectively made. However, the interior of the pellet probably remained metallic V_6O_{13} . Given that the pellet was 0.3 mm thick, and assuming a thin outer layer of V_2O_5 , the temperature dependence of the conductivity of this composite may be expected to show a very small E_a , in contrast with reported³ value at room temperature of 0.42 eV. As this is much larger than the $E_a = 0.07$ eV measured in V570 at room temperature, we examined the conductivity versus temperature data of Kachi et al.³ and computed the E_a using these data. The value of E_a is found to be 0.02 eV at room temperature, and 0.01 eV at low temperatures. These much smaller values are consistent with our hypothesis that the sintered pellet of Kachi et al.³ consisted of metallic V_6O_{13} enveloped in an ostensibly thin outer layer of V_2O_5 , formed due to relaxation during the cooling of the pellet after it was sintered. The re-computed E_a of this sintered pellet at low temperature (0.01 eV) is consistent with the value of E_a (~0.03 eV) calculated from the data of Kawashima et al.² for single-crystalline V_6O_{13} below the M-S transition temperature. This supports the conjecture that the surface of the pellet had relaxed into V_2O_5 , within which the bulk of the metallic V_6O_{13} was embedded.

V. SUMMARY AND CONCLUSIONS

Strongly (00 l)-oriented composite films of V_2O_5 and V_6O_{13} have been grown on fused quartz at temperatures ≥ 560 °C by MOCVD. Such textured growth stems from the tendency for minimization of interfacial energy when growth occurs on a smooth, amorphous substrate. Films grown below 560 °C are composed of a mixture of V_2O_5 , V_6O_{13} , and V_4O_9 , with no tendency for any preferred orientation. When the growth temperature is increased from 560 to 580 °C in steps of 10 °C, a reentrant-type behavior in the dominant phase of the film alternating between V_2O_5 and V_6O_{13} is observed, as evidenced by XRD and RBS analyses. Such a growth trend is related to the close relationship between the crystal structures of V_2O_5 and V_6O_{13} , which, in turn, is reflected in the proximity of the two oxide phases on the binary V–O phase diagram. It is proposed that the intriguing reentrant-type growth stems also from the nature of the growth process that employs a precursor with built-in V–O bonds. These factors combine to make the range of conditions in which either pure V_2O_5 or pure V_6O_{13} is deposited extremely narrow, rendering the formation of a thin film composite of the two phases more probable than not. Resistance measurements of the film dominated by strongly oriented and highly connected single crystalline platelets of V_6O_{13} show no evidence for S-M transition known to occur in single crystals of V_6O_{13} at 150 K. Instead, the film undergoes a semiconductor-to-semiconductor (S-S) transition. This may be understood from the (unintended)

oxidation of the edges of V_6O_{13} platelets to V_2O_5 during the cool-down to room temperature, as observed by SEM and confirmed by TEM. As such, the platelets of metallic V_6O_{13} are in fact connected to one another through semi-conducting V_2O_5 , suppressing the S-M transition, and resulting in a S-S transition. The transformation of the edges to V_2O_5 is the result of the relaxation of crystallites of V_6O_{13} into the thermodynamically more stable V_2O_5 , which occurs during the postdeposition cooling of the films to room temperature. Such a relaxation/transformation explains the previously reported observation of a S-S transition in polycrystalline V_6O_{13} material, rather than a S-M transition. Indeed, the electrical data on our thin films help reconcile the measurements on sintered V_6O_{13} . The topotactic conversion of all samples into (00 l)-oriented V_2O_5 through post-deposition annealing in oxygen is consistent with these observations. The results presented here, therefore, point to the importance of controlling the conditions under which oxide films and oxide ceramics are cooled from their formation temperature, and has implications for the stability of the composition and properties of transition metal-containing films/fine particles, because of their large surface area/volume ratio. Thus, the present study presents a coherent picture of the close relationship between the binary phase diagram of a transition metal–oxygen system, and the CVD of thin films of the oxides of the metal from precursors containing metal–oxygen bonds.

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