COHERENT V_2O_3 PRECIPITATES IN α - Al_2O_3 CO-IMPLANTED WITH VANADIUM AND OXYGEN

LAURENCE A. GEA, L. A. BOATNER, JANET RANKIN*, AND J. D. BUDAI

Solid State Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831.

*Brown University, Providence, RI 02912

ABSTRACT

The oxides of vanadium VO_2 and V_2O_3 are of fundamental and practical interest since they undergo structural phase transitions during which large variations in their optical and electronic properties are observed. In the present work, we report the formation of buried precipitates of V_2O_3 in sapphire by ion implantation and thermal annealing. It was found that the co-implantation of oxygen and vanadium was required in order to form nanophase V_2O_3 precipitates. Additionally, these precipitates, which formed only following an anneal of the co-implanted sample under reducing conditions, are coherent with the sapphire lattice. Two epitaxial relationships were observed: $(0001)V_2O_3// (0001)\alpha-Al_2O_3$ and $(11-20)V_2O_3// (0001)\alpha-Al_2O_3$. This finding is in agreement with results obtained elsewhere for thin films of V_2O_3 deposited on c-axis-oriented sapphire.

I. INTRODUCTION

Several oxides of vanadium are known to exist due to the relatively large number of possible valence states characteristic of this element. Two of the commonly occurring oxides, VO_2 and V_2O_3 , undergo a temperature-induced crystallographic phase transition that is accompanied by large changes in their electrical and optical properties [1,2], and correspondingly, these changes represent the physical basis for a number of vanadium-oxide-based devices [3]. The oxide V_2O_3 , which has a narrow homogeneity range [4], is monoclinic below the phase transition temperature ($\sim 150^\circ C$) and has the hexagonal corundum structure above the transition temperature. Preparation methods and associated characterization results have been reported previously for both bulk [5] and thin-film forms of V_2O_3 . Thin films of V_2O_3 have been formed using sputtering [6], electron-beam deposition [7], and sol-gel processes [8], and the characteristics of these films have been shown to depend on the particular deposition technique employed. The purpose of the present investigation is to form and characterize buried nanophase V_2O_3 precipitates in Al_2O_3 , and presumably, such clusters may also exhibit property variations that depend on the specifics of the formation methods employed. Here, the highly non-equilibrium process of V and O ion co-implantation is employed in conjunction with subsequent thermal annealing under slightly reducing conditions in the formation of vanadium oxide precipitates. This process is shown to result in the production of V_2O_3 precipitates that are crystallographically coherent with respect to the host Al_2O_3 lattice.

Ion-implanted single crystal Al_2O_3 or sapphire has been the subject of numerous previous studies (for a review, see Ref. [9]). These investigations have shown that the non-equilibrium nature of ion implantation can lead to the formation of unexpected phases in Al_2O_3 and that the solid solubility of the implanted ion plays an important role in determining the characteristics of the implanted region. For some ionic species that are ion implanted into sapphire, a significant loss of the implant is reported following a thermal anneal. In the case of high-dose implants, the ion-beam-damaged Al_2O_3 lattice is observed to recrystallize (amorphous $\rightarrow \gamma$ phase $\rightarrow \alpha$ phase) as the annealing temperature is raised above $1000^\circ C$ [10], and in such cases, the distribution of the implanted species during annealing has been shown to be governed by this epitaxial regrowth process [11]. If the solubility of the implanted ion is high (as in the case of Cr [12]), one may observe the formation of a solid solution or the formation of precipitates [13]; if the solubility is low, the implanted ions may diffuse to the front surface of the sample along with the epitaxial recrystallization interface of the host lattice (at least in those cases where the ion-damaged layer extends to the sample surface.)

Preliminary studies [14] indicated that vanadium implanted at high fluences (10^{17} ions/cm²) into α - Al_2O_3 diffuses out of the implanted layer during thermal anneals (in the

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temperature range of 900 to 1100 °C) in an oxygen ambient, and losses of up to 70% of the implanted V ions were observed. In order to enhance the retention of V in ion-implanted sapphire, co-implantation of oxygen and vanadium was utilized. Using this approach, and by employing appropriate annealing conditions, it was possible to form crystallographically coherent precipitates of V_2O_3 in the (0001) near-surface region of α - Al_2O_3 . Details of this process and of the characteristics of the modified surface layer are given in the following sections.

2. EXPERIMENTAL

The V and O co-implantations were made into c-axis-oriented α - Al_2O_3 single crystals that were optically polished and then, prior to implantation, annealed in flowing O_2 for 5 days at 1350 °C in order to remove damage due to the polishing process. Implantation with V ions was performed at room temperature at an energy of 300 keV and a fluence of 10^{17} ions/cm². Co-implantation with oxygen ions was performed at 120 keV (at room temperature and a fluence of 2×10^{17} ion/cm²), 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 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 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 Co-Implantation and Annealing - Formation of V_2O_3 Precipitate

The RBS spectra of α - Al_2O_3 co-implanted with vanadium and oxygen at energies of 300 and 120 keV respectively are shown in Fig. 1(a). The distribution of the vanadium ions is gaussian with a mean projected range of 150 nm - in good agreement with theoretical predictions given by the TRIM code [15]. The RBS results clearly show that V/O co-implantation produces a significant amount of damage in the near-surface region of the sapphire crystal. Channeling and rotating-random RBS yields for aluminum overlap over the space of several channels, indicating that a buried amorphous layer was formed at a depth of about 160 nm, which corresponds to the location of the implanted V and O ions. Annealing in a reducing atmosphere (Ar with 4% H_2 in argon), produces a significant reorganization of the lattice (figure 1b). The dechanneling yield for the Al RBS signal is about 50% and fairly constant. The drop in the aluminum yield, which is visible at a depth corresponding to the location of the vanadium atoms, suggests that the vanadium-rich region is also ordered. The distribution profile of the vanadium atoms exhibits a slight evolution, and the distribution is wider than in the as-implanted state.

Observations of the sample surface with an optical microscope reveal that the annealed surface is not flat but, in fact, exhibits a high density of small pits or "craters" (diameter ~ 15 μ m and a depth of ~15 to 60 nm). These surface features are separated by about 40 μ m. Some of the "craters" are partially covered with a thin layer of surface material indicating that they resulted from the breaking of surface blisters. Such surface features are likely to influence significantly the RBS spectra, however, a substantial fraction of the vanadium atoms is clearly substitutional in the Al sublattice. This substitution, together with the relatively good crystallization of the surface, suggests that a phase containing some vanadium that is oriented with respect to the sapphire lattice has formed. X-Ray-diffraction experiments were subsequently performed to investigate the existence of such a phase. Figure 2 shows the θ -2 θ scan of the annealed, co-implanted sample and provides clear evidence of the formation of the V_2O_3 phase. Two peaks at angles $2\theta = 36$ degrees and 38.9 degrees, corresponding to (11-20) V_2O_3 and (0006) V_2O_3

Figure 1(a) : V and O co-implanted in Al_2O_3

Figure 1(b) : Al_2O_3 co-implanted and annealed

Figure 2 : V and O co-implanted in (0001) Al_2O_3

respectively, and a third peak at $2\theta = 41.7$ degrees, corresponding to $(0006)\text{Al}_2\text{O}_3$, are visible on the same scan. This indicates an orientational relationship between two orientations of V_2O_3 precipitates and the Al_2O_3 host crystal. Furthermore, the X-ray rocking curves (not shown) are consistent with a three-dimensional orientational relationship for both types of V_2O_3 precipitates with respect to the substrate. A normalization of the X-ray intensities indicates that both (0001) and $(11-20)$ orientation of V_2O_3 are present in similar amounts. Lattice parameters of the hexagonal lattice of V_2O_3 were also determined as: $a = 4.997 \text{ \AA}$ from the $(11-20)$ V_2O_3 peak and $c = 13.9 \text{ \AA}$ from the (0001) V_2O_3 peak. These parameters are different from the values obtained from a powder pattern analysis ($a = 4.954 \text{ \AA}$ and $c = 14.0083 \text{ \AA}$): i.e., the value for a is larger by 1%, and the value for c is also smaller by 1%. This suggests that the precipitated V_2O_3 is either not pure or is not in its equilibrium (unstrained) state. In fact, similar values for lattice parameters have been obtained for bulk V_2O_3 containing chromium impurities [1]. These values are also in good agreement with the lattice parameters for V_2O_3 at a temperature of 600 K [1]. The fact that only $\alpha\text{-Al}_2\text{O}_3$ is present in the layer indicates that $\alpha\text{-Al}_2\text{O}_3$ has epitaxially recrystallized from the amorphous or highly damaged state. The room-temperature phase of V_2O_3 has the hexagonal corundum structure, which is consistent with some of the V_2O_3 precipitates having their c -axis aligned with the c -axis of sapphire. The presence of the $(11-20)$ precipitates aligned with the c axis of sapphire is more surprising; however, such a relationship has been noted previously [8] for V_2O_3 films grown on c -axis sapphire and attributed to the low mismatch (4%) between some ionic positions on the two types of planes. Because the V_2O_3 precipitates are epitaxial with respect to the $\alpha\text{-Al}_2\text{O}_3$ lattice, one would expect a relatively low RBS/channeling yield. Residual defects such as cavities [10] are, however, likely to be found in the recrystallized layer, and clearly, the phase formation is not homogeneous, as evidenced by the presence of broken blisters on the sample surface.

Cross-section TEM experiments confirm the results described above. Figure 3 shows a TEM micrograph of the interface between the $\alpha\text{-Al}_2\text{O}_3$ sub lattice and a V_2O_3 precipitate that is 70 nm thick and about 1 μm long and lies parallel to the surface near the middle of the implanted layer (thickness 250 nm). The epitaxial relationship is clearly evident in this micrograph. A difference between the lattice parameters of Al_2O_3 and V_2O_3 is also observed, in good agreement with the results obtained using X-Ray diffraction analysis ($a = 4.997 \text{ \AA}$, $c = 13.9 \text{ \AA}$) and the lattice parameters of sapphire ($a = 4.758 \text{ \AA}$, $c = 12.991 \text{ \AA}$). Investigation of another region of the same sample (not shown) reveals the presence of smaller precipitates in the vicinity of a hole representing a broken surface blister.

3.2 Parameters Influencing the Formation of V_2O_3

In the case of impurities with various possible valence states such as vanadium, the annealing atmosphere is frequently a determining factor in the phase-formation process. In order to investigate the influence of this parameter, samples were annealed in pure oxygen for 30 minutes. In this case, however, no evidence of the V_2O_3 phase was found from the XRD measurements. Moreover, RBS analysis showed that vanadium had diffused to the sample surface resulting in a V loss of about 20%. This influence of the pure O_2 annealing atmosphere on the distribution of vanadium is similar to the effect observed for Al_2O_3 samples implanted only with vanadium: i.e., an oxidizing atmosphere induces a significant loss of the implanted atoms, as opposed to an anneal in a reducing atmosphere. This result suggests that for both single-ion and co-implantation, the loss of vanadium occurs via the formation of a volatile oxide. Two types of oxides having relatively low melting points [i.e., V_2O_5 (640°C) and a mixed oxide AlVO_4 (695°C)] may be involved in this loss of the implanted species.

The co-implanted samples initially used in this study were introduced directly into the annealing furnace which was set at a temperature of 1000°C . In order to avoid or minimize the undesirable formation of blisters on the surface of co-implanted samples that were rapidly heated, other V and O-implanted samples were introduced into a cold furnace that was subsequently heated to 1000°C at $3^\circ\text{C}/\text{min}$. Observations of the resulting surface by optical microscopy showed no evidence of broken surface blisters. Accordingly, the RBS analysis of these samples yielded significantly different results as compared to those shown in figure 1b, suggesting that, in fact, different phases may have formed. XRD and TEM investigations are currently in progress in order to investigate the possible formation of higher oxides of vanadium under these conditions.

Figure 3 : HRTEM photograph of the V_2O_3 - Al_2O_3 interface

The co-implantation of vanadium and oxygen at lower energies (i.e., 150 keV and 55 keV respectively) results in the formation of a 140 nm-thick amorphous layer that reaches the sample surface. Annealing of these samples (without ramping the annealing temperature) in the 4% H_2 reducing atmosphere at 1000 °C results in the formation of V_2O_3 precipitates. The energy of implantation, i.e., the proximity of the surface does not have an influence on the nature of the phase that is formed nor on its orientation with respect to the sapphire lattice. However, XRD investigations show that for the low-energy implantation, the orientation $(0001) V_2O_3 // (0001) Al_2O_3$ is predominant. The X-ray-diffraction peak is also broader than for the case of the high-energy implantation, indicating that the precipitates are either smaller or strained. The remaining damage, as revealed by RBS examination, is consistent with the existence of deformation in the near-surface region. Numerous blisters are visible in this case, but only a fraction of these have broken to produce surface pitting.

4. SUMMARY AND CONCLUSIONS

The present results show that the co-implantation of vanadium and oxygen into sapphire followed by an anneal in a reducing atmosphere at 1000 °C results in the formation of coherent V_2O_3 precipitates. Two orientations are found : $(0001)V_2O_3 // (0001)Al_2O_3$ and $(11-20)V_2O_3 // (0001) Al_2O_3$. This suggests that the V_2O_3 phase is formed as the sapphire lattice recrystallizes from the amorphous state. The use of a reducing atmosphere results in the formation of the lower oxide V_2O_3 . Some aluminum is also probably incorporated in V_2O_3 as suggested by the values obtained for the lattice parameters.

The modified surface layer is not homogeneous as evidenced by the presence of craters that are apparently produced by blistering and exfoliation resulting from the use of relatively rapid heating conditions during the anneal. Assuming that all of the implanted vanadium reacts to form V_2O_3 (The co-implantation ratio was two oxygen for one vanadium), 25% of the implanted oxygen (i.e., 5×10^{16} ions/cm²) is in excess. Al_2O_3 does not exhibit any deviation from stoichiometry, and previous work has shown [16] that the implantation of oxygen into sapphire and subsequent annealing can lead to the formation of blisters on the surface. The presence of the surface "craters" on our samples suggests that a similar aggregation of the excess oxygen has occurred. However, the size and depth of the craters is not totally consistent with the size expected for O_2 aggregation at a fluence of 5×10^{16} ions/cm². Accordingly, the observed blistering and exfoliation may also be associated with the formation of volatile oxides as the excess oxygen diffuses out of the implanted layer.

In conclusion, the present results indicate that through the careful control of annealing and implantation conditions, it is possible to form buried, coherent nanophase precipitates of V_2O_3 in Al_2O_3 while minimizing undesirable void, blister, and surface-pitting effects. The ability to produce this type of V_2O_3 particle/host system offers new opportunities for the study of structural phase transitions of buried precipitates and of the effect of interactions between the host lattice and the imbedded precipitate on the physical and electronic property changes that occur at the phase transition.

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