Phys. Scr. 92 (2017) 114007 (8pp)

https://doi.org/10.1088/1402-4896/aa90a3

Investigation of electron beam lithography effects on metal-insulator transition behavior of vanadium dioxide

H Yuce¹, H Alaboz¹, Y Demirhan¹, M Ozdemir^{1,2}, L Ozyuzer^{1,2} and G Aygun¹

E-mail: ozyuzer@iyte.edu.tr

Received 26 April 2017, revised 25 September 2017 Accepted for publication 3 October 2017 Published 25 October 2017



Abstract

Vanadium dioxide (VO₂) shows metal-insulator phase transition at nearly 68 °C. This metalinsulator transition (MIT) in VO2 leads to a significant change in near-infrared transmittance and an abrupt change in the resistivity of VO₂. Due to these characteristics, VO₂ plays an important role on optic and electronic devices, such as thermochromic windows, meta-materials with tunable frequency, uncooled bolometers and switching devices. In this work, VO2 thin films were fabricated by reactive direct current magnetron sputtering in O₂/Ar atmosphere on sapphire substrates without any further post annealing processes. The effect of sputtering parameters on optical characteristics and structural properties of grown thin films was investigated by SEM, XRD, Raman and UV/VIS spectrophotometer measurements. Patterning process of VO₂ thin films was realized by e-beam lithography technique to monitor the temperature dependent electrical characterization. Electrical properties of VO₂ samples were characterized using microprobe station in a vacuum system. MIT with hysteresis behavior was observed for the unpatterned square samples at around 68 °C. By four orders of magnitude of resistivity change was measured for the deposited VO₂ thin films at transition temperature. After e-beam lithography process, substantial results in patterned VO2 thin films were observed. In this stage, for patterned VO₂ thin films as stripes, the change in resistivity of VO₂ was reduced by a factor of 10. As a consequence of electrical resistivity measurements, MIT temperature was shifted from 68 °C to 50 °C. The influence of e-beam process on the properties of VO₂ thin films and the mechanism of the effects are discussed. The presented results contribute to the achievement of VO₂ based thermochromic windows and bolometer applications.

Keywords: vanadium dioxide, metal insulator transition, e-beam lithography, magnetron sputtering

1

(Some figures may appear in colour only in the online journal)

1. Introduction

Transition metal oxides have been investigated widely due to their peculiar electrical and optical properties. Vanadium dioxide (VO₂) indicates a reversible metal insulator transition (MIT) at \sim 68 °C [1, 2]. It has been reported that MIT behavior of VO₂ strongly varied in wide range with crystal quality, grain size, grain boundaries and defects related to self-doping and the other factors [3, 4]. While VO₂ has monoclinic crystal structure with insulator phase at below the MIT temperature

 $(T_{\rm MIT})$, the material has tetragonal rutile crystal structure with metallic phase at above $T_{\rm MIT}$ [5, 6]. During the transition, the change in the volume of VO₂ crystal is around 1%–2% [7]. In insulator phase, the energy bandgap of VO₂ is around 0.65 eV [8]. There have been two views on the origin of MIT in VO₂; Peierles transition and Mott–Hubbard transition. Peierles transition arises due to the change in crystal structure, and Mott–Hubbard transition takes places due to electron-electron correlations [9]. MIT in VO₂ can be induced by heating [10], doping [11, 12], ion bombardment [13] and UV light [14].

¹ Department of Physics, Izmir Institute of Technology, 35430 Urla, Izmir, Turkey

² Teknoma Technological Materials Ltd, 35430 Urla, Izmir, Turkey

Table 1. Deposition	parameters and	morphology	of VOs s	amples
Table 1. Deposition	Darameters and	11101101101027	UL VU2 S	annoies.

Sample	Reactive oxygen ratio (%)	Deposition time (min)	Average grain size (nm)	Thickness (nm)	Electrical properties
A	2.00	45	NA	310	MIT
В	2.00	22.5	<20	120	Non-transition (metallic)
C	2.25	22.5	NA	125	MIT
D	2.50	22.5	150	124	Non-transition (insulator)
E	3.00	22.5	150	127	Non-transition (insulator)

Insulator VO₂ has high transmittance whereas metallic VO₂ becomes opaque to near-IR radiation [15, 16]. MIT behavior of VO₂ is not only accompanied by significant change in infrared transmittance but also sharp change in resistivity. The transition takes place in approximately 80 fs, which is useful property for switching applications [17]. Moreover, MIT in VO₂ exhibits hysteresis behavior which can be tuned. These characteristics can be useful in many areas of optics and electronics, such as thermochromic windows [18, 19], tunable frequency meta-materials [20], detectors [21–24] and switching devices [25, 26]. Sensor applications require negligible hysteresis with high resistance drop during phase transition while the storage type devices require relatively large hysteresis [27].

There are various techniques to fabricate VO₂ films, such as pulsed laser deposition [28], chemical vapor deposition [29], atomic layer deposition [30], spray pyrolysis [31] thermal oxidation [32], sol-gel method [33] and magnetron sputtering [34, 35]. Being the most suitable technique in terms of large area growth, uniform deposition and high crystal quality [36], magnetron sputtering technique has advantageous in many respects to the others techniques.

Since it has been a challenging task to grow high quality VO₂ thin films, various substrates have been used as seen from the literature [15, 37]. The microstructure of deposited VO₂ thin films depends on lattice matching and surface energy of the substrates. Although silicon substrates are relatively cheaper and widely used in microelectronics, it is quite challenging to deposit high quality VO₂ films due to unavailability of its native oxide layer on the silicon substrates [37]. However, the sapphire substrates are commonly used for achieving high quality VO₂ thin films due to the fact that it has high thermal conductivity compared to the other ones.

In this study, VO_2 thin films were successfully grown on c-cut sapphire without any post annealing processes. The structural, optical and electrical properties of these grown thin films were investigated. The grown VO_2 films were patterned by e-beam lithography for the electrical measurements. The effect of structure size, patterning process on resistivity and MIT characteristics of VO_2 thin film were investigated. It is observed that e-beam patterned stripes with narrowed width (e.g. high aspect ratio ranging from 44 to 220) have peculiar properties. These will be discussed in detail in results and discussion part. The main outcome of this study is highly important that $T_{\rm MIT}$ was decreased from 68 °C to 50 °C as a result of e-beam lithography processing.

2. Experimental procedure

VO₂ thin films were deposited on c-cut sapphire (Al₂O₃ (0001)) using high purity (99.95%) vanadium (V) target by DC magnetron sputtering technique [38, 39]. Substrates were cleaned with acetone and DI water by means of ultrasonic cleaner. The vacuum chamber was evacuated to a base pressure of 1.2×10^{-6} mbar and the substrate was kept at 550 °C during deposition. In order to get rid of any contaminations of target's surface, 10 min pre-sputtering was performed on the target prior to deposition. VO2 thin films were grown under 8.5×10^{-3} mbar of O_2 and Ar mixed gas pressure environment and 50 W of sputtering power. The substrates were rotated at 15 rpm in order to improve the uniformity of the film during the deposition process. Oxygen gas ratio of the sputtered thin films was varied in order to investigate the growth conditions of VO₂ thin films having sharp resistivity changes at T_{MIT} . Sample deposition parameters and the properties of the discussed films can be seen in table 1. In our experiments, firstly 310 nm VO₂ (named sample A) was grown on sapphire substrate during 45 min. According to analysis results, high quality VO₂ with the high change in resistivity depending on the temperature was observed. After that, in order to obtain thinner VO₂ film, we reduced deposition time from 45 to 22.5 min. Therefore, we obtained 125 nm vanadium oxide thin films with various unexpected phase at different oxygen concentrations. According to optimized parameters of the sample A, deposition time was reduced to 22.5 min at the same oxygen concentration (2.00%), and we deposited 125 nm VO_x with 2.00% oxygen rate (named sample B). For sample B, MIT was not observed. Due to that, oxygen concentration was increased up to 3.00% (named sample C for 2.25% O2, sample D for 2.50% O₂, sample E for %3.00 O₂) with 22.5 min deposition time. However, for 125 nm VO_x thin films, high quality VO2 thin film like sample A could not be obtained. 125 nm grown VO_x thin films except sample C did not exhibit MIT. As considering all grown films, only sample A and sample C show a transition. When especially electrical analysis results were examined, it is clear that sample A is more quality with high changing resistivity rate than sample C.

Structural and morphological properties of the films were characterized by field emission scanning electron microscopy (FE-SEM, Philips Quanta) equipped with energy dispersive spectroscopy (EDS, Oxford X-act). X-ray diffractometry (XRD, Philips PANanalytical X'Pert System) was used for the structural properties of the grown VO₂ thin films. The

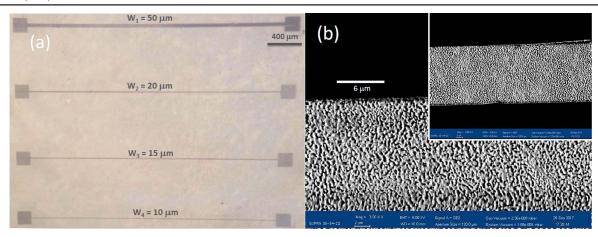


Figure 1. In order to investigate e-beam effect on VO_2 thin films, the VO_2 strips with varied dimensions were designed and fabricated. (a) The optical image of e-beam patterned VO_2 thin film (sample A, 310 nm thickness) strips with 50, 20, 15 and 10 μ m strip widths (W) and 2.2 mm strip length is given. (b) SEM image of 20 μ m width strip edge. The black region is sapphire. The inset shows the full width of the strip which corresponds to 20 μ m.

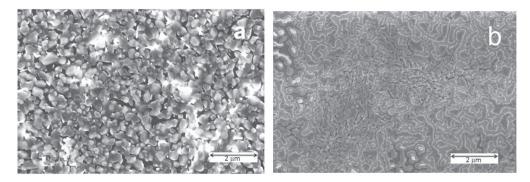


Figure 2. Field emission scanning electron microscope (SEM) images of 310 nm VO₂ thin film (sample A) (a) and 125 nm VO₂ thin film (sample C) (b) with 2 μ m length scale bars. (Among all grown vanadium oxide thin films given in table 1, sample A and sample C have both shown MIT.)

XRD measurements were performed from 10° to 80° for 2θ using Cu K_{α} radiation ($\lambda=1.5406\,\text{Å}$) with step size of 0.04° and time step of 1 s. Optical transmittance spectra of samples at normal incidence were taken between 200 and 1200 nm using spectrophotometer (UV/VIS Spectrophotometer, Perkin Elmer) with a precisely controlled homemade heating mechanism. The thickness of the grown thin films was measured by a surface profilometer (Vecco DEKTAK 150). Raman measurements were taken by a confocal Raman spectroscopy (Scientific Instruments). The resolution of the Raman measurements was $2.0\,\mathrm{cm}^{-1}$. Argon laser with 514 and 633 nm excitation wavelengths having 120 mW (514 nm laser) and 20 mW (633 nm laser) power were used for the Raman analysis.

Deposited high quality VO₂ thin films were patterned by e-beam lithography (Raith e-line e-beam lithography system) to investigate the effects of e-beam on MIT characteristics of aforementioned films. For this purpose, the VO₂ films were coated with AZ5214 photoresist at 3000 rpm for 50 s. Photoresist coated films were heat treated for 30 min in a furnace kept at 90 °C. After the film was patterned by e-beam, it was exposed to ultraviolet light (OAI Mask Aligner) for 7 s. Later, it was put in developer solution and rinsed with deionized water. Followed by hard bake process at 120 °C, Ar ion

milling was performed. The samples were water cooled during etching of VO_2 to create strips. Remaining photoresist was stripped away with acetone at the last step of the patterning process [40, 41]. Final structure of shaped VO_2 stripes and a representative SEM picture were given in figure 1. The discussion of the images were deferred to a later part of this paper.

Electrical measurements of VO_2 samples were done between 30 °C and 100 °C with usage of microprobe station (Janis Microprobe Station). A Labview controlled computer program was used to record the measurements done by a Keithley sourcemeter.

3. Results and discussions

3.1. Structural properties

Surface morphologies of the grown VO_2 thin films having different O_2/Ar flow rates and deposition durations were investigated using SEM (figure 2). There are many variables such as substrate, growth temperature, deposition rate and sputtered ion energy affecting the quality of the grown vanadium oxide films. In this study, we investigated two

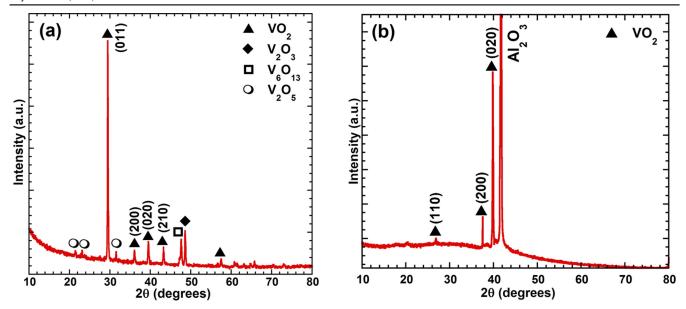


Figure 3. XRD spectrum of sample A (a) and sample C (b) which shows MIT behavior. Here, it is seen that sample A -310 nm film thickness with 2.00% oxygen concentration- exhibits high intensity VO₂ diffraction peak. However, XRD diffraction peaks of sample C -125 nm film thickness with 2.25% oxygen concentration—belong to VO₂ are at lower intensity.

parameters, namely oxygen concentration in grown vanadium oxide films and the thickness of the films. These two variables in our experiments affect grain size and surface morphology of the thin films. As shown in table 1, sample A and C exhibit MIT among deposited thin films.

Figure 2 shows SEM images of samples A and C. While sample A has small grains (figure 2(a)), sample C has meander like structure (figure 2(b)). It is concluded that increasing deposition time and decreasing oxygen concentration of the films convert meander like grains to small grains. This effect can be explained with the diffusion and migration of adsorbed atoms; increasing deposition time gives additional time to adatoms for diffusion and migration on the substrate surface which is essential for nucleation and growth [42].

The XRD patterns of as grown thin films at different O2 flow rates and growth duration were collected for 2θ between 10° and 80° . There are two important peaks observed at $\sim 29^{\circ}$ and 39° related to VO₂ as seen in figure 3(a). These can be assigned to (011) and (020) diffraction peaks [42]. Since the film is quite thin for sample C, a strong peak at $2\theta \sim 41^{\circ}$ is detected belonging to sapphire substrate [43] as shown in figure 3(b). According to XRD results, the films consist of mixed phases, i.e. VO_2 , V_2O_3 , V_2O_5 and V_6O_{13} [43, 44]. It can be understood from the XRD peaks that 2.00% oxygen to argon ratio is a reasonable choice to grow 310 nm thick vanadium oxide films in the form of mainly VO₂ phase. In addition, in case of thickening the grown film, the orientation of vanadium oxide crystal changes compared to substrate orientation, and this leads to consist of more polycrystalline structure as in sample A. Due to the change in crystal orientation depending on the film thickness, the peaks which are the highest intensity belong to sample A and C are different from each other.

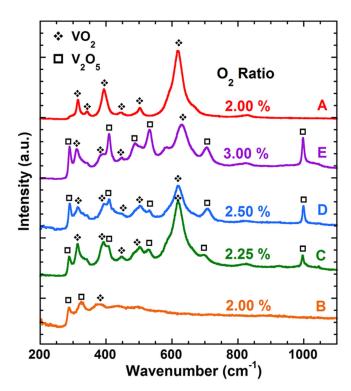


Figure 4. Raman spectra of thin films deposited at different O_2/Ar flow ratios. Note that sample A is thicker than the rest of the samples. According to the Raman spectra of sample A and sample B, main observed vanadium oxide Raman modes are disappeared with decreasing film thickness. Also, in case of decreasing O_2/Ar flow ratio, the grown vanadium oxide thin films with the same thickness (sample B, C, D and E) exhibit more metallic properties.

Raman microscopy analyses were carried out at room temperature for each sample in order to investigate the oxygen flow ratio effects on the phases of vanadium oxide films (figure 4). In order to prevent phase transition due to heating effects during the measurement, laser intensity was

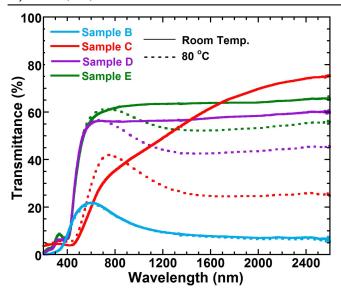


Figure 5. Optical properties of deposited VO₂ thin films with different oxygen flow ratios at room and above transition temperatures. Note that solid lines correspond to room temperature measurement and dashed lines for 80 °C ones.

minimized to its lowest possible value. Raman analysis show that VO2 and V2O5 coexist in grown thin films except for sample A. Raman peaks detected at 313, 342, 392, 445, 502 and 617 cm⁻¹ correspond to VO₂ phase as reported in the literature [45]. The main V–V band at 617 cm⁻¹ belongs to VO₂ phase. Besides VO₂ peaks, the detected signals at 288, 408, 488, 530, 704 and $997 \, \text{cm}^{-1}$ correspond to V_2O_5 characteristic peaks [46]. The highest Raman intensities belonging to VO₂ phase with a lower V₂O₅ intensity mode are detected for sample C grown at 2.25% oxygen ratio compared to the other ones having the same thickness. As a result, it can be concluded that 2.25% oxygen ratio for 125 nm thick film includes more abundant peaks corresponding to strong vibrational modes of VO₂ phase. As increasing O₂ ratio from 2.25% to 3.00%, the intensity of V₂O₅ phase increases while that of VO₂ phase decreases. The Raman peak at 285 cm⁻¹ is assigned to V₂O₅ phase of sample B [46]. Also, the broad peak at around 320 cm⁻¹ could be belong to amorphous V₂O₅ [47]. For sample B, there is another broad peak at around $386 \,\mathrm{cm}^{-1}$ which is shifted by $\sim 6 \,\mathrm{cm}^{-1}$ compared to the Raman peak of sample A at 392 cm⁻¹. This Raman shift may be related to chemical bond of the molecule. These results are supported by XRD analysis that when the oxygen gas ratio increases above 2.25%, the percentage of VO2 decreases while V₂O₅ phase increases.

3.2. Optical properties

Transmittance spectra measured at room temperature and 80 °C of grown VO_2 thin films (samples B, C, D and E) grown under different O_2 flow rates are shown in figure 5. Due to higher thickness of sample A (see table 1), transmittance measurements of all samples are not comparable. Therefore, the transmission spectrum of sample A was not set in this graph. Due to phase transition, the transmittance of the

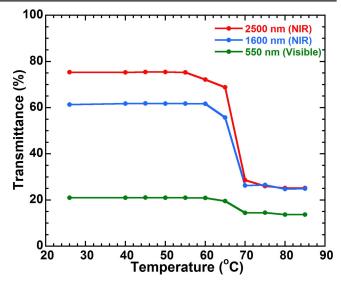


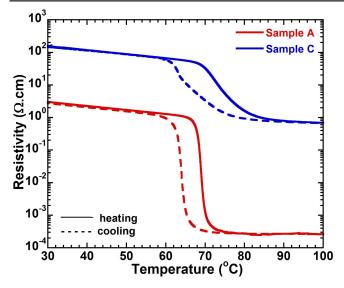
Figure 6. Temperature dependent transmission change is seen for various wavelengths in sample C.

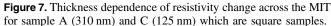
films decreases in near-IR region above MIT temperature. As it is clearly seen from the plots, VO₂ thin films show high optical transmission in their insulating state, i.e. at room temperature, while low optical transmission in their metallic state in IR region above MIT temperature, namely 80 °C. Moreover, transmittance change was not observed in the film grown under 2.00% O₂ (sample B) flow rate. Since the as grown film is already in metallic phase, transmission at all temperatures, as expected, is low in IR region corresponding to the metallic case behavior. For grown thin films with 2.50%–3.00% O₂ ratio, the transmittance variation rates are almost the same, being around 8%–15%. As it can be clearly seen in figure 5, VO2 thin film grown under 2.25% oxygen ratio had the MIT, and showed the highest change in transmittance at IR region. Above transition temperature, VO₂ has metallic phase resulting in an increment of electron concentration in the conduction band.

Figure 6 indicates the temperature dependent transmittance of deposited 125 nm VO_2 thin films grown under 2.25% oxygen flow ratio at the wavelengths of 1600 and 2500 nm for near infrared and 550 nm for visible regions. In visible region, transmittance varies 7% with temperature, and it is about 21% at low temperatures. In addition, transmittance change at MIT region is around 36% for 1600 nm and 50% for 2500 nm wavelength. It is concluded that transmittance of insulator VO_2 phase is higher for 2500 nm than that of 1600 nm wavelength.

3.3. Electrical properties

It is known that mixed phases of vanadium oxide systems need to be optimized in terms of sputtering parameters to yield high quality pure VO_2 phase. One of the most important properties that determine film quality is the resistivity drop at $T_{\rm MIT}$. It is indicated that the change in resistivity depends on uniformity of the film [48], strain, grain size and boundaries [3, 4, 49]. Epitaxially grown VO_2 films are known to be the





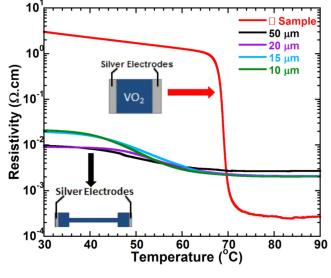


Figure 8. Temperature dependence of resistivity (during heating) for square sample A and the stripes with various widths.

best qualified films, and they exhibit resistivity changes an order of four at transition temperature [50]. Their hysteresis width of temperature changes from 0.5 °C to 2 °C [51]. Recent studies support that resistivity changes in high quality VO_2 films is about 10^4 for magnetron sputter deposited VO_2 films [26]. In our experiments, the sputtering conditions were optimized to obtain VO_2 thin films having 10^4 resistivity drop at $T_{\rm MIT}$.

Figure 7 shows the resistivity of these films in the measurement range between 30 °C and 90 °C. The size of square samples was $4 \text{ mm} \times 4 \text{ mm}$. Note that the square samples were cut from large VO2 grown substrate, and silver electrodes were deposited. Square samples were not exposed to any e-beam process. It is clearly seen that the resistivity of sample A at transition temperature decreases more than 10⁴ of magnitude. $T_{\rm MIT}$ is about 68 °C, and the hysteresis loop width is about 4 °C for sample A, which are quite good values for DC sputtered VO₂ thin films [52]. In addition, it is observed that resistivity change across transition decreases by a factor of 10² for sample C. Therefore, it can be concluded that the films including high oxygen concentration with mixed phases show less resistivity change at transition temperature. The deposition time is an important factor to observe MIT in VO₂. When deposition time decreases to 22.5 min from 45 min, grown films are exposed to high temperature with 550 °C for less time. This leads to reduce the reactions of scattered V atoms with oxygen atoms. In this instance, instead of VO₂, other vanadium oxide phases take place. Because of the reason, Sample B could not exhibit MIT at nearly 68 °C. Sample B exhibits more metallic properties compared to the other grown vanadium oxide thin films due to exposing lower reactions with oxygen atoms. For the other samples, in case of increasing oxygen concentration (from 2.00% to 3.00%) with 22.5 min deposition time, it is necessary that new deposition parameters like deposition pressure should be determined in order to observe MIT. Under sample D and sample E fabrication conditions, there is more than enough oxygen present to react with V atoms. The excess of oxygen concentration leads to coexist unexpected secondary phases and VO₂ phase. Thus, these secondary phases prevent or reduce MIT in grown vanadium oxide thin film. Due to the excess of the oxygen concentration, sample D and sample E do not exhibit MIT properties.

Figure 8 shows temperature dependence of resistivity for a square sample and the e-beam lithography patterned VO₂ stripes. Note that the square sample is not patterned and measured as grown. The square sample is shown as an inset picture of figure 8, whereas the optical microscopy and SEM images of stripes can be seen in figure 1. The length of the stripes was 2.2 mm and the widths of the stripes were changed from 10 to 50 μ m. Therefore, aspect ratios were ranging from 220 to 44. It has been observed that the resistivity of VO₂ stripes decreased down to around $10^{-2} \Omega$ cm at room temperature (figure 8). It can be also seen that the $T_{\rm MIT}$ shifted to about 50 °C. On the other side, the resistivity drop was only one order for the stripes at $T_{\rm MIT}$. As a summary, when the electrical properties of the square sample are compared to those of stripes, three distinct changes occur: (i) the resistivity value at room temperature decreases, (ii) resistivity changes at MIT get smaller, (iii) $T_{\rm MIT}$ shifts to 50 °C from 68 °C which is getting closer to room temperature, and (iv) the resistivity value at room temperature increases. These variations could be related to the e-beam patterning processes of the stripes. We investigated the influence of soft bake, developer and hard bake on the electrical properties of VO₂ films. However, there was not any change in electrical results for VO₂. The stripes of VO2 films were exposed to electrons with 10 keV energy during e-beam lithography process held around 1.3×10^{-6} Torr vacuum. Under this circumstance, electron beam could affect the structure of grown VO2 thin film. During e-beam lithography process, applied electron current leads to local heating on the surface of the film. In case of taking place local heating in high vacuum ambiance, a number of oxygen might release from VO2 thin film.

Therefore, the reduction in oxygen concentration of grown VO2 film leads to consist of secondary phase which are in metallic phase of vanadium oxide compounds. Since the electrons prefer low resistance paths, it is reasonable that we get low resistivity at room temperature for e-beam patterned samples. In contrary to this, the secondary phases increase the resistance above $T_{\rm MIT}$ for patterned samples. As a result, we observe distinct properties of VO2 stripes produced after e-beam lithography processes than those of square sample. Moreover, as we know from the literature studies, since the MIT in V_2O_3 and V_6O_{13} occurs, respectively, at -105 °C [53] and -123 °C [54], they are in metallic phases of vanadium oxide at the temperatures of our measurement region. In order to create patterned VO₂ structures, there are various methods, such as lift-off process [55]. Compared to their works which include lift-off method, we examined electron beam effect on VO₂ thin film. In order to create patterned vanadium oxide stripes, VO₂ thin film was shaped by electron beam lithography. In our works, during electron beam writing on VO2 thin film, the film was exposed to electron beam with 10 keV energy. Our works show that electron beam lithography leads to decrease the change in resistivity of patterned stripes compared to VO₂ thin film. In order to give shape to VO₂ film, because of the negative effect of electron beam lithography, lift-off process could be better option for now. In this case, new research and studies will be required in order to prevent negative effect of electron beam lithography. Because electron beam lithography provides significant advantages in terms of its high resolution property for nanotechnology. Furthermore, SEM picture in figure 1(b) demonstrates large roughness of the sample. While the details of picture reveals grains as given in figure 2(a), figure 1(b) could be between figures 2(a) and (b) in terms of the surface morphology. So this change could be caused by e-beam influence on stripes.

3.3.1. Raman analysis results of patterned vanadium oxide stripes. Because of the nano-stripes, we are not able to look at XRD study to find crystal structure of patterned stripes. Furthermore, XPS studies cannot obtain local data from these stripes. On the other hand, we analyzed vanadium oxide stripes by confocal Raman spectroscopy, and Raman analysis results is shown in figure 9.

Due to strong resonance effect, in order to observe the Raman peaks at 192 and 222 cm⁻¹, 633 nm laser is better than 514 nm one. Because of this, in order to observe all phonon modes and prevent weak signals, 633 nm laser was used for Raman analysis of patterned samples. In figure 9, the vibration bands of VO_2 were observed by the peaks at 192, 222, 260, 306, 337, 386, 442, 497 and 613 cm⁻¹. These peaks are consistent with the literature [45]. After e-beam process, patterned vanadium oxide stripes (width range from 20 to $10 \,\mu\text{m}$) were analyzed by Raman spectroscopy. As shown in figure 9, the peak at $192 \,\text{cm}^{-1}$ was observed at lower intensity compared to the patterned stripes. The intensity variation between the stripes and VO_2 thin film for bands at $192 \,\text{cm}^{-1}$ may be due to differences in vanadium oxide crystal orientations. The Raman peak at $442 \,\text{cm}^{-1}$ which was

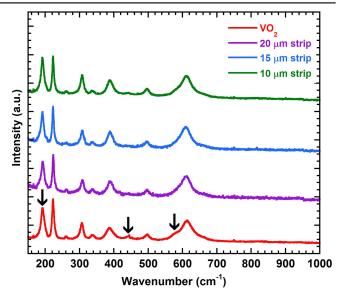


Figure 9. Raman spectrum of VO_2 and patterned vanadium oxide stripes (width range from 20 to 10 μ m).

observed for VO₂ film was vanished for all patterned vanadium oxide stripes. According to Raman analysis of VO₂ film, there is a shoulder located at around 580 cm⁻¹. This shoulder was vanished in Raman analysis of patterned vanadium oxide stripes. These results show that not only variation of crystal orientation but also weaker crystalline properties occurred due to the e-beam exposure. Raman studies are also in agreement with the electrical measurements given in figure 8. It can be seen that the resistivity drops in the stripes at room temperature support that the secondary phases occurred in e-beam patterned structures. Therefore, it can be concluded that the obtained crystal structure variations are caused by e-beam patterning of stripes.

4. Conclusion

In summary, we have obtained high quality DC magnetron sputtered VO_2 thin films on c-cut sapphire substrate. Various oxygen concentrations were performed and optimized to obtain VO_2 films with a sharp resistivity drop across MIT. The change in resistivity at transition temperature of VO_2 thin film is around by a factor of 10^4 , and it is convenient for electrical switching applications. Moreover, the grown VO_2 thin films exhibit nearly 50% transmission change in near-IR region, which is promising for optical applications, such as thermochromic windows.

The grown VO_2 films having 10^4 resistivity drop were used for the electrical characterization of patterned stripes. For these measurements, e-beam lithography and Ar ion etching processes were used for the purpose of patterning the grown VO_2 films in the form of stripes. As a result, we have investigated the effect of e-beam patterning on MIT characteristics of VO_2 films when the electrical characteristics of the stripes and square samples are compared. It is observed that $T_{\rm MIT}$ shifts close to room temperature after patterning the VO_2 films by e-beam lithography. E-beam causes a change in oxygen concentration of grown VO_2

thin film (figure 8), the metallic phase of vanadium oxide compounds becomes dominant. Secondary phases of VO_x might originate from low oxygen concentration due to local heating under high vacuum. Formed metallic phase of the secondary phase in VO_x causes a drop of resistivity of the film at room temperature while the degradation of ideal oxygen concentration leads to a decrease in the ratio of resistivity values (MIT rate) at $30\,^{\circ}\text{C}-90\,^{\circ}\text{C}$. Lastly, the change in resistivity of the VO_2 stripes is an order of magnitude, and transition temperature shifts from $68\,^{\circ}\text{C}$ to $50\,^{\circ}\text{C}$. Shifting T_{MIT} to a closer region of room temperature might be important in terms of many applications, such as thermochromic windows and bolometers.

Acknowledgments

This research is partially supported by TUBITAK (The Scientific and Technological Research Council of Turkey) with the project number 113F349 and partially by the University Research Foundation (BAP) with the project number of 2015-IYTE-42. Additionally, we thank to Applied Quantum Research Center (AQUREC) of IZTECH for the research facilities offered us with this study.

References

- [1] Balu R and Ashrit P V 2008 Appl. Phys. Lett. 92 21904
- [2] Gopalakrishnan G, Ruzmetov D and Ramanathan S 2009 J. Mater. Sci. 44 5345
- [3] Nag J, Payzant E A, More K L and Haglund R F Jr 2011 Appl. Phys. Lett. 98 251916
- [4] Nagashima K, Yanagida T, Tanaka H and Kawai T 2007 J. Appl. Phys. 101 26103
- [5] Fillingham P J 1967 J. Appl. Phys. **38** 4823
- [6] Guiton B S, Gu Q, Prieto A L, Gudiksen M S, Park H and Amer J 2005 Chem. Soc 127 498
- [7] Liu K, Cheng C, Suh J, Tang-Kong R, Fu D, Lee S, Zhou J, Chua L O and Wu J 2014 Adv. Mater. 26 1746
- [8] Yi X, Chen C, Liu L, Wang Y, Xiong B, Wang H and Chen S 2003 Infrared Phys. Technol. 44 137
- [9] Imada M, Fujimori A and Tokura Y 1998 Rev. Mod. Phys. 70 1039
- [10] Donev E U, Lopez R, Feldman L C and Haglund R F 2009 Nano Lett. 9 702
- [11] Goodenough J B 1971 J. Solid State Chem. 3 490
- [12] Krammer A, Magrez A, Vitale W A, Jeanneret P, Guibert E, Whitlow H J, Ionescu A M and Schüler A 2017 J. Appl. Phys. 122 045304
- [13] Gupta A, Singhal R, Narayan J and Avasthi D K 2011 J. Mater. Res. 26 2901
- [14] Wu J M and Liou L B 2011 J. Mater. Chem. 21 5499
- [15] Jiang M, Cao X, Bao S, Zhou H and Jin P 2014 Thin Solid Films 562 314
- [16] Yuce H 2015 MS Thesis Izmir Institute of Technology (http://hdl.handle.net/11147/4585)
- [17] Ruzmetov D, Gopalakrishnan G, Deng J, Narayanamurti V and Ramanathan S 2009 J. Appl. Phys. 106 83702
- [18] Kato K, Song P K, Odaka H and Shigesato Y 2003 Japan. J. Appl. Phys. 42 6523
- [19] Cui H N, Teixeira V, Meng L J, Wang R, Gao J Y and Fortunato E 2008 Thin Solid Films 516 1484

[20] Dicken M J, Aydin K, Pryce I M, Sweatlock L A, Boyd E M, Walavalkar S and Atwater H A 2009 Opt. Express 17 18330

- [21] Chen C, Yi X, Zhao X and Xiong B 2001 Sensors Actuators A 90 212
- [22] Gauntt B D, Dickey E C and Horn M W 2009 J. Mater. Res. 24 1590
- [23] Fieldhouse N, Pursel S M, Horn M W and Bharadwaja S 2009 J. Phys. D: Appl. Phys 42 055408
- [24] Alaboz H, Demirhan Y, Yuce H, Aygun G and Ozyuzer L 2017 Opt. Quantum Electron. 49 238
- [25] Stefanovich G, Pergament A and Stefanovich D 2000 J. Phys.: Condens. Matter 12 8837
- [26] Ruzmetov D, Gopalakrishnan G, Ko C, Narayanamurti V and Ramanathan S 2010 J. Appl. Phys. 107 114516
- [27] Narayan J and Bhosle V 2006 J. Appl. Phys. 100 103524
- [28] Kim D and Kwok H 1994 Appl. Phys. Lett. 65 3188
- [29] Maruyama T and Ikuta Y 1993 J. Mater. Sci. 28 5073
- [30] Dagur P, Mane A U and Shivashankar S 2005 J. Cryst. Growth 275 1223
- [31] Mousavi M, Kompany A, Shahtahmasebi N and Bagheri-Mohagheghi M-M 2013 *Phys. Scr.* **88** 6
- [32] Yoon J, Kim H, Mun B S, Park C and Ju H 2016 J. Appl. Phys. 119 124503
- [33] Partlow D, Gurkovich S, Radford K and Denes L 1991 J. Appl. Phys. 70 443
- [34] Li S Y, Namura K, Suzuki M, Niklasson G A and Granqvist C G 2013 J. Appl. Phys. 114 033516
- [35] Kusano E, Theil J and Thornton J A 1988 J. Vac. Sci. Technol. A 6 1663
- [36] Shigesato Y, Enomoto M and Odaka H 2000 Japan. J. Appl. Phys. 39 6016
- [37] Youn D H, Kim H T, Chae B G, Hwang Y J, Lee J W, Maeng S L and Kang K Y 2004 J. Vac. Sci. Technol. A 22 719
- [38] Tuna O, Selamet Y, Aygun G and Ozyuzer L 2010 J. Phys. D: Appl. Phys 43 055402
- [39] Ozdemir M, Kurt M, Ozyuzer L and Aygun G 2016 Eur. Phys. J. Appl. Phys. 75 30401
- [40] Turkoglu F, Koseoglu H, Demirhan Y, Ozyuzer L, Preu S, Malzer S and Kadowaki K 2012 Supercond. Sci. Technol. 25 125004
- [41] Demirhan Y, Saglam H, Turkoglu F, Alaboz H, Ozyuzer L, Miyakawa N and Kadowaki K 2015 Vacuum B 120 89
- [42] Zhang H, Wu Z, He Q and Jiang Y 2013 Appl. Surf. Sci. 277 218
- [43] Luo Y, Zhu L, Zhang Y, Pan S, Xu S, Liu M and Li G 2013 J. Appl. Phys. 113 183520
- [44] Zhu N-W, Hu M, Xia X-X, Wei X-Y and Liang J-R 2014 Chin. Phys. B 23 048108
- [45] Zhao Y, Lee J H, Zhu Y, Nazari M, Chen C, Wang H and Fan Z 2012 J. Appl. Phys. 111 053533
- [46] Piccirillo C, Binions R and Parkin I P 2007 Chem. Vapor Depos. 13 145
- [47] Öksüzoğlu R M, Bilgiç P, Yıldırım M and Deniz O 2013 Opt. Laser Technol. 48 102
- [48] Son L N, Tachiki T and Uchida T 2011 Japan. J. Appl. Phys. 50 025803
- [49] Ruzmetov D, Zawilski K T, Narayanamurti V and Ramanathan S 2007 J. Appl. Phys. 102 113715
- [50] Tashman J W et al 2014 Appl. Phys. Lett. 104 063104
- [51] Berglund C and Guggenheim H 1969 Phys. Rev. 185 1022
- [52] Gurvitch M, Luryi S, Polyakov A and Shabalov A 2009 J. Appl. Phys. 106 104504
- [53] Wu C, Feng F and Xie Y 2013 Chem. Soc. Rev. 42 5157
- [54] Eguchi R, Yokoya T, Kiss T, Ueda Y, Tajima H, Yamazaki J and Shin S 2002 Physica B 312 600
- [55] Yamin T, Havdala T and Sharoni A 2014 Mater. Res. Express 1 046302