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Research paper

Investigation of Annealing Temperature on Vanadium Dioxide Thin Films

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Abstract

Vanadium dioxide (VO_2) thin film is a material that has multiple functionalities and smart response that give good news for device engineers and material scientist. One of the applications of VO_2 thin film is for smart windows that could help to reduce the impact of global warming from buildings and to reduce expenditure on equipment or other methods to cool buildings. Annealing temperature is one of the importance parameters in VO_2 thin films fabrication. The optimum annealing temperature is required in order to produce good properties of thin films. In this research, the properties of VO_2 thin films were examined. All samples were prepared by the sol-gel spin coating method. The thin films were annealed at different annealing temperatures of 475˚C, 500˚C, 525˚C, 550˚C and 575˚C. The properties of thin film in term of structural, optical and electrical properties were investigated by using field emission scanning electron microscope (FESEM), ultraviolet-visible (UV-Vis-NIR) spectrometer and Current-Voltage measurement respectively. FESEM was used to produce the images of the samples' structure, the diameter of each nanoparticle and the thickness of samples. An I-V two-probe instrument was used to characterize the electrical properties of VO_2 thin films with calculated resistivity and conductivity due to the differentiation of annealing temperature. An ultraviolet-visible spectrometer was used to characterize the optical properties of VO_2 thin film; to show the absorbance and transmittance plots as well as calculated energy band gap. The results show that the thickness and the grain size of the thin films increase with annealing temperature. However, the increase in the absorbance and transmittance is inversely proportional to the annealing temperature.

Keywords: *electrical properties; optical properties; sol-gel method; spin-coating method; structural properties; vanadium dioxide (VO_2)*

1. Introduction

The world needs to pay attention to the dangers of global warming which can be addressed by Green Nanotechnology. One of the consequences of global warming is the use of fossil energy and one way to reduce energy consumption is to use smart windows. These windows use thermochromic materials to create a vitality sparing properties that can reverse the lighting and solar heat gain from the outside environment [1], [2]. Vanadium dioxide is an inorganic compound with the formula of VO_2. It is one of the materials for a reversible semiconductor–metal transition (SMT) at a temperature of about 68^{0}C with the dramatic change in electric and optical properties [3]. Below 68 ^{0}C temperature, VO_2 act as a semiconducting and transmitting material whereas it is metallic and infrared reflecting above the transition temperature and low-temperature monoclinic. The thermochromic properties of materials are able to change color due to temperature and switching feature to near room temperature [4], [5].

Vanadium dioxide was discovered in 1959 where it is a popular material for research purposes and device application possibility. The color of VO_2 is dark blue solid. VO_2 is amphoteric, which is dissolves in non-oxidizing acids to give the blue vanadyl ion, $[VO]^{2+}$ and in alkaline to give the brown $[V4O9]^{2-}$ ion, or at high pH $[VO4]^{4-}$. Vanadium is in list of group five elements in the periodic table. This material is rarely found in nature but may be produced artificially.

There are many different methods for the preparation of VO_2 thin films like ~~a~~ dip coating, spin coating, sputtering, spray pyrolysis, chemical vapor deposition, and electrochemical deposition. For better processing, spin coating method is usually used in the fabrication with sol-gel technique [6]. The process of sol-gel techniques are stable to heat and can be fabricated at a lower temperature [7]. This technique does not require sophisticated equipment, as it is simple and relatively cheap to apply [8]. Spin coating is a standard process involving the process of depositing a small amount of fluid or solution onto the centre of a substrate and spin the substrate at a specific speed. The acceleration of the centripetal will make the solution spread over the entire substrates. The thickness of the thin films can be changed depending on the speed of spin coating. By increasing the speed, the solution may spread or spill to the surrounding that causes the thickness of thin films to decrease. Therefore, sol-gel spin coating technique was chosen to use in this research.

One of the important parameters in VO_2 thin film fabrication is the annealing temperature. The annealing temperature of 525^{0}C is typically required to obtain VO_2 thin film with good properties ~~as~~ [9]. This annealing temperature is undesirable high and prohibition for low-cost coating on temperature with sensitive substrates [10]. VO_2 thin film also diminishes sharply in optical transmission in the infrared spectrum [11].

The main objective of the research is to fabricate and characterize the VO_2 thin films with different annealing temperatures range from 475˚C to 575˚C by using sol-gel spin coating technique.

2. Method

VO_2 thin films were deposited on quartz substrates. Before the deposition process began, the quartz substrates were cleaned in order to ensure that there are no organic contaminations on the quartz substrates. The dimension of 2x2 cm^2 of quartz substrates were immersed in a beaker containing acetone, methanol and de-ionizer (DI) water and placed into an ultrasonic bath consecutively. It took 10 minute for each step to make sure the substrates were free from undesired particle. Then the substrates were blown with dry nitrogen gas for drying. The cleanliness of the quartz substrates is important since they may affect their condition for the next process and to produce good quality of thin films.

The solution used to obtain VO_2 thin films were composed of vanadium oxytriisoproxide $VO(OPr^i)_3$ as alkaline and 2-propanol Pr^iOH as a solvent for making a precursor. In this study, the molarity of precursor is 0.6M. 3.5ml of $VO(OPr^i)_3$ and 26.5ml of Pr^iOH were mixed and stirred with a magnetic stir at room temperature for 10 minutes. During the stirring, the beaker was coved using aluminium foil; this is because to avoid the precursor from any unwanted material and water that may disturb the performance of precursor. The precursor is very sensitive to the humidity and quickly forms viscous red sol when contact with water [10]. After 10 minutes of stirring, 0.3ml of precursor was taken with a syringe to drop into the spin coating.

VO_2 thin films deposition were used static spin coated method, means the precursor was dropped by syringe into spin coating in static condition. After dropping precursor, it takes 90 second for the duration times to spin coated the quartz substrate. The program of spin coating was set with 1000rpm for speed and 3500rpm for acceleration. Then, the substrates were dried in a furnace at 70˚C. The process was repeated for the second layer. After spin coated, the thin films become a yellow colour, then the substrates were annealed for 5 hours 20 minutes. In order to improve crystallinity of the thin films, there were different annealing temperatures (475˚C, 500˚C, 525˚C, 550˚C and 575˚C) were prepared for each substrate. The thin films have a strong and good in adhesion at this stage.

For the metallization process, the metal contact was deposited on the sample for the purpose of current voltage (I-V) measurement. Half of the thin films were covered by mask with kepto tape as a sticker to hold the mask on the thin films. The equipment used for the metal contact is thermal evaporator (TE) with platinum (Pt) as metal. The thickness of the Pt is 40 nm as shown in Fig. 1. Since Pt has a high density, so its resistivity is high and it can be easily to measure using two probe measurements.

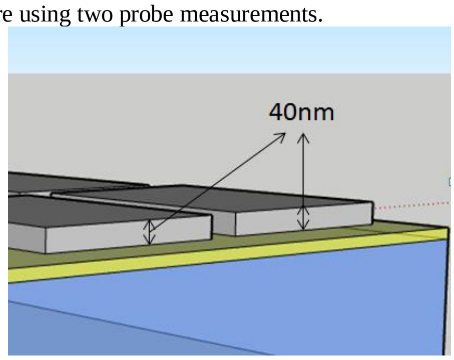

Fig. 1: The side view of sample with Pt metal contact.

The characterization of VO_2 thin films were performed by different measurement techniques. The surface morphology and the thickness of VO_2 were characterized by field emission scanning electron microscope (FESEM). The I-V measurement was used to measured current response that conducted by using two probes equipment. The ultraviolet-visible (UV-Vis-NIR) spectrometer was used to characterize the optical properties of the VO_2 thin films. Fig. 2 shows flow chart of the overall process of the experiment.

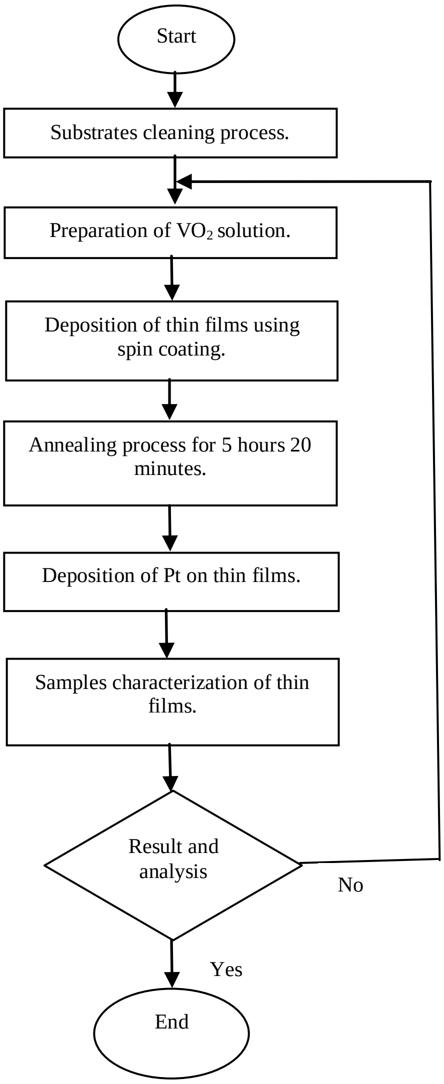

Fig. 2: Flow chart of the experiment.

Fig. 3 shows the top view of samples with Pt as the metal contact. The dimension of metal contact is 0.3x0.3 cm^2. Two sets of five samples with different annealing temperatures were prepared in this experiment. The second set of samples was required for the I-V measurement purpose since these samples need to deposit metal contact on top of the thin film. The metal contact was not required for other measurements.

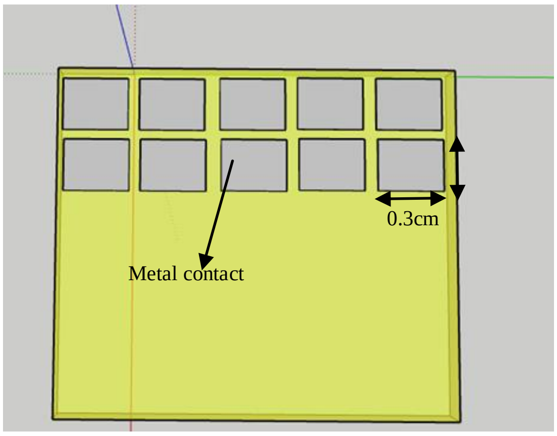

Fig. 3: Top view of the sample with Pt as the metal contact.

3. Results and Discussion

Fig. 4 shows the surface morphology images of VO_2 thin film annealed at (a) 475°C, (b) 500°C, (c) 525°C, (d) 550°C and (e) 575°C. The average grain size of VO_2 thin films are 258.33nm, 240.33nm, 300.33nm, 344.33nm and 592.00nm for samples with annealing temperature of 475°C, 500°C, 525°C, 550°C and 575°C respectively. From the images, it proved that grain size of nanoparticles was observed and estimated to be increased when the temperature increased from 475°C to 575°C and the surface morphology mostly irregular shape. When the temperature is increased the nanoparticle of VO_2 becomes rough. The higher the annealing temperature of VO_2 thin film, the larger the grain size of VO_2 nanoparticle [12].

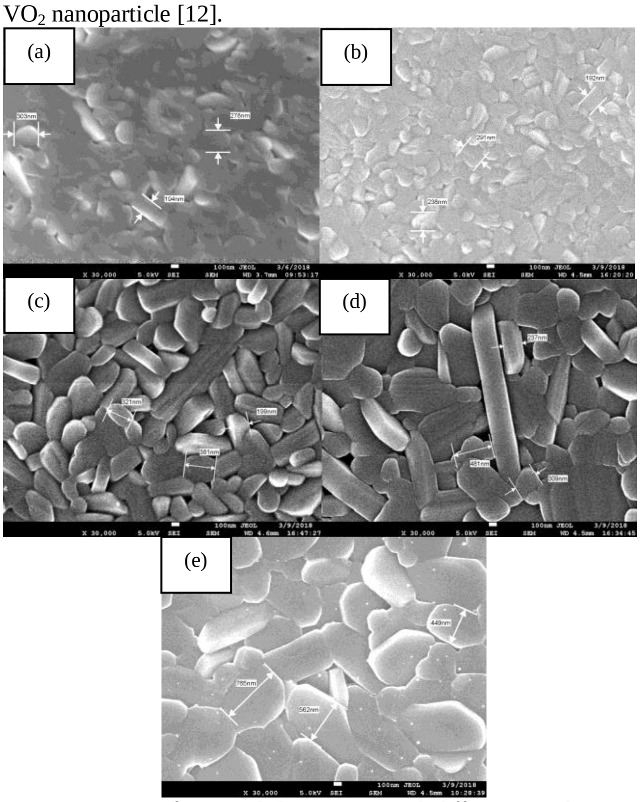

Fig. 4: FESEM surface morphology images with different annealing temperature of (a) 475°C, (b) 500°C, (c) 525°C, (d) 550°C and (e) 575°C.

The thickness of VO_2 thin films were measured using FESEM. The samples were cut using diamond cutter to measure the sample's cross section. The calculated average thickness of VO_2 thin films are 166nm, 181nm, 256nm, 277nm and 980nm as the annealing temperature increase from 475˚C to 575˚C respectively. The thickness parameter is very important due to the surface phenomena which alter the properties of the materials [5]. As the annealing temperature increased, the crystalline size of the semiconductor material is enhanced [13], [14]. In general, due to the shrinking of film thickness, the surface energy favours the suppression of grain growth it is depend on annealing temperature [15]. Fig 5 shows one example of the sample's cross-section from FESEM image for the thickness measurement.

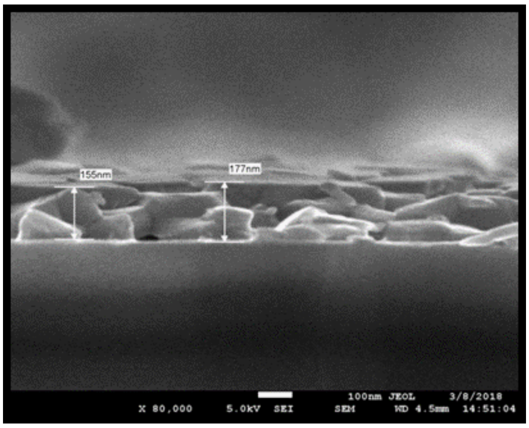

Fig. 5: Sample cross-section from the FESEM image.

Fig. 6 shows the I-V plot that obtained from the two-probe measurements. The ohmic comportment of thin films was indicated by linear I-V curve plot for all samples and can observed the current value at fixed voltage in this experiment [16]. As the annealing temperature increased, the enhancement of electrons conductivity also increased. During the measurement, the result of current in graph was in micrometer (μm) unit, this is because the value is acceptable and it was high to produce a good performance device.

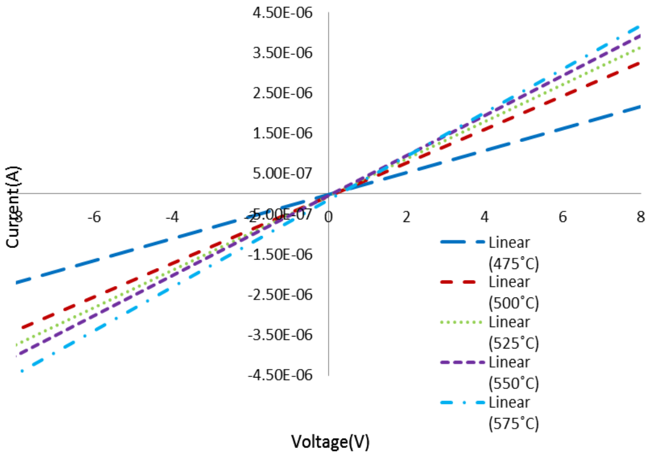

Fig. 6: I-V measurement of VO_2 thin films with different annealing temperatures.

The value of VO_2 thin films resistivity and conductivity with annealing temperatures are shown in Table 1. As the resistivity increases, the annealing temperature also increases. For conductivity, the values are inversely proportional to the values of resistivity. At higher annealing temperature, absorption of oxygen is reduced on the grain boundaries, due to the activity of dense process [17].

Table 1: The resistivity and conductivity values of VO_2 thin films

Sample	Annealing temperature (°C)	Resistivity (Ωm)	Conductivity $(\Omega m)^{-1}$
A	475	0.9243	1.0819
B	500	0.6376	1.5684
C	525	0.8157	1.2259
D	550	0.8482	1.1790
E	575	2.8214	0.3544

The transmittance and absorbance spectrum were measured using UV-Vist spectrometer. The sample can be supervised, when the beam of ultraviolet or visible through it. The transmittance spectra for the VO_2 thin films with different annealing temperatures are plotted in Fig.7 at a wavelength ranging from 450nm to 750nm. The nanostructure shows high transmittance at low temperatures. Studies showed that balance of VO_2 nanostructures absorption of cross section is the primary driver of the dielectric optical response. This happens before the phase transition reaches the nanoscale due to plasmon resonance [5]. In general, the annealing temperature decreases, due to maximum of transmittance transformation of the film to infrared radiation increments [18].

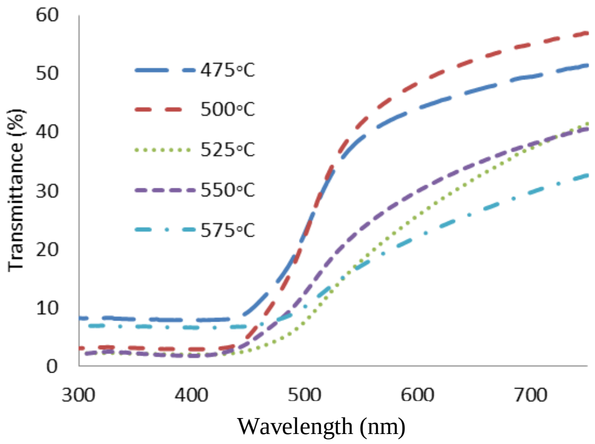

Fig. 7: The transmittance spectra for different annealing temperatures.

Fig. 8 shows the absorption spectra for the wavelength between 300nm and 750nm. The reaction of the absorption of the spectra starts at 300nm and the higher absorption occurred at wavelength at 450nm. It shows that the UV absorption properties for all samples occur at absorption edge of 450 nm. From the observation, at approximately 450 nm was a sharp absorption corresponding to the direct transition of electron surrounded by the edges of the conduction band and the valence band. From the absorbance values, the absorbance coefficient, α can be determined as shown in Fig. 9.

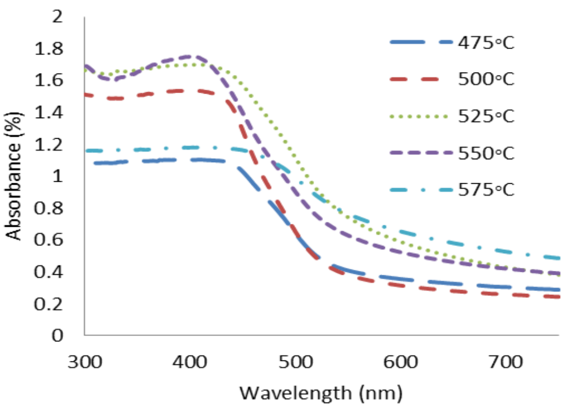

Fig. 8: The absorbance spectra for different annealing temperatures.

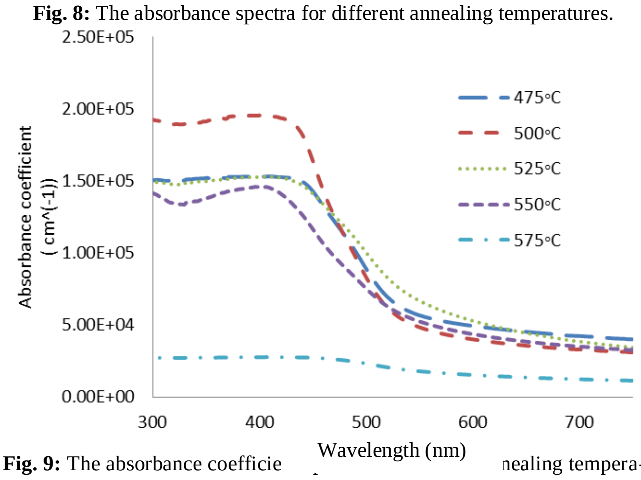

Fig. 9: The absorbance coefficie nealing temperatures.

Optical energy band gap is the product of absorbance coefficient and photon energy with the power of two. The values of optical energy band gap are shown in Fig. 10 by using reciprocal gradient. From the plot, the optical band gap energy are 2.28 eV, 2.35 eV, 2.30 eV, 2.31 eV and 2.47 eV of as deposited samples annealed at 475°C, 500°C, 525°C, 550°C and 575°C respectively. The results show the optical energy band gap increases with annealing temperature. The optical band gap energy is low at lower annealing temperature due to the formation of oxygen ion in VO_2 thin film which creates a glitch of energy levels just below the conduction band [19]. The glitch of energy levels makes for the electrons to move easily through the conduction band [20].

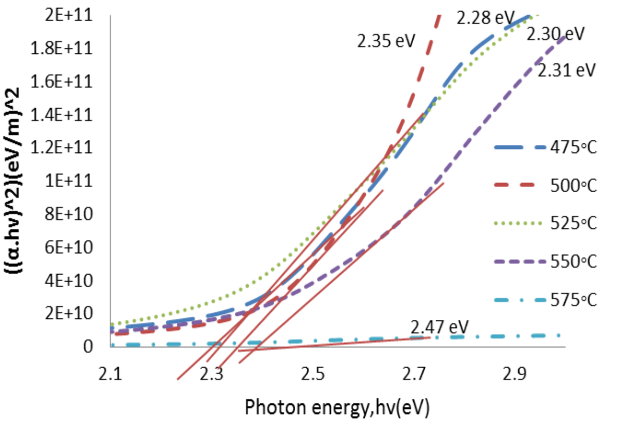

Fig. 10: The optical energy band gap for different annealing temperatures.

4. Conclusion

VO_2 thin films were prepared using sol-gel spin coating method. The thin films were annealed at different temperature range between 475°C and 575°C. The thickness and the grain size increase as the annealing temperature increase, while the absorbance and transmittance decrease as the annealing temperature increase. The results indicate that sample at 525°C annealing temperature has better properties due to moderate absorption and I-V measurement.

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