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OPTICALLY ACTIVE SURFACES FORMED BY ION IMPLANTATION AND THERMAL TREATMENT

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Abstract

Embedded VO₂ precipitates have been formed in single-crystal sapphire by the ion co-implantation of vanadium and oxygen and subsequent thermal annealing. The embedded VO₂ particles have been shown to exhibit an optical switching behavior that is comparable to that of continuous thin films. In this work, the mechanisms of formation of these optically active particles are investigated. It is shown that precipitation of the vanadium dioxide phase is favored when the thermal treatment is performed on an ion-damaged but still crystalline (rather than amorphized) Al₂O₃ substrate. The best optical switching behavior is observed in this case, and this behavior is apparently correlated with a more-favorable dispersion of VO₂ small particles inside the matrix.

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Recent results have established that it is possible to form crystallographically coherent vanadium dioxide precipitates that are embedded in single-crystal sapphire by the ion co-implantation of vanadium and oxygen followed by an appropriate thermal treatment (1). Vanadium dioxide exhibits a reversible phase transition (2) from a semiconductor (monoclinic structure) to a metal (tetragonal structure) upon heating above a transition temperature of about 70°C. The phase transition of the embedded VO₂-precipitate phase was monitored using infra-red transmission measurements as a function of temperature. The curve obtained on heating exhibits decreasing optical transmission during the transition to the opaque metallic state of VO₂ and, on cooling, exhibits an increasing optical transmission in returning to the transparent semi-conducting state. These transitions occur at two different temperatures (exhibiting hysteresis), in agreement with the behavior observed for both thin films and single crystals of VO₂. However, differences were observed in the maximum transmission change Δ , the sharpness of the transition S (the temperature range necessary for the complete optical switching), and the transition temperature T_C. The aim of the present work is to provide a basis for understanding the observed anomalies between the ion-implantation-produced VO₂ precipitates and either thin-film or bulk VO₂.

In order to understand the role played by various parameters (e.g., the precipitate size, thermal stresses, or oxygen content) on the characteristics of the hysteresis (i.e., Δ , S, and T_C) it was necessary to first investigate the more-basic mechanisms that lead to the precipitation of such a phase. For this purpose, c-axis-oriented sapphire specimens were implanted with 2 to 20 X 10¹⁶ V ions · cm⁻² at

300 K and 77 K and subjected to a 10 min. thermal treatment in pure flowing argon at temperatures ranging from 500 to 1000°C. Stoichiometric co-implantation of oxygen was performed on all the samples prior to the thermal treatment, since the presence of oxygen was shown to enhance the optical-switching properties, in agreement with previous findings concerning the growth of thin films of VO₂ deposited on sapphire (3,4). Characterization of the microstructures was carried out by means of X-ray diffraction (XRD) measurements and Rutherford Backscattering Spectroscopy (RBS) in the channeling geometry. Optical transmission measurements were made using an IR spectrophotometer (wavelength fixed at 3.4 μm) equipped with a heating stage.

Optical-switching curves for precipitates of VO₂ embedded in α-Al₂O₃.

Figure 1 shows the optical transmission of a sapphire specimen implanted with vanadium (2×10^{17} V ions · cm⁻²) and oxygen ($4 \cdot 10^{17}$ O ions · cm⁻²) and annealed at 900°C. As the temperature is scanned between 30 and 90°C, the transmission change for the precipitate system is somewhat smaller ($\Delta = 55\%$) than that of a continuous thin film of VO₂ taken as a reference ($\Delta \sim 100\%$). It should be noted here that Δ is different from the optical contrast used previously by various authors to describe the optical-switching quality of thin films. In the present case, Δ is defined as the difference between the optical transmission at 30°C and the transmission at 90°C, normalized to the room-temperature transmission: $\Delta = (Tr_{30} - Tr_{90}) / Tr_{30}$. The

change in optical transmission of VO_2 with temperature is primarily governed by the switching of individual domains or grains (5) and, in the case of the present $\text{VO}_2/\text{Al}_2\text{O}_3$ nanocomposite system, the transmission change is, therefore, mainly dependent on the number of precipitates. In fact, Δ can provide a measure of the surface coverage of the precipitates as a first approximation, e.g., the surface coverage would be approximately 55% in the case of the $2 \times 10^{17} \text{ V ions} \cdot \text{cm}^{-2}$ implant.

As can also be seen in Figure 1, the sharpness of the transition (i.e., ~ 20 degrees) is about five times that observed for a VO_2 thin film, indicating that extra energy is required to overcome barriers to the propagation of the crystallographic shear in the case of embedded VO_2 precipitates – particularly in the high-temperature region.

Finally, regarding the transition temperature, the switching transition occurs at a temperature that is 4 to 10 degrees higher than that reported for the best thin films of VO_2 (6). Possible candidates for this difference between the embedded precipitates and VO_2 thin films are: high thermal stresses due to process temperature of 900-1000°C for VO_2 precipitates as compared to 500-600°C for thin films, Al impurities introduced into the precipitates by the Al_2O_3 matrix, and particle-size effects.

The microstructure of the VO_2 precipitate/ Al_2O_3 host system at room temperature, as determined by X-Ray diffraction using a four-circle diffractometer, was found to be very close to the structure described in the JCPDS 9-142 file (7) but with an indication of some distortions (8). In the case of high-dose ion implantation, the VO_2 precipitates were several microns long (as measured in the

case where the precipitates were near the surface), and they were three-dimensionally crystallographically oriented with respect to the sapphire substrate (3). A coherence length of only 50 nm for the VO_2 phase at room temperature was deduced, however (8). These results indicate that the "50 nm domains" are not dispersed inside the matrix but rather that they are segregated to form long, flat oriented precipitates that are easily detected with an optical microscope. The microstructure and dispersion of the VO_2 phase are certainly of primary importance for understanding the anomalies observed in the hysteretic behavior of the VO_2 precipitate/ Al_2O_3 host system.

Mechanisms of formation of the $\text{VO}_2/\text{Al}_2\text{O}_3$ composite surface: Formation of the embedded switching phase.

Figure 2 shows the normalized transmission change Δ as a function of the annealing temperature for several Al_2O_3 single-crystal samples co-implanted with vanadium and oxygen at various energies and doses. In the three cases: high dose implantation at 300 K (curve 2a), low dose implantation at 300 K (curve 2b), and low-dose implantation at 77 K (curve c), the evolution of the transmission change Δ (which is assumed in a first approximation to be proportionnal to the number of "switchable" VO_2 precipitates) is similar. The precipitates start to form between 600°C and 800°C (region I) and only a partial transmission change is observed. In the 800-900°C range (region II), the transmission change is a maximum, and finally at

1000°C (30 min. anneal), Δ drops dramatically indicating a nearly complete loss of optical switching (region III).

The fact that VO_2 precipitates are formed between 600°C and 700°C (for a dose of 2×10^{17} V ions $\cdot$ cm⁻² at room temperature) is surprising since, in the case of Al_2O_3 , temperatures higher than 800°C are required for the recovery of the ion-damaged lattice to occur (9). This would indicate that vanadium is highly mobile in Al_2O_3 and that the precipitation of VO_2 is somehow independent on the crystalline state of the substrate. The minimum temperature required for the nucleation of the VO_2 phase, however, is higher for lower implant doses (curve 2b) and suggests either that a threshold value exists for the vanadium concentration (e.g., the lower the local concentration, the greater the path leading to precipitation) or that a minimum size for the "switchable" VO_2 domain needs to be exceeded for optical switching to occur within the limits of detection.

A comparison of the curves shown in Figs. 2b and 2c (corresponding to a similar dose of 5×10^{16} V ions $\cdot$ cm⁻²) suggests that the local concentration in the as-implanted state is certainly not a sufficient factor: i.e., a temperature larger than 800°C is required for the precipitates to form in the case of the implant made at 77 K (curve 2c); while in the case of the 300 K implantation, precipitates are present below 800°C (curve 2b). The mechanisms of the sapphire recovery from displacive ion damage can play a major role in the redistribution of the implanted vanadium. In fact, these mechanisms have been shown (9) to depend on the amount of damage in the as-implanted state (amorphization at 77 K and high damage at 300 K), and this effect is illustrated in Figure 3. In this figure, the RBS spectra of the specimens

implanted at 77 K (curve 3a) and 300 K (curve 3b) and annealed at 900°C are shown in both the random and channeling geometry. For the case of the liquid nitrogen temperature implantation, the substitution fraction is close to 100% and the sapphire lattice is nearly completely recrystallized. Furthermore, the depth distribution of the vanadium is larger than in the as-implanted state (not shown), while for the room-temperature implantation, it is narrower. The diffusion coefficient of vanadium in amorphized Al_2O_3 is probably lower than that in the damaged but still crystalline form. The migration and incorporation of V is then governed by the movement of the recrystallization front (9). In the case of the damaged Al_2O_3 crystalline state, the high mobility of vanadium (in conjunction with a favorable annealing atmosphere) allows the nucleation and growth of the VO_2 precipitates in a more "independent" manner in the vicinity of the the damage peak. These results also suggest that the diffusion of vanadium in Al_2O_3 occurs with the help of some lattice defect: e.g., a dislocation or aluminum vacancy. As a consequence, the VO_2 precipitates formed at room temperature are expected to be larger (or at least to cover a larger area since the in-depth distribution is narrower). From the RBS measurements, the depth distribution of VO_2 for the 77 K implant is estimated to be twice that of the 300 K implant. If one assumes that the same amount of VO_2 is formed in both cases, it is possible to estimate the surface coverage for the 77 K implantation to be half that of the 300 K implant. From Figure 2, the value of Δ for the liquid-nitrogen temperature implant (6%) is about half that of the room-temperature implant (15%) – as expected. Although the values for Δ are small for these low doses, the difference between the two cases is larger than the 3%

estimated error. Measurements of the surface coverage by TEM should be carried out, however, to confirm this interpretation.

As far as region III is concerned, the loss of optical switching activity is related to the diffusive loss of precipitates at the surface as detected by optical microscopy. The reason for such an instability will be treated in detail in a subsequent paper.

In summary, the most efficient optical-switching behavior has been observed in implanted Al_2O_3 samples that were not amorphized during the implantation process. The as-implanted damage state determines the nature of the recovery processes of the Al_2O_3 lattice as well as the diffusion mechanisms for the implanted vanadium. The superior optical switching observed for the room temperature implants is believed to be related to the larger in-plane size of the precipitates and other characterization methods are currently being applied in order to verify the proposed mechanism. This research was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

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FIGURE CAPTIONS

FIGURE 1: Optical transmission spectrum at a fixed wavelength ($3.4\ \mu$) showing the characteristic hysteretic VO_2 phase transition for: (a) VO_2 precipitates formed in Al_2O_3 co-implanted with V and O and thermally annealed; (b) a standard thin film of VO_2 deposited on Al_2O_3 [1].

FIGURE 2: Maximum optical transmission change Δ as a function of annealing temperature for single-crystal Al_2O_3 co-implanted with vanadium and oxygen at:

(a) 2×10^{17} V ions $\cdot \text{cm}^{-2}$ at 300 K

(b) 5×10^{16} V ions $\cdot \text{cm}^{-2}$ at 77 K

(c) 5×10^{16} V ions $\cdot \text{cm}^{-2}$ at 300 K

FIGURE 3: RBS spectra of sapphire co-implanted with vanadium (5×10^{16} V ions $\cdot \text{cm}^{-2}$) and oxygen and annealed in pure Ar at 900°C for 10 min;

(a) implantation performed at 300 K

(b) implantation performed at 77 K

Figure 1

Figure 2

Figure 3

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