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Fabrication of High-Quality VO_2 Thin Films by Ion-Assisted Dual ac Magnetron Sputtering

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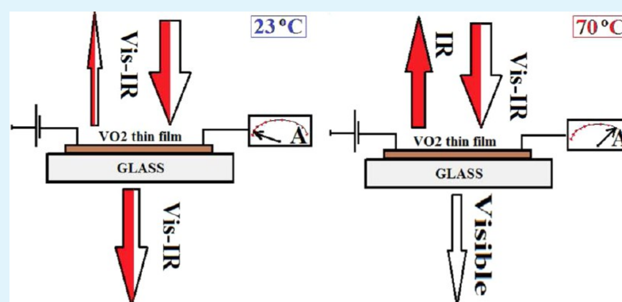
ABSTRACT: The technique of cathodic ac dual magnetron sputtering along with the high energy ionic bombardment is known to yield high-quality thin films in terms of their uniformity and high density. This technique has been applied for the first time to achieve thermochromic VO_2 thin films that show a high optical and electrical contrast between normal and switched states. In this two-step process Vanadium metal films were deposited and subsequently oxidized in optimum conditions to achieve stoichiometric VO_2 films. Typical films switched between more than 40 % to less than 5 % transmission in the infrared region while undergoing an electrical sheet resistance change between 1×10^5 and 1×10^2 Ω/cm^2. The application potential of such VO_2 films in integrated optics is deemed high.



KEYWORDS: *thermochromics, vanadium oxide, ac cathodic sputtering, microstructure, transition temperature, optical switching*

■ INTRODUCTION

Vanadium dioxide (VO_2) thin films are very well known for their efficient thermochromic switching or a metal to insulator transition (MIT) under the influence of temperature. These films are transparent to near-infrared wavelengths at room temperature and become opaque above their natural transition temperature. These reversible optical changes are accompanied by reversible electrical and structural changes.[1,2] Of all the transition metal oxides possessing a stable transition, VO_2 is the oxide with a transition temperature closest to room temperature.[3] The transition temperature in pure VO_2 thin films is found to be around 68 °C and can be modified by a controlled doping of compatible atoms into the film.[4] The insulator (at room temperature) to metal (at higher temperature) transition is also accompanied by a phase change of the film from monoclinic to tetragonal (rutile).[2] Following the discovery of the thermochromic switching properties in VO_2 films by Morin,[1] an enormous amount of research has been carried out on these films. This research interest is fueled in large part by the vast number of application possibilities that exist for this material, from smart windows[5] to infrared filters[6] to optical commuters[7] and imaging systems.[8] The fabrication of integrated optical devices based on VO_2 thin films has been proposed by many researchers.[9−12] This work is motivated by the specific need in this industry for miniaturisation of the telecommunication and imagery components as well as the need to increase their speed of performance. The distinct feature of these photonic and optoelectronic components based on VO_2 films is the possibility that exists to control their properties via electrical, optical, and thermal means. Despite the vast amount of research work carried out thus far on the fabrication of VO_2 thin films, the achieving of stoichiometric VO_2 films in a reproducible way remains a challenge.

Chemical deposition methods like the solution processing have seen significant advances in recent years.[13] These methods offer many distinct advantages. They are technically easier to implement and provide a facile dopant control. These methods are also very economical, especially to apply on large areas. However, the thin films obtained by these methods are known to have a poor mechanical adherence and are often porous which limits their use in integrated optics. The integrated optical applications require these films to be very thin while maintaining a high degree of homogeneity (uniform and dense) and thermochromic switchability. An extremely precise control of thickness and interface state is also needed in these applications due to the interference phenomenon prevalent. The physical vapor deposition (PVD) techniques are deemed good candidates to address all these challenges. Amongst these, RF and DC magnetron sputtering are the most commonly used techniques in the microelectronic industry for obtaining high quality depositions. However, these techniques suffer the disadvantages of having low deposition rate and relying on high-cost maintenance systems.

In this work we have carried out the deposition and study of high-quality VO_2 thin films by the cathodic *ac* dual magnetron sputtering aided by ion beam bombardment. This technique

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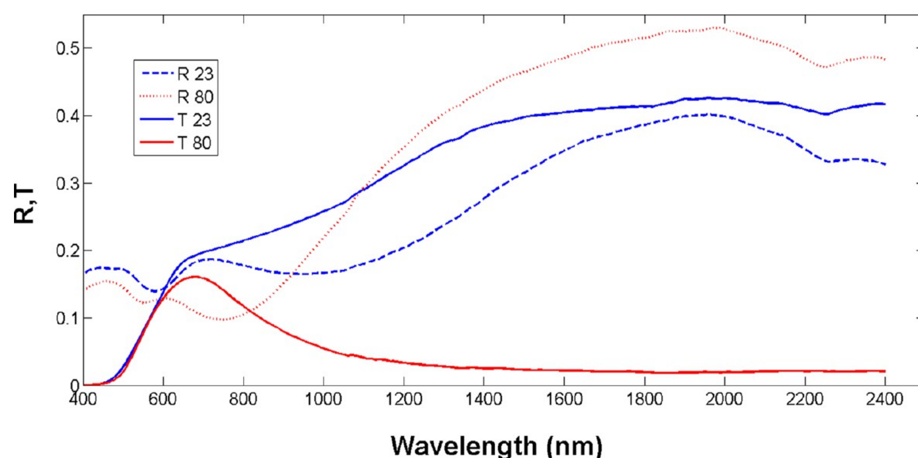

Figure 1. Transmission and reflection at 10° of incidence angle of VO_2 at 23 and 80° Celsius.

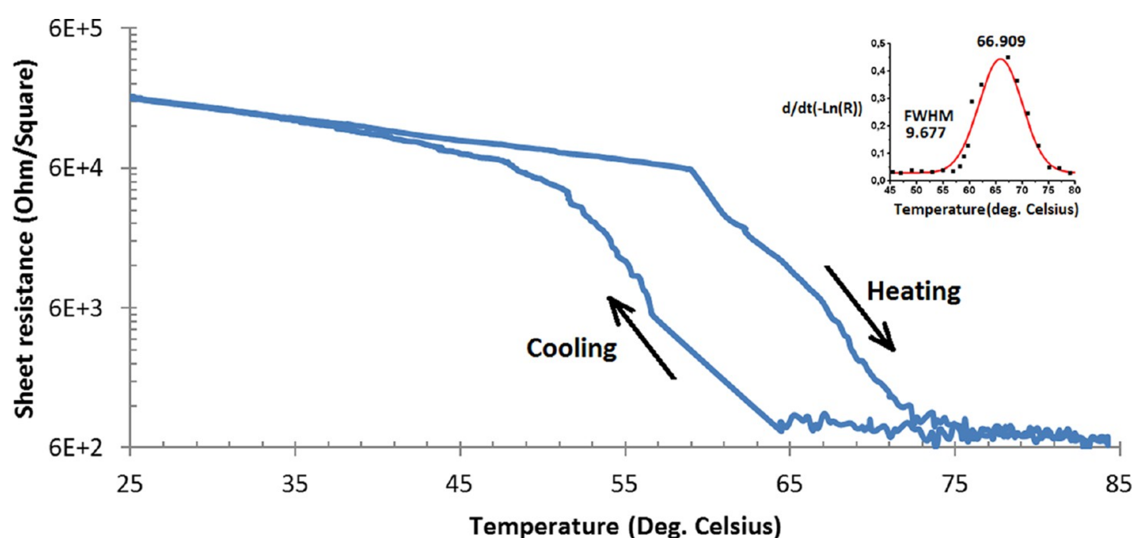

Figure 2. Sheet resistance in ohm/sq is mesured by four probes method versus the temperature. In inset, the derivative of the temperature in the heating branch give the transition temperature and its peak width.

provides the unique opportunity of yielding dense films even at low film thickness ($\lambda/2$ or $\lambda/4$ where λ is the working wavelength) and with high deposition rates.

EXPERIMENTAL DETAILS

The fabrication of VO_2 thin films in this work was carried out in two steps. In the first step uniform metallic thin films of vanadium were deposited by the said method with varying degree of oxygen (0 to 24 sccm) in the vacuum chamber and then all the samples were thermally oxidized in a carefully controlled atmosphere to obtain stoichiometric VO_2 films. The initial deposition was carried out on 1 mm thick clean glass substrates by ion assisted ac cathodic dual magnetron sputtering. The utilisation of the ac powered dual magnetron enabled us to achieve a high rate of deposition of 0.3 nm/s. A Kaufman type ion source with a cathode cage for neutralizing the ion flux was used to compact the deposited film. Two high-purity (99.99 %) 6″ diameter vanadium targets were sputtered in a 0.46 m^3 chamber at a working pressure of 1×10^{-4} Torr with a gas mixture of oxygen and argon. The chamber was initially pumped down to a pressure of 10^{-7} Torr and backfilled with the working gas mixture. The substrate temperature during deposition was maintained at 120 °C. The vanadium thin films thus deposited were gray in colour and of metallic nature. These films were subsequently oxidized by thermal annealing in a vacuum furnace at a temperature of 520 °C in the presence of 0.1 mTorr of oxygen to obtain the VO_2 thin films. The duration of this oxidation varied between 15 and 120 min. The coloration of the films after the oxidation varied from light to dark maroon, clearly indicating the transformation of the more metallic vanadium into the dioxide.

The optical characterization of the films was carried out by a Cary-5000 spectrophotmeter in the wavelength range between 300 and 2500 nm. The film thickness was measured using a profilometer Dektak 150 from Veeco Instruments Inc (NY, USA). The surface morphology of the films was examined by an atomic force microscope (AFM) as well as by a scanning electron microscope (SEM). The electrical resistance and its variation with temperature was measured by a four-point system from Lucas Labs (Gilroy, CA,USA) using a Keithley 2750 multimeter equipped with a model 7700 multiplexer (Keithley Instruments Inc., Cleveland, OH,USA). The four-point system was controlled by a Labview program. A laboratory built heater filament assembly was used to gradually heat the samples above the MIT temperature and to a maximum of 80 °C using a temperature controller. The film stoichiometry was measured using a Kratos x-ray electron spectroscopy (XPS). This system is provided with a large radius electrostatic analyzer, a detection system with 8 channels, a double x-ray Al−Mg source without monochromator and an Al source with monochromator. The system also has an electron gun of very low energy for the effective neutralization of electrostatic charge that appears on the electrically insulating samples during their exposure to the beam of monochromatic X-rays. This spectrometer is housed in a vacuum system with a base pressure of 5×10^{-10} Torr.

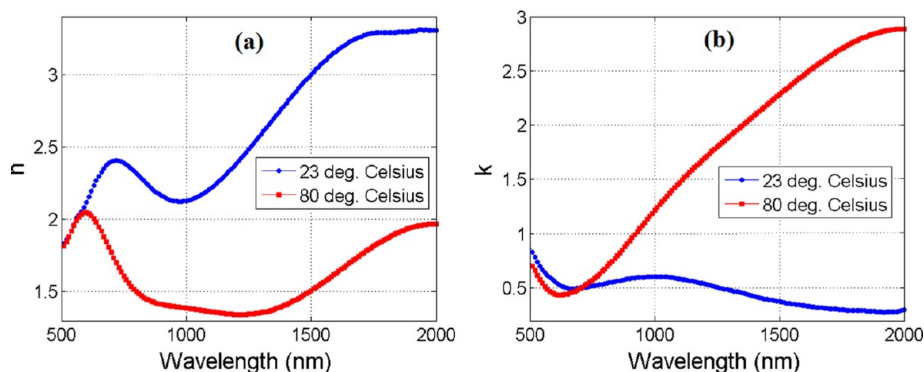

Figure 3. Ellipsometric measurements at ambient and high temperature of (a) the refractive index and (b) the extinction coefficient versus the wavelength.

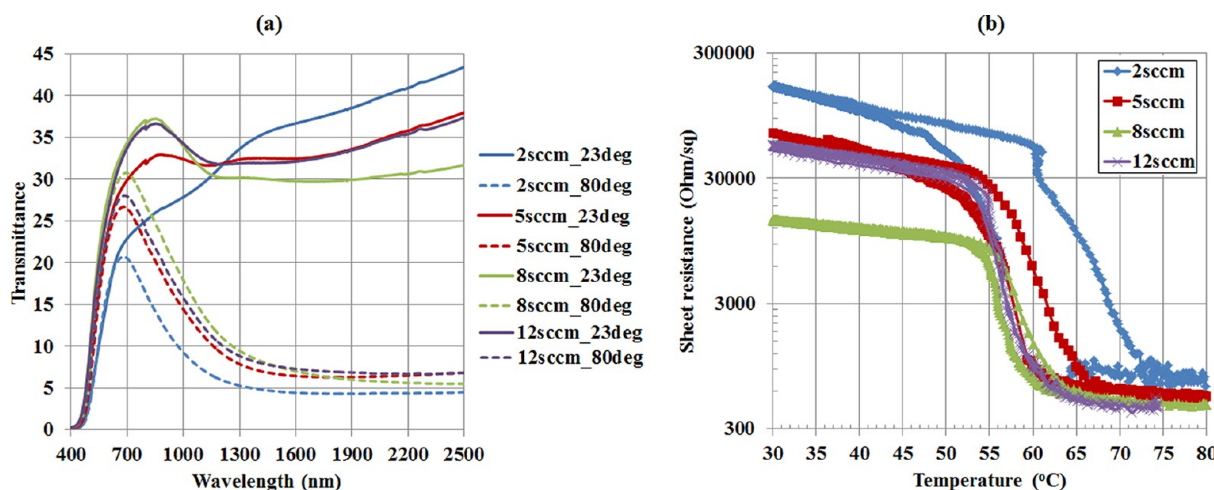

Figure 4. (a) Transmittance of VO_2 thin films fabricated with different oxygen flow at ambient and high temperature. (b) Sheet resistance VO_2 thin film fabricated with different oxygen flows versus the temperature.

■ RESULTS AND DISCUSSION

In Figure 1 are shown the transmittance (T) and reflectance (R) spectra of a VO_2 thin film above (80 °C) and below (23 °C). These results pertain to a sample that was deposited with no oxygen (0 sccm) in the chamber and subsequently oxidized like the other films. From the Dektak measurements, it is found that the initial metallic Vanadium films had a thickness of around 70 nm and the film thickness nearly doubled after their annealing and oxidation. The optical and electrical measurements show a highly efficient thermochromic changes in these films. As seen from Figure 1, the maximum optical change in this film occurs at the wavelength of 2400 nm where the film transmittance changes from around 42% at ambient (23 °C) to 2% at higher temperature (80 °C). The corresponding changes in the electrical resistance are shown in Figure 2 where the film undergoes a resistance change of the order of 3, from 1×10^5 Ω/cm^2 to 1×10^2 Ω/cm^2. The thermal dependence of resistance exhibits a hysteresis, as shown in this figure. From the differential change shown in the inset of Figure 2, we can infer that the phase transition during the heating cycle is centered around 66 °C and the spread is about 9.7 °C around this value.[14] For this film, the transition temperature is quite close to that of the value of 68 °C reported for the bulk.[1] In Figure 3 are shown the changes occurring in the optical constants (n, k) of the film. Significant changes in both n and k have been observed when the film undergoes thermochromic phase change. At ambient (23 °C) dielectric state, the film exhibits a relatively low k value (0.8 to 0.3) and significantly high n value (1.8 to 3.3) in the spectral region studied. At higher temperature and upon phase change, the k value rises drastically with increasing wavelength. At the wavelength of 2000 nm, a drastic change in k value between 0.3 at room temperature to 2.9 at higher temperature is seen. An equally important, but less wavelength dependent decrease in n value is seen. At the wavelength of 2000 nm, a decrease from 3.3 at room temperature to 1.9 at higher temperature is observed. These important changes in transmittance (T), reflectance (R), sheet

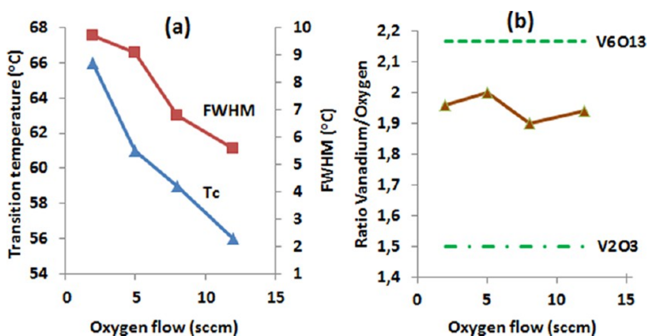

Figure 5. (a) Transition temperature and the peak width of its derivative in the heating branch; (b) ratio of vanadium/oxygen measured with XPS.

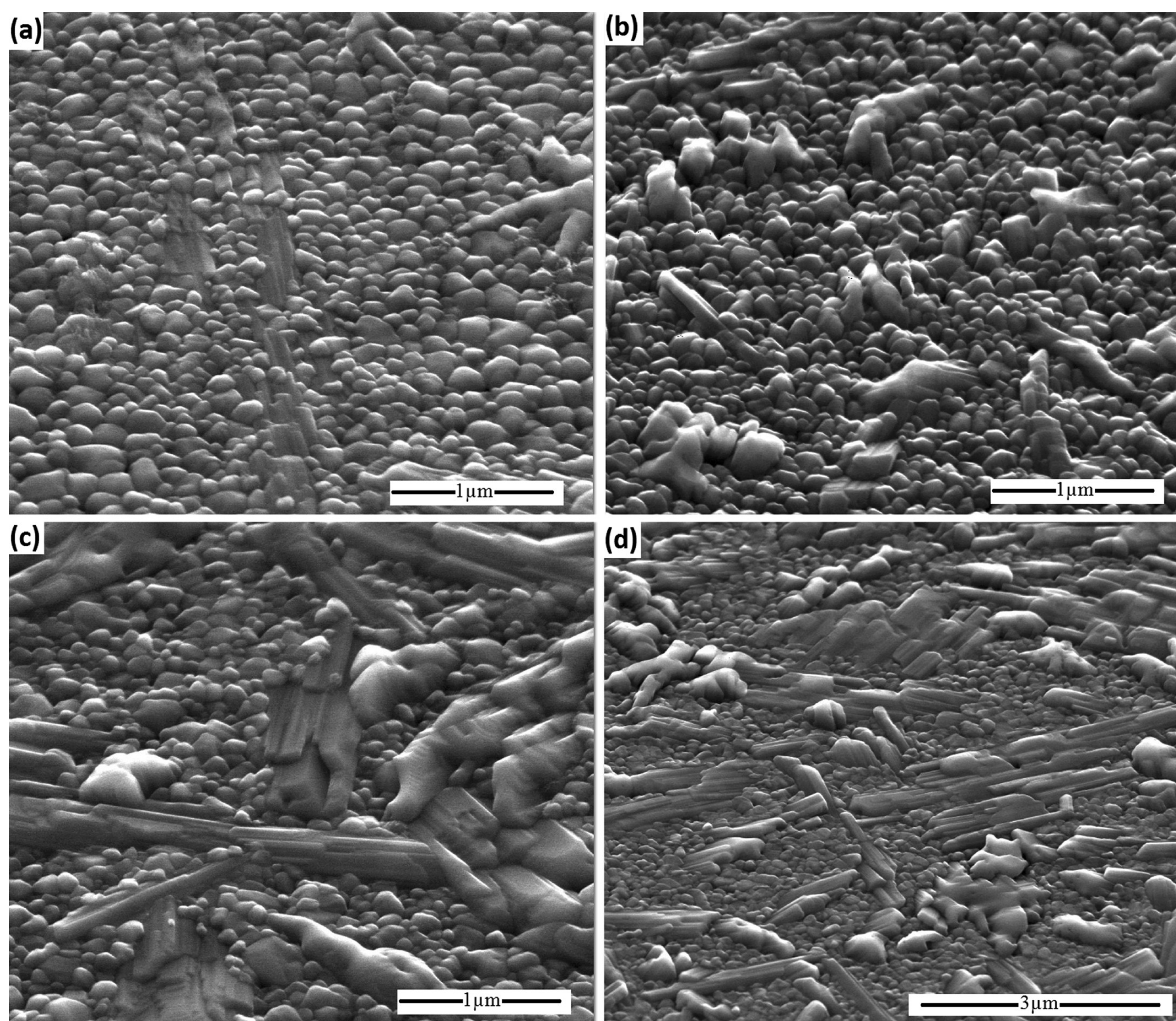

Figure 6. SEM images of the samples fabricated with (a) 2, (b) 5, (c) 8, and (d) 12sccm of oxygen flow rates and subsequently heated at 520 °C in 100 mtorr of O_2.

resistance, and the optical constants are very important both from the physics point of view as well as for applications.

VO_2 thin films were also deposited with varying amounts of oxygen (2 to 24 sccm) in the deposition chamber and later oxidized as described earlier. The film thickness, as measured by Dektak, for these films varied between 80 and 100 nm. All the as-deposited films with an oxygen flow of less than 18 sccm exhibited a gray color and a metallic behavior with a sheet resistance of less than 350 Ω/cm^2 and reflectivity of higher than 80% in the near infrared region (1500–2500 nm).

However, the as-deposited film obtained with an oxygen flow of 18 sccm or more in the chamber had yellowish to orange colour indicating the probable formation of the Vanadium pentoxide (V_2O_5).[15] Such films also had a dielectric behavior with a very high sheet resistance on the order of 1×10^5 Ω/cm^2. The reaction between Vanadium and oxygen for the formation of lower vanadium oxides (VO_x) such as VO_2 is known to require a high critical temperature which in turn depends on the partial pressure if oxygen. Griffithsand et al.[16] have established that a temperature higher than 300°C with an oxygen partial pressure of 2 mTorr is essential for the formation of VO_2. In Figure 4a are given the transmittance change of the samples deposited with varying degree of oxygen (2 to 12 sccm) and oxidized later. At room temperature, these films show a transmittance of 32 to 44% in the visible and near infrared region. When the temperature is raised above the transition temperature, the transmittance in the near infrared region falls to a lower value (4–7%) with relatively little change in the visible region. Such samples showing a very effective transmittance switching in the infrared part and maintaining a high transmittance in the visible region are very interesting for smart window application for heat management purpose. A theoretical calculation of the transmittance values using the matrix method and the known refractive index at the wavelength of 2500 nm[17] and assuming a film thickness of 140 nm was carried out. Transmittance values of 40 and 7% at low and high temperatures, respectively, were obtained. This calculation assumes a thin layer without any defects. Our experimental measurements are in fairly good agreement with these theoretical values. In Figure 4b are shown the drastic change in sheet resistance undergone by each of these samples. A steep decrease in the sheet resistance of the films is seen as a function of increasing oxygen flow during the film deposition. Another important consequence of the increased oxygen flow is the diminution in the transition temperature. From a transition temperature of 66 °C for a sample with the least amount of oxygen flow a decrease in temperature to 56 °C is seen for a sample with the most oxygen flow. As can be seen from Figure

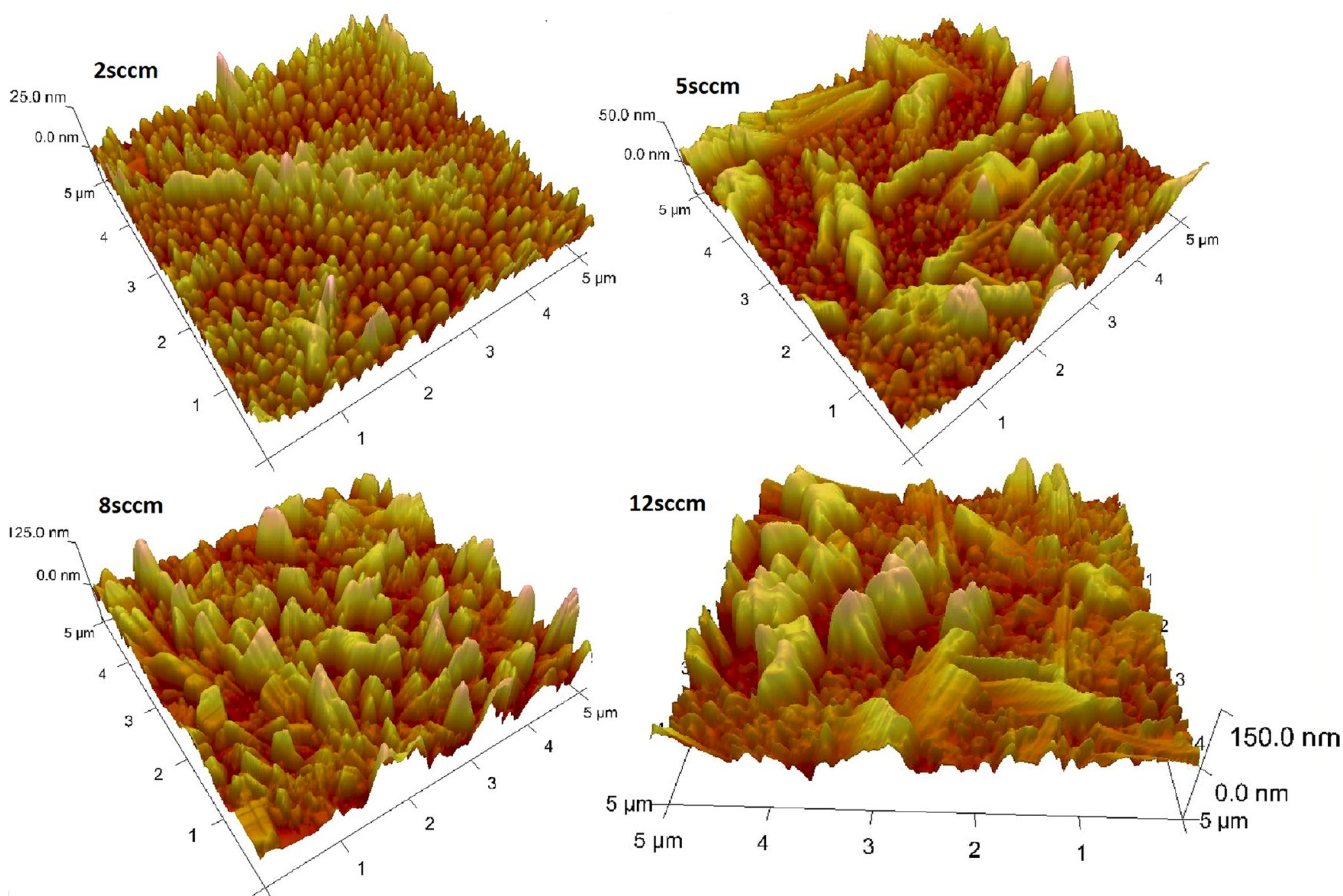

Figure 7. AFM pictures of the samples fabricated with 2, 5, 8, and 12 sccm of oxygen flow then heated at 520 °C in 100 mtorr of O_2.

Table 1. RMS Roughness and the Length (L)/Width (l)/Height (H) of the Crystallites Measured by AFM

O_2 flow (sccm)	2	5	8	12
RMS (nm)	25.7 ± 2.1	36.7 ± 1.7	32.0 ± 1.7	34.7 ± 2.3
L (nm)	118 ± 27	2312 ± 175	2065 ± 571	>2000
l (nm)	118 ± 30	448 ± 84	569 ± 66	513 ± 162
H (nm)	59 ± 05	158 ± 07	113 ± 15	106 ± 14

4b, this decrease in transition temperature is also accompanied by a decrease in area of hysteresis loop. These results are shown in Figure 5a where the FWHM of the hysteresis curve and the transition temperature decrease systematically with increasing oxygen flow. The FWHM of the transition hysteresis decreases from 9.7 to 5.6 °C. Figure 5b also shows the stoichiometry of these films as measured by the XPS technique. The XPS spectral analysis revealed the presence of oxygen, carbon and vanadium as well as traces of potassium, magnesium, calcium and fluorine, probably from contaminants. To measure the stoichiometry, we recorded high-resolution spectra of O1s and V2p1/2. The spectra of V2p1/2 showed two components of vanadium (V4+ and V5+), respectively associated with the corresponding components O1 (4 +) and O3 (5 +).[18−20] The O/V ratio is found to vary between 1.9 and 2 for our samples. This is compared with the other well known stable phases of vanadium oxides (V_2O_3 and V_6O_{13}).[4] We have also performed an XRD analysis on one of our films to confirm that it was indeed polycrystalline. The observed spectral lines are attributed to VO_2(M) phase which confirms both stoichiometry and phase.

The atomic force microscopy (AFM) and scanning electron microscopy (SEM) were carried out on these films with varying degree of oxygen flow. The SEM images of the VO_2 samples are given in Figure 6. A systematic increase in grain size is seen with increasing oxygen flow. The film prepared with 2 sccm oxygen flow exhibits a very highly granular structure. These nanograins evolve progressively into columnar microstructures with preferred orientation, with increasing oxygen flow. These SEM observations are confirmed by the atomic force micrographs shown in Figure 7. The parameters associated with these images are shown in Table 1. The grain growth seems to proceed according to the Volmer−Weber model wherein a strong adatom−adatom interaction is expected because of the mismatch between the lattice parameters of VO_2 and the glass substrate.[21] As can be seen from both Figures 6 and 7, there is a gradual evolution of the grains into columns with increasing oxygen flow. The 2 sccm sample presents a predominantly granular surface with a RMS roughness of 25 nm. The 5 sccm sample exhibits the development of some columns with an increased roughness of 36 sccm. The other samples (8 and 12 sccm) show an increased column density with a slight decrease in the roughness triggered by the coalescence of grains.

An interesting feature of our samples is the high optical and electrical contrast they show with thermochromic phase transition, despite their small thickness. This seems to be due to the absence of film porosity and weak diffusion. The

variation of transition temperature with oxygen flow seems be more correlated to the microsctructure and not correlated to film stoichiometry. The link between the phase transition and the microstructure of the VO_2 thin films has been investigated by several groups.[22−25] Lopez et al.[22] have studied the dependence of the MIT and hysteresis loop on particle size in VO_2 thin films prepared by ion implantation in fused silica. In their work they have used the theory of heterogeneous nucleation statistics with a phenomenological approach. Donev et al.[23] have arrived at the conclusion that size effect is responsible of thermal hysteresis loop by studying Raman scattering at the surface of VO_2 thin films prepared by pulsed laser deposition. Brassard et al.[24] have reported similar effect on VO_2 thin films produced by rf magnetron reactive sputtering. Similar variation to ours in transition temperature was observed by Suh et al.[25] The major difference in their case is the systematic shift of the hysteresis curve with changing annealing temperature, whereas in our case, we have observed the flattening of the hysteresis curve due to the shifting of only the heating leg of the curve, while the cooling leg remained relatively less affected. Our results and the analysis show that the flattening of the hysteresis curve by about 10 °C is eventually correlated to the grain size.

CONCLUSION

VO_2 thin films have been deposited by ion assisted dual magnetron ac cathodic sputtering. High-rate and high-quality VO_2 thin films can be deposited with a near perfect reproducibility. The films exhibit a high-efficiency thermochromism with a high optical and electrical contrast. The uniformity and the high density of the films with a nanostructure and phase transition that can be controlled through the oxygen flow render the films very apt for integrated optical applications.

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Notes

The authors declare no competing financial interest.

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