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OPTICAL SWITCHING OF COHERENT VO_2 PRECIPITATES EMBEDDED IN SAPPHIRE

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ABSTRACT

In this work, we report the formation of a new type of active or "smart" surface that is produced by ion implantation and thermal processing. By co-implanting vanadium and oxygen into a single-crystal sapphire substrate and annealing the system under appropriate conditions, it was possible to form buried precipitates of vanadium dioxide that were crystallographically oriented with respect to the host Al_2O_3 lattice. The implanted VO_2 precipitate system undergoes a structural phase transition that is accompanied by large variations in the optical transmission which are comparable to those observed for thin films of VO_2 deposited on sapphire. Co-implantation with oxygen was found to be necessary to ensure good optical switching behavior.

1. INTRODUCTION

Vanadium dioxide has been studied for a number of years in single-crystal form [1], and more recently, thin films of VO_2 have been investigated due to the large variations in their electronic and optical properties that occur as the oxide undergoes a thermally induced crystallographic transformation from a monoclinic to a tetragonal structure. This structural phase transition is also accompanied by a semiconducting-to-metal transition that is characterized by a change in the VO_2 electrical conductivity of over two orders of magnitude. Changes in the properties of vanadium dioxide that occur at the phase transition are not only of interest from the fundamental point of view: The transition temperature of ~68°C is close to ambient temperature (and can be easily altered by appropriate doping or by growing VO_2 in a thin-film geometry), making this material suitable for a variety of practical applications - particularly in the area of forming "smart" or interactive surfaces, i.e., surfaces that are capable of performing both sensing and actuating functions. In particular, the properties of VO_2 thin films have been investigated for technological applications that include: thermal sensors, optical switches, and optical storage media [2,3]- as well as mirrors for infrared lasers [4] and laser-pulse protection devices. In the present work, a new method for the formation of VO_2 precipitates that are "embedded" in the near-surface region of a transparent host matrix has been developed by employing ion implantation coupled with subsequent thermal processing [5]. The "surface-composite" VO_2/Al_2O_3 system formed using this approach exhibits characteristics that are believed to be advantageous for both technological applications and for carrying out fundamental investigations. In the present case, the near-surface layer containing the active elements in the form of VO_2 precipitates is protected from environmental interactions and degradation effects. Furthermore, it is anticipated that new materials properties and effects are likely to arise at the phase transition as a result of interactions between the VO_2 precipitates and the host matrix. Additionally, "size effects" are also expected as the size of the precipitates is decreased by controlling the processing conditions. The present study focuses, in particular, on the development of a new technique for forming embedded VO_2 precipitates and on characterizing their optical-switching behavior in an Al_2O_3 host matrix.

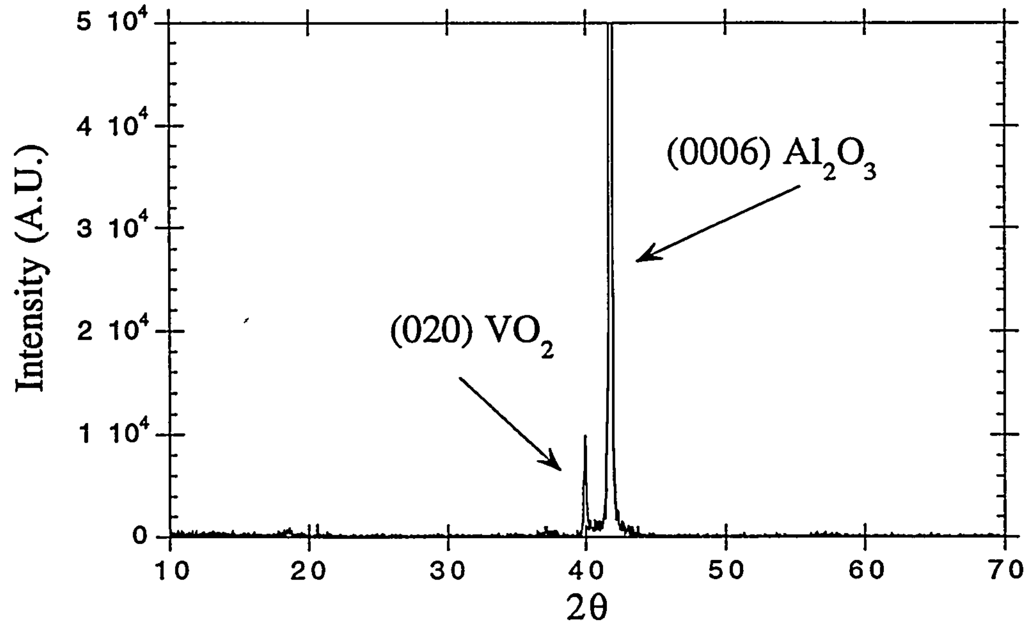

Figure 1 : XRD of sapphire co-implanted (V + O) and annealed

2. EXPERIMENTAL

Room-temperature implantations of V and O were performed on *c*-axis-oriented α-Al_2O_3 single crystals, and the vanadium and oxygen ions were co-implanted at a stoichiometric ratio of 1: 2. Implantation energies in the range of 55 to 300 keV were appropriately calculated and selected to insure the superimposition of both the vanadium- and oxygen-implant distributions in the same Al_2O_3 near-surface region. Thermal annealing of the co-implanted specimens was carried out in an Ar atmosphere at temperatures ranging from 700 to 1000°C for annealing times of 10 to 30 mins. The implanted surfaces were subsequently analyzed using Rutherford backscattering (RBS)/channeling techniques in order to follow the recrystallization behavior and recovery of the ion-damaged Al_2O_3 host lattice as well as the possible diffusion or substitution of vanadium atoms induced by the thermal treatment. Formation of the precipitated VO_2 phase was determined and confirmed by X-ray diffraction techniques and by optical-transmission measurements made using a Perkin-Elmer model 580 double-beam spectrophotometer equipped with a programmable heating stage.

3. RESULTS

An X-ray θ-2θ scan of a (0001)-oriented single-crystal sapphire substrate co-implanted with vanadium (at a fluence of 2×10^{17} ions.cm^{-2}), stoichiometrically implanted with oxygen in the ratio of two oxygens for each vanadium, and finally annealed at 900°C for 10 mins. is shown in figure 1. The intense peak observed at 41.75° is characteristic of the (0006) reflection of the sapphire substrate. A second peak is observed at an angle of 39.9° which is not related to any form of Al_2O_3. This peak indicates that a new precipitated phase has formed following the V and O co-implantation and thermal treatment. Because this reflection corresponds to an inter-planar spacing that could be attributed to more than one vanadium oxide, optical transmission measurements were performed as a function of temperature (at a fixed wavelength of 3.4 μm) in order to confirm unequivocally the presence of VO_2.

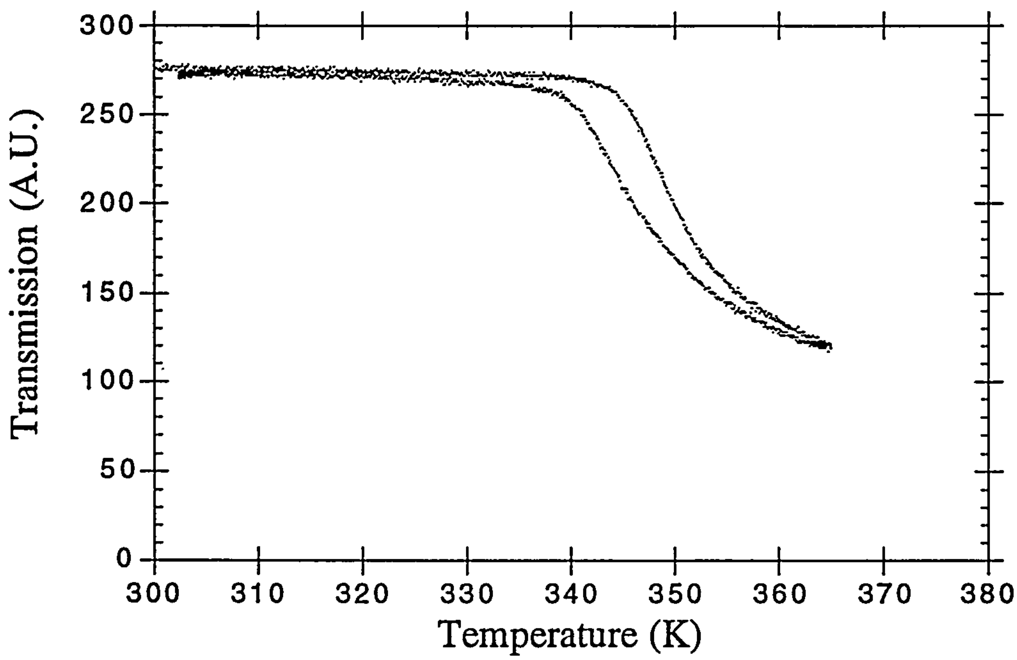

Figure 2 : Optical transmission as a function of temperature of Al_2O_3 co-implanted with V and O and annealed

Figure 2 shows the optical transmission of the VO_2/Al_2O_3 system as the temperature is cycled from room temperature to 90°C, i.e., through the characteristic VO_2 phase-transition-temperature region. The near-surface "composite" system formed by the occurrence of VO_2 precipitates in sapphire exhibits a large variation in its optical properties (i.e., a change in the transmission from 70% to 35 % is observed) at a transition temperature of ~77°C. The magnitude of this transmission change is to be compared with the change of 60% to 5 % typically obtained for thin VO_2 films deposited directly on sapphire substrates of similar thickness [6]. The relatively smaller magnitude of the change in absorption observed in the present case is believed to be due, in part, to the non-continuous character of the active layer as well as to possible precipitate/host-lattice-interaction effects. The observed variation of the optical transmission with temperature for our system is reversible with a hysteresis of 5°C. This is comparable to the behavior reported for the best vanadium dioxide thin films. The transition temperature of 77°C, taken at the mid-point of the heating curve, is comparable to the transition temperature of ~73°C measured for thin films of VO_2 deposited on sapphire by several methods [6,7]. The effects of precipitate/host-lattice interactions are assumed to be responsible, at least in part, for the relatively higher phase-transition temperature of ~77°C found for the embedded VO_2 precipitates as compared with the thin-film transition temperatures near ~73°C.

The X-ray diffraction peak at 39.9° could be correlated with the (020) reflection of a monoclinic (low-temperature) form of VO_2. Although this reflection is not present on the JCPDS powder diffraction files for VO_2 [8], it was found to be kinematically allowed with an intensity 3% that of the (001) reflection [9]. No peak related to the intermediate γ-phase of Al_2O_3 is visible in figure 1, indicating that the sapphire lattice has completely recrystallized into the alpha alumina form from the as-implanted amorphous state. It is important to note that the orientational relationship between the c-axis sapphire lattice and the vanadium dioxide phase is similar to that in evidence for several thin films of VO_2 grown on similarly oriented sapphire substrates [9,10]. This similarity in the orientational relationship was also previously observed by us for V_2O_3 precipitates formed in sapphire by ion-implantation techniques [11] and has also been found for V_2O_3 thin films deposited on sapphire.

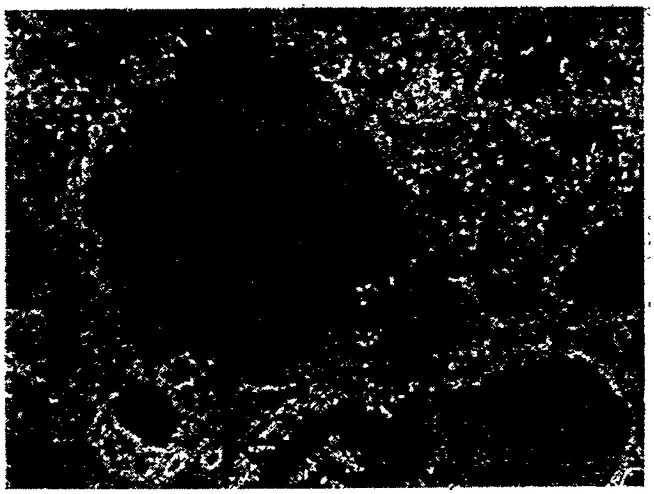

Figure 3 : Optical micrograph of the sapphire surface, showing the orientation of the precipitates

Figure 3 shows the optical micrograph obtained for an Al_2O_3 single-crystal sample co-implanted with vanadium and oxygen and annealed at 1000°C for 30 mins. In a small region where the surface has spalled off, the buried VO_2 precipitates are visible. Their alignment along directions following the symmetry of the hexagonal sapphire lattice reveals their in-plane orientational relationship relative to the Al_2O_3 host. Detailed TEM and XRD characterizations of the in-plane orientation relationships are currently ongoing.

It is well known that the switching properties of VO_2 thin films are strongly dependent, not only on the particular growth process employed, but also on various deposition parameters (such as the partial pressure of oxygen and the deposition temperature) that are utilized in a given growth process. We anticipate an even stronger dependence of the system properties on the processing conditions in the present case of the formation of a buried VO_2 precipitate phase because of the complex growth processes that are involved in the implantation, solid state reaction, and recrystallization of the implanted materials. In the following paragraph, we will consider only the effect of oxygen content on the formation and switching properties of VO_2 precipitates formed by ion implantation and thermal processing.

Figure 4 shows the RBS spectrum of a sample co-implanted with vanadium (10^{17} ions.cm^{-2}) and oxygen (2 X 10^{17} ions.cm^{-2}) at energies of 150 keV and 55 keV respectively and annealed for 30 mins. in argon at 1000°C. No significant diffusion of the implanted vanadium was observed during the anneal in going from the as-implanted, amorphous state (not shown) to the final state. However, the recrystallization is relatively good (a 20 % channeling yield is obtained). Figure 5 represents the RBS spectrum of a similar sapphire substrate implanted only with vanadium at an energy of only 150 keV (10^{17} ions.cm^{-2}). The channeling yield is not as good in this case (40%), and there is clearly some long-range diffusion of vanadium toward the interior of the Al_2O_3 substrate. As noted in the previous paragraph, the thermal-treatment conditions selected here favor the formation of vanadium dioxide. In the case of vanadium implantation alone (i.e., in the absence of the co-implantation of oxygen), the formation of vanadium dioxide competes with the recrystallization of α-Al_2O_3 from the amorphous state. This may induce some long-range diffusion of the vanadium atoms. Because the local concentration of vanadium is altered, different switching behavior is likely to occur. Figure 6 represents the hysteresis curve of sapphire implanted only with vanadium and compared with that found for sapphire co-implanted with both vanadium and oxygen.

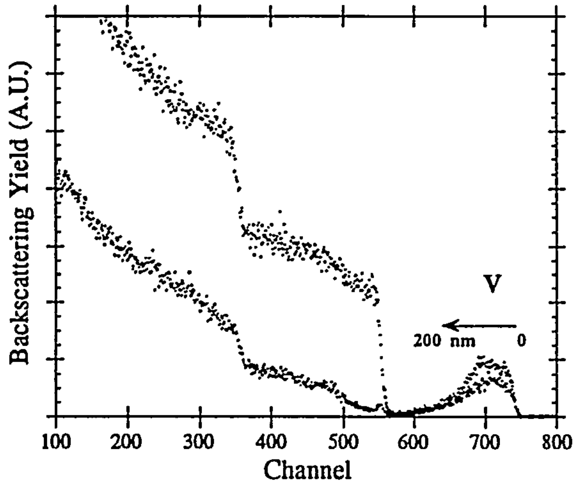

Figure 4 : Sapphire co-implanted (V + O) and annealed

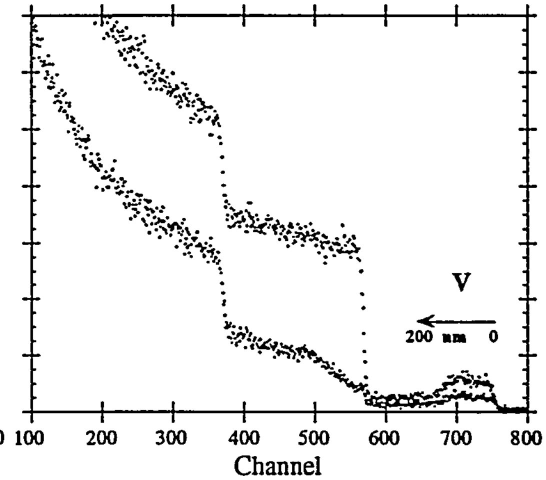

FIGURE 5 : Sapphire implanted with vanadium and annealed

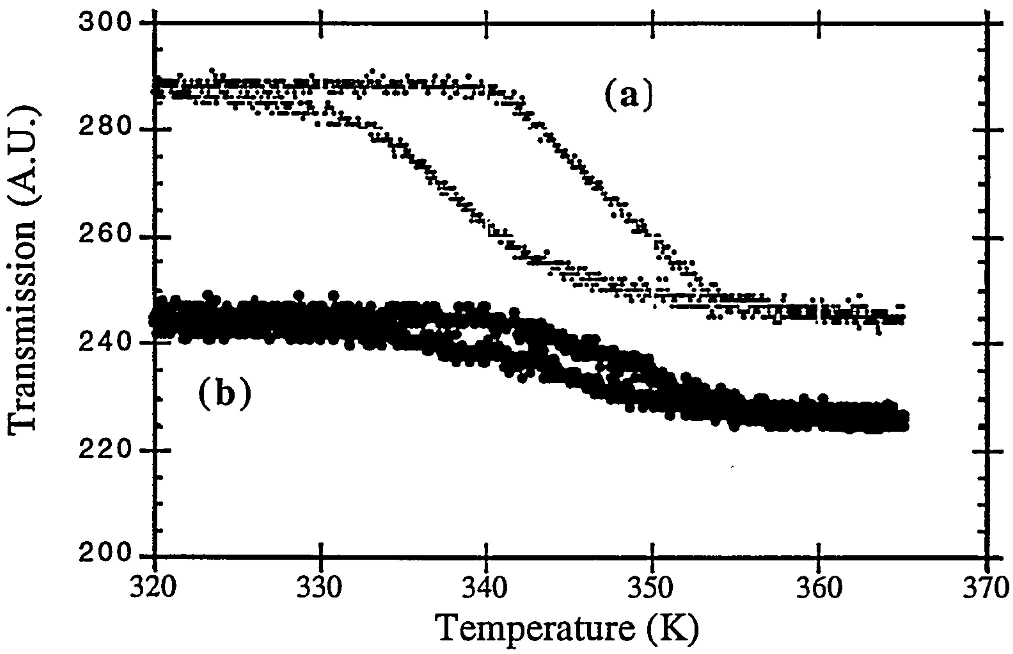

Figure 6 : Optical switching of sapphire
(a) co-implanted with V and O,
(b) implanted with V and annealed

The characteristic switching behavior is indeed clearly different : in the case of the vanadium implantation only, the hysteresis curve is flat, and a relatively small variation in the optical transmission is observed. When co-implantation is performed, the switching range is significantly wider but without the occurrence of a significant change in the phase-transition temperature. Although the precise effects on the precipitate size and microstructure are not established at the present time, co-implantation with oxygen clearly improves the optical switching properties of the VO_2-precipitate/Al_2O_3 surface "composite" system.

3. CONCLUSION

The present study shows that it is possible to form buried, crystallographically coherent precipitates of vanadium dioxide in sapphire single crystals by a two-step process of ion implantation and thermal treatment. These VO_2 precipitates undergo a phase transition which exhibits variations in the optical properties that are comparable to those observed for thin films of VO_2 deposited on sapphire. Additionally, it has been shown that co-implantation with oxygen is necessary to obtain the best optical switching characteristics.

In the case of the optically active, switchable surfaces formed here, the active VO_2 phase is protected from the environment. Furthermore, the observation of new materials properties is anticipated as the size of the active precipitates is decreased, and investigations of this type are currently under way along with studies of the formation of VO_2 precipitates in host-substrate materials other than Al_2O_3. This approach to the formation of optically active near-surface regions by ion implantation and thermal processing is believed to offer new opportunities for the creation of "smart" surfaces.

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