CONF-950412--48

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Structure & Properties of Multilayered Thin Films
Spring 1995 Materials Research Society Meeting

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April 1995

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prepared by
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Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, Tennessee 37831-6056
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC
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under contract DE-AC05-84OR21400

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THE FORMATION Al_2O_3/V_2O_3 MULTILAYER STRUCTURES BY HIGH-DOSE ION IMPLANTATION

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ABSTRACT

High-resolution TEM, RBS-channeling and x-ray-diffraction techniques have been used to characterize multilayered structures formed by the high-dose co-implantation of vanadium and oxygen into single crystals of α-Al_2O_3. Thin, two-dimensional multilayered structures have been formed by implanting *c* -axis and ***a*** -axis-oriented single crystals of Al_2O_3 at room temperature with vanadium (10^{17} ions/cm^2 at 300 keV) and oxygen (2 X 10^{17} ions/cm^2, 120 keV) followed by a rapid anneal at 1000°C. Cross-sectional TEM studies showed that this process produced a buried layer of V_2O_3 located about 120 nm below the Al_2O_3 surface. X-ray-diffraction investigations revealed that this layer is epitaxially oriented in three dimensions with respect to the host Al_2O_3 lattice. The orientational relationship was subsequently confirmed by RBS/channeling techniques. V_2O_3 exhibits a first-order phase transition at about 155 K that is accompanied by striking changes in its electrical and optical properties, and this phase transition was observed through in-situ TEM cooling studies of cross-sectional samples.

1. INTRODUCTION

Vanadium sesquioxide V_2O_3, undergoes a thermally-induced crystallographic phase transition that is accompanied by large changes in its electrical and optical properties [1,2] at a temperature of about 155 K. The temperature of the phase-transition may vary depending on the form of V_2O_3 (e.g. bulk crystal or film) and on the processing method employed in the growth of thin films [3]. V_2O_3 has a narrow homogeneity range [4]. It is monoclinic below the phase transition temperature and has the pseudo-hexagonal corundum structure above the transition temperature. It has been previously shown by the present authors that it is possible to form buried V_2O_3 precipitates in Al_2O_3 by high-dose co-implantation of vanadium and oxygen followed by rapid thermal annealing [5]. This process has been shown to result in the production of V_2O_3 precipitates that are crystallographically coherent with respect to the host Al_2O_3 lattice thus allowing the formation of Al_2O_3/V_2O_3 multilayer systems. However, due to the excess of implanted oxygen (oxygen fluence / vanadium fluence = 2) and the rapid thermal annealing (room temperature to 1000 °C in less than 2 mins.), the resulting crystal surfaces were not of good quality. Here we report the formation of similar multilayer structures that are characterized by an improved surface quality. Furthermore, the effect of the crystallographic orientation of the sapphire substrate on the formation of such layers is investigated. The results of TEM investigations of the implantation-produced structures that are present both below and above the phase transition temperature are also described.

2. EXPERIMENTAL

The V and O co-implantations at room temperature were made into *c* -axis and ***a*** -axis-oriented α-Al_2O_3 single crystals that had been optically polished and subsequently annealed in flowing O_2 for 5 days at 1350 °C in order to remove damage due to the polishing process. Then, implantation with V ions was performed at room temperature at an energy of 300 keV and a fluence of 10^{17} ions/cm^2. Co-implantation with oxygen ions was performed at 120 keV (at room temperature and a fluence of 2 X 10^{17} ion/cm^2), so that both the implanted vanadium and oxygen were located at the same depth in the Al_2O_3 crystal. Thermal annealing of the co-implanted Al_2O_3 specimens was carried out at 1000 °C for 30 min. in a reducing atmosphere (4% H_2 in

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Ar). The implanted surfaces were analyzed using Rutherford backscattering (RBS)/channeling techniques in order to determine the V distribution and lattice damage. X-ray-diffraction techniques and cross-section transmission electron microscopy (TEM) were employed in determining the precipitate relative orientation, composition, and structure. The phase transformation near 155K was observed using a Gatan-single tilt cooling holder in a Philips 420 electron microscope. The X-ray diffraction measurements were performed using a rotating-anode Cu K_α source, a focusing LiF monochromator, and a Huber four-circle diffractometer.

3. RESULTS

3.1 Formation of V_2O_3 precipitates in sapphire

Co-implantation of α-Al_2O_3 with vanadium and oxygen at energies of 300 and 120 keV produces a buried amorphous layer at a depth of about 160 nm, which corresponds to the location of the implanted V and O ions. Rapid thermal annealing in a reducing atmosphere (Ar with 4% H_2 in argon), produces a significant reorganization of the material (Figure 1a) ; i.e., the channeling yield is indicative of a partial recrystallization of the layer. A significant surface roughness is produced by this process - as evidenced by the presence of "craters" or pits associated with the formation and subsequent breaking of oxygen "blisters". These surface defects are responsible, at least in part, for the observed relatively low RBS/channeling yield. Also, numerous cavities and defects which were observed by cross-section TEM can account for the imperfect recrystallization. XRD and TEM results, however, clearly show the presence of V_2O_3 precipitates that are three-dimensionally oriented with respect to the sapphire lattice, i.e. precipitates that have recrystallized from the amorphous/highly damaged state to the corundum form of V_2O_3. The observed structures are schematically represented in Figure 2.

In order to improve the surface quality of the implantation-produced multilayers, other V and O-implanted samples were introduced into a cold furnace that was subsequently heated to 1000 °C at 3 °C/min. Observations of the resulting surface by optical microscopy showed no evidence of broken surface blisters. Accordingly, the RBS analysis (Figure 1b) of these samples yielded significantly different results as compared to those shown in Figure 1a. From the surface to about 100 nm, the sapphire lattice is almost perfectly recrystallized (channeling yield of 7 %). The backscattered yield then increases from a depth of 100 nm with a peak occurring at a depth of about 150 nm. This depth corresponds to the peak concentration of the vanadium distribution. This result suggests that significant distortions occur in this particular zone. The vanadium distribution is similar to that shown in Figure 1a, indicating that the heating rate has no effect on the shape of distribution of the implanted atoms. However, in the case of the slow annealing rate, defects are more likely to recombine, thereby inhibiting the trapping of oxygen in defect clusters. Furthermore, XRD shows that V_2O_3 precipitates are also formed which are three-dimensionally oriented with respect to the sapphire substrate. The lattice parameters for V_2O_3 do not differ significantly from the values observed for rapidly heated samples (Table I).

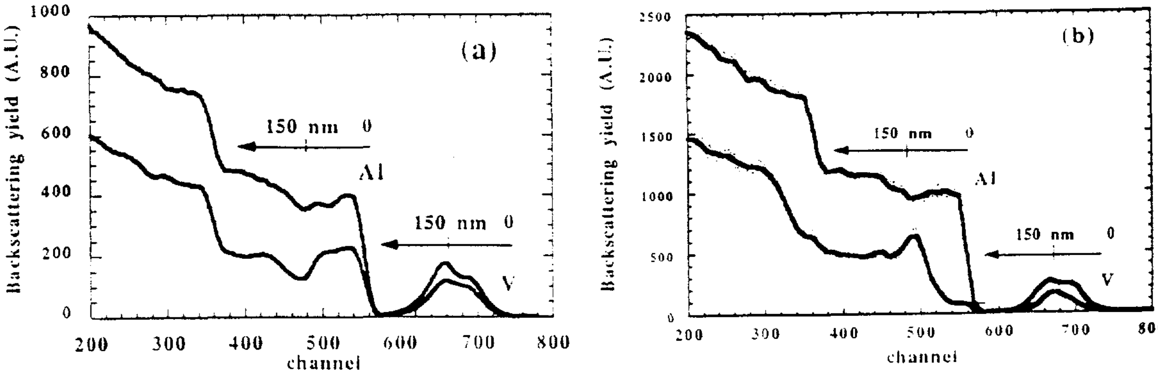

Figure 1 : RBS of Al_2O_3 co-implanted with V and O : (a) rapid anneal (b) slow anneal

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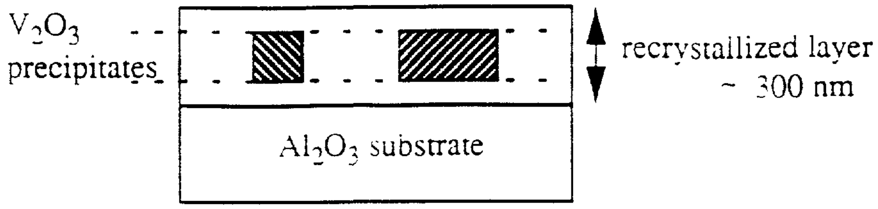

Figure 2 : Schematic of the multilayer system

3.2 Influence of the crystallographic orientation of the substrate on the formation of Al_2O_3/V_2O_3 multilayers

The effect of the crystallographic orientation of the substrate was studied by co-implanting a (110)-oriented sapphire crystal under the same conditions as those described above - followed by a rapid thermal anneal. The RBS spectrum is very similar to that obtained for the c-axis-oriented sapphire (Figure 1a). In particular, the vanadium distributions are similar, indicating no effect of the crystallographic orientation of the sapphire substrate on the vanadium diffusion due to thermal annealing. The XRD results for (110)-oriented Al_2O_3 substrates are presented in the next paragraph in comparison with the results obtained previously for c-axis-oriented sapphire.

3.2.1. Phase formation in (110)-oriented Al_2O_3

In agreement with the RBS results, XRD analysis also shows that V_2O_3 precipitates form in (110)-oriented sapphire and that they are three-dimensionally aligned with respect to the sapphire substrate. Details of the lattice parameters, precipitate size, and orientational relationships with respect to the substrate are given in Table I.

For each orientation, two types of domains coexist. For (001)-oriented sapphire, both domains are present in about the same proportion. For (110)-oriented sapphire, the second domain is present in a reduced percentage.

3.2.2 Lattice parameters of the embedded precipitates

In both orientational cases, the lattice parameters of the V_2O_3 precipitates are different from the bulk values presented in the powder diffraction files. The measured ***c*** parameter is smaller by - 0.8%, while for the ***a*** parameter, a difference of + 0.6 % is found.

***Table I** : XRD Results of V_2O_3 precipitate formation in (001) - and (110) - oriented sapphire (rapid heating)*

precipitates	(001) Al_2O_3 substrate	(110) Al_2O_3 substrate
main domain	**(001) V_2O_3 // (001) Al_2O_3** **(3D orientation)**	**(110) V_2O_3 //(110) Al_2O_3** **(3D orientation)**
secondary domain	(110) V_2O_3 // (001) Al_2O_3	(012) V_2O_3 //(110) Al_2O_3
precipitate size	38 nm	25-30 nm
lattice parameters of V_2O_3 main prec. (mismatch / Al_2O_3)	c= 13.9 Å (7%)	**c= 13.845 Å (6.6%)** a = 4.986 Å (4.8%)
bulk lattice param. of V_2O_3 (JCPDS)	**c = 14.008 Å** (mismatch /Al_2O_3 = 8%) a =4.954 Å (mismatch / Al_2O_3 = 4%)	

Table II : Thermal expansion coefficients of V_2O_3 and Al_2O_3

	α thermal expansion coefficient ($10^{-6}K^{-1}$)			
	Al_2O_3		V_2O_3	
direction	// a axis	// c axis	// a axis	//c axis
300K	5.4	5.4	20.2	- 8.6
1300K	10.4	9.7	8.3	- 2.4
[REF]	6	6	7	7

Both extrinsic stress and intrinsic stress may account for such differences. Extrinsic stress is related to the difference between the thermal expansion coefficients of the precipitate and the substrate and is the major source of stress in thin-film growth. The thermal expansion coefficients α for sapphire and vanadium sesquioxide are given in Table II.

From these values, we can determine the sign of the thermal stress (tension or compression) of a vanadium oxide precipitate in sapphire, as the system is cooled from 1273 K to room temperature. In the following discussion, only the main precipitates are considered ie only those with the following orientations : (110) V_2O_3 // (110) Al_2O_3.

Along the ***c*** -axis direction (parallel to the surface), the thermal expansion coefficients of sapphire and vanadium sesquioxide are opposite in sign. As the system cools down, the V_2O_3 precipitate will expand along the (001) direction while the substrate will shrink : thus, the precipitate will be in compression along the (001) direction. Compression along the (001) direction is expected to induce a modification in the value of *c* . From the values given in Table I, it can be seen that the measured *c* value is smaller than that of the bulk value. This is consistent with the precipitate being in compression along the c-axis (Fig. 3).

A consideration of the role of thermal expansion in the formation of the precipitates allows us to account for the observed deviations of the lattice parameters relative to the bulk values normally obtained from an X-ray powder diffraction pattern. However, the lattice parameters of V_2O_3 can be affected by another type of stress [8]. Intrinsic stress is related to the precipitate itself and can arise from oxygen non-stoichiometry, impurity substitution, grain boundaries, lattice coherence and other sources. V_2O_3 normally forms in a relatively narrow compositional range and deviations from stoichiometry are possible, but it appears that the formation of precipitates under the solid-state chemical conditions represented by the Al_2O_3 host favors the formation of the V_2O_3 phase. This phase formation occurs even though excess oxygen was implanted in the present case, and the excess oxygen atoms oxygen atoms tend to agglomerate to form clusters upon thermal annealing. As the system cools down from the process temperature, and the vanadium sesquioxide precipitate grows, some aluminum atoms from the matrix may be incorporated in the precipitate in substitutional sites. It is difficult, however, to determine to what extent this process is likely to occur. Aluminum substitution in vanadium oxide (i.e. a solid-solution formation of aluminum oxide and vanadium oxide) has previously been shown to induce a change in the lattice parameters of vanadium oxide and lead to an increase in the volume of the unit cell [1]. However, the direction of the changes (reduction/ increase of ***a*** and ***c***) is not documented.

The lattice mismatch between the precipitates and the substrate is significant. As a consequence, one might expect a relatively high concentration of defects at the interface - including dislocations or grain boundaries inside the precipitate itself. Although it is difficult to

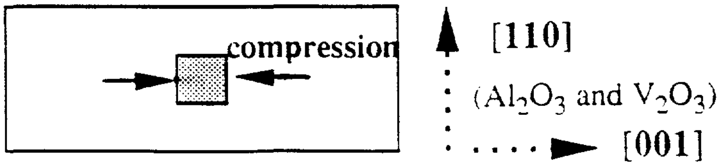

Figure 3 *: sign of the thermal stress of the V_2O_3 precipitates in (110) oriented sapphire*

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Figure 4a : Cross-section TEM of a V_2O_3 precipitate at 240 K

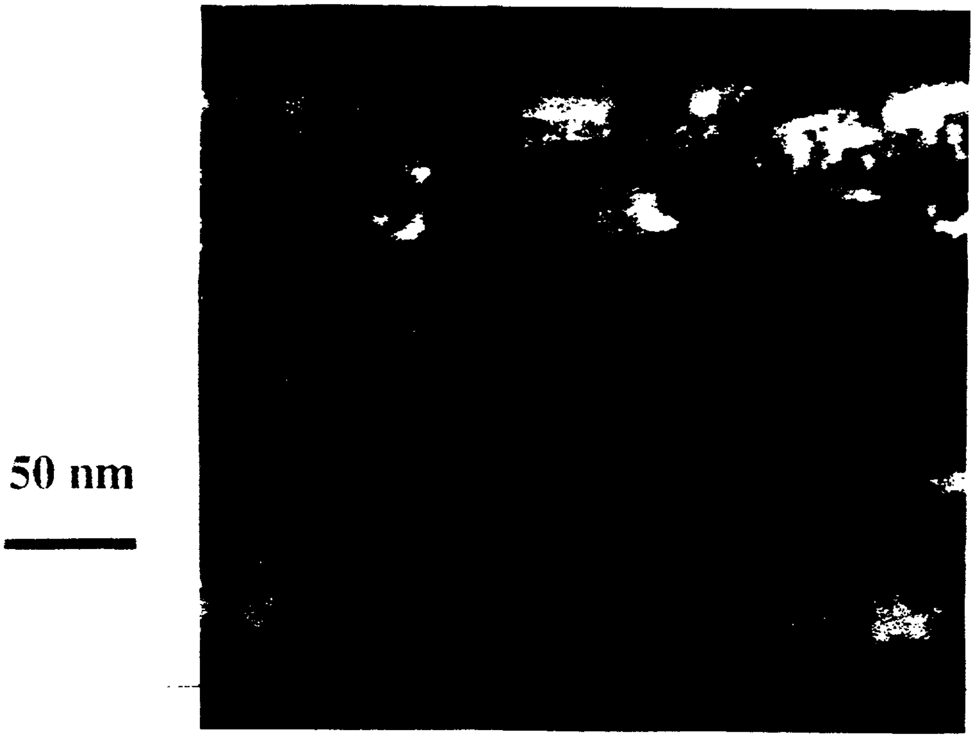

Figure 4b : Cross-section TEM of a V_2O_3 precipitate at 120 K

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determine its relative role vis-a-vis other possible interactions, the effect of extrinsic stress resulting from the difference in thermal-expansion coefficients of V_2O_3 and Al_2O_3 is sufficiently important that stress is likely to be one of the significant parameters in modifying the lattice constants of embedded V_2O_3 precipitates. As a consequence, the stress state of the precipitate is likely to influence the phase transition of V_2O_3 upon cooling through the transition temperature. Published data report a change in the transition temperature of single crystals of V_2O_3 under either stress or hydrostatic pressure - as well as a change in the magnitude of the electrical and optical properties [7, 8]. On the other hand, adding an insulating oxide (e.g. Cr_2O_3) to the metallic room -temperature phase of V_2O_3 has been shown to inhibit the crystallographic transformation of bulk V_2O_3. One might expect similar behavior with the addition of Al_2O_3 to V_2O_3, i.e. with Al substitution in V_2O_3.

3.3 TEM observations of the buried V_2O_3 phase in sapphire

Figure 4a represents a TEM micrograph of a three-dimensionally aligned precipitate of V_2O_3 in (001)-oriented Al_2O_3. The precipitate is about 1 µm in length and 70 nm thick and lies parallel to the surface at a depth of about 100 nm. The size of the precipitate as measured on the micrograph is significantly larger than the average size of 38 nm obtained from the XRD investigations. However, the precipitate shown on the micrograph is clearly not a single crystal. The darker lines that cross the precipitates indicate the presence of grain boundaries. Furthermore, the size as given by the XRD data represents a coherence length which, in fact, gives the average size of the coherent planes - free of defects. Clearly the material is not defect-free ; in the region near the interface numerous dislocations are visible. Both grain boundaries and dislocations may account for the observed lattice mismatch as discussed in the preceding paragraph. The use of a cold stage has allowed us to follow the precipitate as it cools down through the phase-transition temperature. Reproducible changes were observed which occurred at a temperature of 155 K. Figure 4b represents the same precipitate (the sample has been slightly translated) at a temperature of 120 K. The grain boundaries that were visible at higher temperatures are now difficult to observe at low temperature. Furthermore, some alignment phenomena have occurred along the direction parallel to the sample surface. This result seems to be in agreement with the movement of atoms as expected along the basal plane of the high temperature hexagonal phase of V_2O_3 that is produced on cooling the material through the phase transition [1, 9].

4. SUMMARY AND CONCLUSIONS

The present results show that the formation of three-dimensionally oriented V_2O_3 precipitates by co-implantation and annealing in sapphire is essentially independent of the crystallographic orientation of the sapphire substrate. Furthermore, the lattice-parameter values of V_2O_3 (***a*** and ***c***) as obtained by XRD differ from the bulk values (JCPDS 34-187) : ***a*** is larger than the bulk value while ***c*** is smaller. Thermal-stress considerations indicate that the V_2O_3 precipitates in (110)-oriented sapphire are in compression along the ***c*** -axis (parallel to the surface) - accounting, at least in part, for the difference between the measured values for the precipitates and the bulk values. The crystallographic transition of the V_2O_3 precipitates has been observed by TEM as the sample was cooled from room temperature to temperatures below the transition temperature of 155 K. The variation in the optical properties, which occurs at the transition of these systems, is currently under investigation.

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