Optical and electrical properties of sputtered vanadium oxide films

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Thin films of vanadium oxide with thickness of 0.1 to 0.2 μm were deposited on Si_3N_4/Si substrate by reactive rf magnetron sputtering. The oxide films were sputtered using a vanadium metal target in various ratios of Ar and O_2 gases. The O_2 content in the mixed atmosphere has a significant influence on the metal-insulator transition characteristics of the oxide films. The oxide film deposited in an Ar/O_2 ratio of 98/2 exhibited high optical transmission of 70% to 80% in wavelength from 2 to 10 μm in insulating state while very low transmission of less than 5% in metallic state. Films prepared with higher O_2 concentration showed no metal-insulator transition. In low O_2 concentration, films showed characteristics of having both a broader transition region spanning over 30 °C and a lowered transition temperature which are similar to those of doped vanadium oxide films. © *2004 American Vacuum Society.* [DOI: 10.1116/1.1676417]

I. INTRODUCTION

Smart materials were known for many years for their changes in optical and electrical properties upon the influence of external parameters such as temperature and electric field. The changes in these properties are usually the results of metal-insulator phase transitions of the materials.[1] These changes can be quick and reversible. In the case of vanadium oxides with oxygen combination in 2-, 3-, 4-, and 5-valent states, the change of resistivity can be as much as several orders.[2] In the family of vanadium oxides, much attention has been drawn to VO_2 (2-valent state) due to the fact that its transition temperature (T_c) is close to room temperature.[3] Also, its T_c can be controlled and reduced by doping the oxide film with impurities such as tungsten and titanium.[4,5] However, as T_c is reduced, one usually obtains a broader transition that may not be desirable in some applications. Optical transmission characteristics of VO_2 also change over the metal-insulator phase transition. This property may be useful in applications that require digital or analog switching of optical signal. While efforts have been focused on applications concerning spectral range from visible to about 3 μm in the near infrared (IR) region, there are few research works to study and optimize far IR switching of vanadium oxides. IR switching devices in the 10 μm range may benefit IR imaging systems and IR spectrometers. In this work, as-deposited VO_2 thin films without doping were prepared using reactive rf sputtering techniques under various conditions. The results of electrical and optical properties of the films are presented and examined for possible use in far IR switching applications.

II. EXPERIMENTAL PROCEDURES

In this work, a procedure was established to create VO_2 thin films on a Si_3N_4/Si substrate by reactive rf magnetron sputtering. The 0.6-μm-thick Si_3N_4 insulating layer was deposited on the (100) Si substrate using plasma enhanced chemical vapor deposition. The vanadium oxide film deposition takes place in a cylindrical stainless steel vacuum chamber. Its diameter and depth are 57 and 28 cm, respectively. In the chamber, there is a 2-in.-diam planar magnetron gun (US GUN II) on which the 2 in. vanadium target (99.7% purity from Target Materials, Inc. of Ohio) in the form of a disk is located. A substrate holder equipped with substrate heating element faces the gun and this holder can be turned to or away from the target. The rf system (Advanced Energy RFX-600) supplies rf power to the gun at 13.56 MHz through an impedance matching network (Advanced Energy ATX-600) which adjusts its impedance to maintain minimum reflected power. In the chamber, high vacuum is established by first using a rotary pump and then a turbo-molecular pump (Balzers THS-512) having a typical air pumping speed of 400 l/s. In addition, a 54-cm-diam, four-turn Meissner coil assists the turbo-molecular station by capturing water vapor inside the chamber. Water vapor represents 70% to 95% of the residual gas below pressure of 10^{-3} Torr. The Meissner coil which provides 17 000 l/s pumping capability is freon cooled by a fast-cycle cryocooler (Polycold PFC-200). With this arrangement, a desirable base pressure of 10^{-6} Torr can be reached in 45 min.

Prior to the deposition, the chamber is evacuated to a base pressure of 5.0×10^{-6} Torr. High-purity Ar gas as the ion supplier gas for the plasma formation and O_2 gas as the reactive gas are fed into the chamber through piezoelectric valves which provide an accurate gas flow control of $\pm0.5\%$. Using a throttle valve, the pumping speed of the vacuum system is adjusted to a rate so that the chamber pressure during sputtering is maintained at 10 mTorr under continuous pumping. Under the same sputtering pressure, one can maintain the reproduction of a specific deposition condition. The depositions were performed with different substrate temperatures from 200 to 400 °C. The rf power during the deposition was 100 W. After the deposition, the films were cooled down to room temperature. No post-annealing was performed on the vanadium oxide films.

In addition, a 15 min pre-sputtering step is carried out

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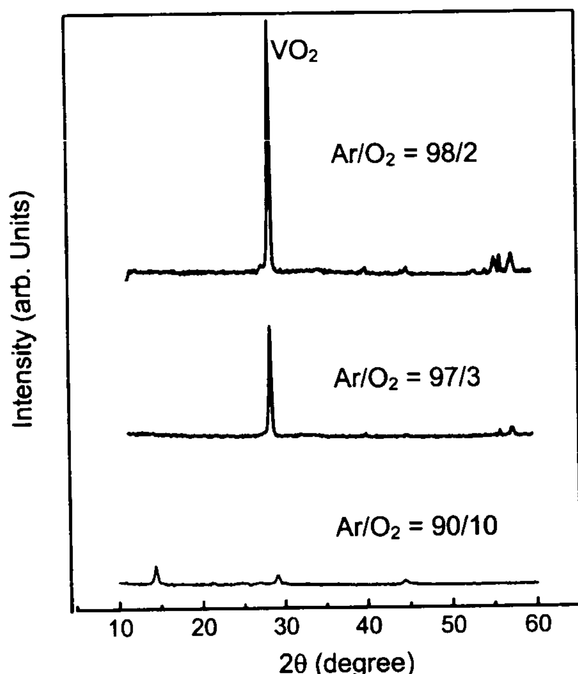

FIG. 1. X-ray diffraction of vanadium oxide films sputtered under different argon and oxygen concentrations.

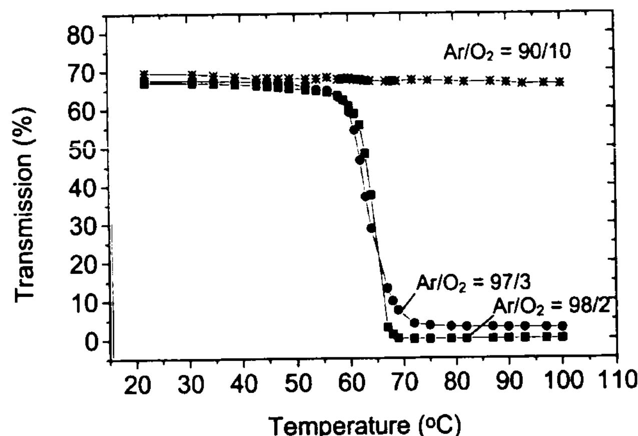

FIG. 2. Optical transmission at 3 μm of the vanadium films sputtered under different oxygen concentrations as a function of temperature.

prior to the deposition onto the substrates. This pre-sputtering step is to remove the first few atomic layers of the target which are subjected to atmospheric pollution or chemical contamination. During the pre-sputtering step, the substrate is turned to a position far from the target and the plasma. After the pre-sputtering, the substrate holder rotates and brings the substrate to the deposition position.

The film thickness was measured using a DekTak 3030 surface profiler. Under these sputtering conditions, the thickness of each oxide film was about 0.2 μm that translates to a deposition rate of about 7 nm/min. A standard four-point probe method was used for the electrical resistance measurements of the films. Film stoichiometric analysis was performed using x-ray diffractometer in the 2θ ranges from 10 to 60° with Cu $K\alpha$ radiation. The spectral transmission of the films as a function of temperature was obtained using an ARC SpetraPro-300i spectrometer (600–13 500 nm wavelength range) and a sample heater. The effect of deposition temperature on optical transmission at wavelength of 3 μm was also examined. All the resistivity and optical transmission measurements as a function of temperature were performed with increasing temperature.

III. RESULTS AND DISCUSSION

In the first series of experiments the sputtering conditions were established to yield VO_2 films suitable for optical switching. Vanadium oxide films were prepared at a various gas mixture of Ar/O_2. The stoichiometry of the films was examined using x-ray diffraction technique. The results are shown in Fig. 1. According to the figure, a mixed structure containing VO_2 and other phases was obtained at high concentration of O_2. At Ar/O_2 of 90/10 or 10% of O_2, the film shows a (011) diffraction peak with low intensity at $2\theta = 27.8°$ that corresponds to the presence of VO_2. The other unidentified peaks may be associated with oxygen-rich phase due to high oxygen atmosphere. As the concentration of O_2 was reduced, VO_2 content in the film increased. The (011) diffraction peak emerged at 3% of O_2. In the case of film sputtered in 2% of O_2, strong (011) peak was obtained, indicating the formation of highly oriented VO_2 in the films. The full width at half maximum of the VO_2 (011) peak was about 0.5°. The other two peaks are at 55.5 and 56.2°, respectively, which have intensity 20 times less than that at (011).

In the second series of experiments the optical transmission of the VO_2 films as a function of temperature was examined during metal-insulator phase transition so as to identify films having suitable characteristics for optical switching. It is noted that all films were prepared using the same deposition conditions and at a substrate temperature of 400 °C but at different O_2 concentrations. The optical transmission curves of films at a wavelength of 3 μm as a function of temperature are shown in Fig. 2. It clearly shows that T_c is about 65 °C and this is true only for the films deposited in low O_2 concentration. Furthermore, VO_2 films with the O_2 concentration ratio of 98/2 yielded the lowest transmission (~3%) in the metallic state while maintaining high transmission (~67%) in the insulating state. The phase transition region is narrow and steep (less than 10 °C). Metal-insulator phase transitions are clearly seen from the film. This sharp transition is desirable for digitally optical switching. Figure 3 shows the spectral transmission up to 10 μm as a function of temperature. The rf-sputtered VO_2 film exhibits very high optical transmission between 60% and 80% over a wide spectrum in the insulating state. In the metallic state, the optical transmission of VO_2 films is low implying that this film can be used for optical switching over a broad spectral range.

A metal-insulator phase transition also implies a change of film electrical resistance which is important especially when the film is electrically connected to the switching devices. A standard four-point probe method was used to mea-

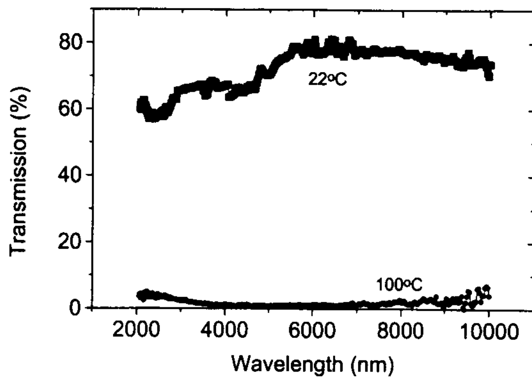

FIG. 3. Spectral transmission of VO_2 films in insulating and metallic states.

sure the electrical resistance of the film. As the substrate was heated in air from 22 to 100 °C, the electrical resistance of the film was measured. The corresponding film resistivity (Ω cm) is shown in Fig. 4. The resistivity was on the order of 10 Ω cm when the substrate temperature was below T_c. As the substrate temperature continued to rise, the resistivity dropped sharply. Above 70 °C, the resistivity of the VO_2 film became 10^{-3} Ω cm, a four decades difference. In the region below T_c, the film showed a typical semiconductor characteristic of decreasing of electrical resistance as temperature increased. In the region above T_c, the film showed one of metal characteristics of increasing in electrical resistance as temperature increased. These results confirmed the metal-insulator transition of the sputtered film. The resistivity-temperature profile also closely matches the transmission-temperature profile. This confirms that the modulation of transmission as a function of temperature is mainly due to the metal-insulator phase transition of the film.

As for the films sputtered in less than 2% of O_2 concentration, the optical transmission curve at wavelength of 3 μm is shown in Fig. 5. It is noted that the transition region is broad, spanning 30 °C, and T_c is lower than those of VO_2 films shown in Fig. 2. These characteristics are similar to that of impurity effect in VO_2 films. As mentioned earlier, the effect of doping normally results in VO_2 films with broader transition and lower T_c.

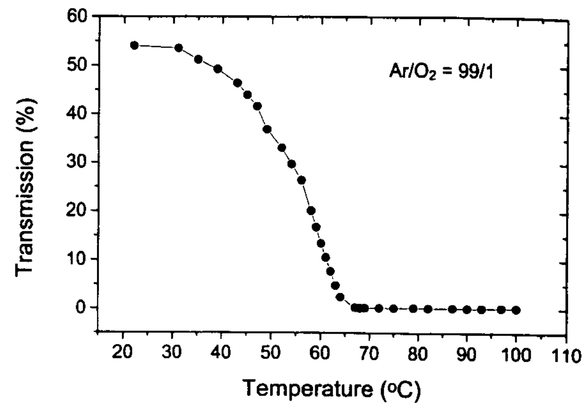

FIG. 5. Optical transmission of a VO_2 film sputtered in low oxygen concentration as a function of temperature.

The effect of substrate temperature (T_s) during deposition on the film characteristics was studied. By keeping all other sputtering conditions unchanged, the optical transmissions of films prepared at various T_s are shown in Fig. 6. While the optical transmissions of all three films are the same in the insulator state, the film prepared at T_s of 400 °C shows both the lowest transmission in the metallic state and the steepest transition. This may be attributed to a larger grain size at higher T_s and a higher VO_2 content in the film at elevated T_s.

IV. CONCLUSIONS

Vanadium oxide films were deposited using reactive rf magnetron sputtering. Various Ar/O_2 concentrations and substrate temperatures were used for the thin film sputtering. Films with thickness of 0.2 μm were obtained at a deposition rate of about 7 nm/min. X-ray diffraction was used to examine the stoichiometry of the film. Optical transmission and electrical resistance measurements as a function of temperature were performed to determine the effects of gas concentration and substrate temperature on the optical and electrical properties of the film. Under the established sputtering conditions, it was concluded that there is less stoichiometric VO_2 in 3% or higher oxygen content during sputtering while

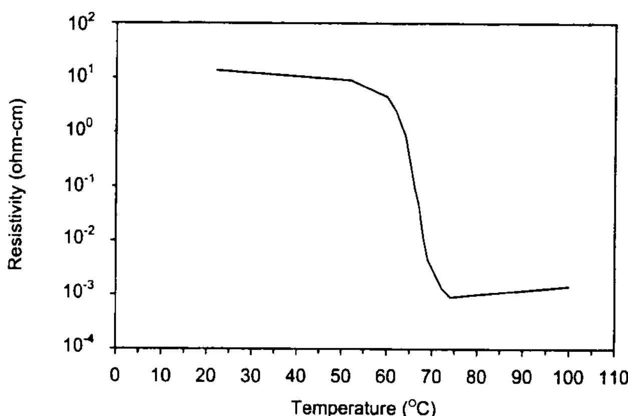

FIG. 4. Resistivity of a VO_2 film as a function of temperature.

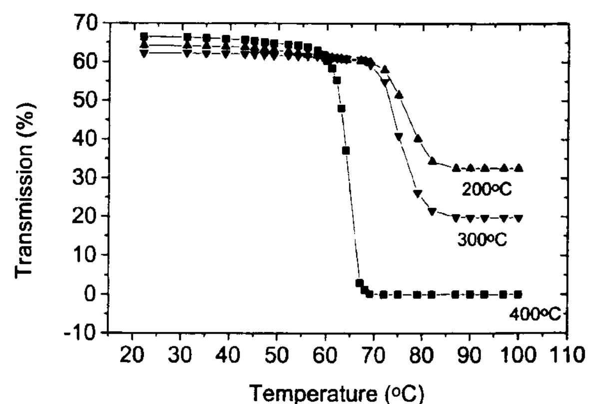

FIG. 6. Optical transmission of films prepared at various substrate temperatures as a function of temperature.

significant stoichiometric VO_2 content with 2% oxygen. This is due to the fact that oxygen partial pressure during the deposition has a significant effect on the formation of VO_2 crystalline phase for high optical transmission in insulating state and low transmission in metallic state. The oxygen content in vanadium oxides also results in a large shift of T_c. The metal-insulator T_c is about 65 °C for the sputtered VO_2 films. Below this T_c, the electrical resistance of the VO_2 films increases. The film becomes more insulating and shows high optical transmission of about 60% to 80% over a broad spectral range that exceeds 10 μm. Above T_c, the films exhibit a sharp drop in optical transmission to below 5%. This high contrast of IR optical switching characteristic is potentially useful in IR optical systems. For those films deposited in low oxygen concentration, they showed optical characteristics similar to that of doped vanadium oxide films having low T_c and broad metal-insulator transition.

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