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# Sintering process and annealing effect on some physical properties of $V_2O_5$ thin films

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Thin films of vanadium pentoxide ($V_2O_5$) on glass substrates were produced by e-beam evaporation technique. The effect of sintering process and annealing temperature on the morphology and optoelectronic properties of these films were studied. The obtained results from scan electron microscope show that, the grain size of $V_2O_5$ films increases with increasing both the temperature of sintering and annealing temperature. The as-deposited films show high transmittance in the visible region that decrease with increasing the temperature of annealing. The films that sintered at 500 $^oC$ represents the high transmittance value about 85 % in the visible region. The electrical resistivity indicates that, the films that sintered at 400 $^oC$ and 600 $^oC$ transform from semiconductor to metal at temperature of 250$^oC$.

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## 1. Introduction

Several theoretical and applied studies on Vanadium pentoxide ($V_2O_5$) materials have been done, due to their industrial importance for many technological applications, such as heterogeneous catalyst [1]. $V_2O_5$ plays also the role of active electrode in a rechargeable lithium battery [2], indeed high electrochemical activity, high stability and ease of thin film formation by numerous deposition techniques led to its use as a highly promising intercalation material in solid state microbattery applications.

Thin films of vanadium pentoxide can be obtained by different techniques like thermal evaporation [3, 4], pulsed laser deposition [5, 6], d. c. magnetron sputtering [7], r.f. sputtering [8,9], flash evaporation [10, 11], and sol-gel technique [12, 13]. It was found that, their microstructure and composition depend strongly on deposition parameters.

It is known that the physical properties of the thin film materials depend on some parameters such as; level and ratio of dopant, substrate temperature, deposition conditions, heat treatment, substrate material, and preparation methods. The sintering process is considered one of the effected parameters which act on the physical properties of thin film materials. Sintering process assist to produce lumps of powder materials in a bulky form without affecting their chemical properties, while their physical properties approach those of single crystal phase [14, 15]. The sintering process is usually carried out in the temperature range $\frac{T_M}{2} \le T \le T_M$ where $T_M$ is the melting point of the material to be sintered [16].

The aim of this work is to study the influence of sintering process and annealing temperature on the morphological, optical and electrical properties of thin films grown by electron beam evaporation technique from a vanadium pentoxide target. The electron beam evaporation technique offers the following advantages: 1) it has a high power density, and hence a wide range of control over evaporation rates, 2) it is used to evaporate materials which have a high melting point, and 3) it provides economical and efficient usage of evaporants.

## 2. Experimental details

The cold pressing technique was employed to convert the $V_2O_5$ powder into tablets form. The sintering process was carried out at three values of temperature of 400 $^oC$, 500 $^oC$, and 600 $^oC$. The time of sintering process was fixed at 5 hours for all samples. The electron beam evaporation was used to deposit the prepared $V_2O_5$ tablets into ultrasonically cleaned microscopic glass substrate. Edwards high vacuum ( $2\times10^{-5}$ Torr) coating unite model E306A was used to this purpose. The rate of deposition and the thickness of the films were controlled to be about 10 nm $min^{-1}$ and 90-100 nm, respectively, by means of a digital film thickness monitor model TM200 Maxtek. Optical measurements (transmittance *T* and reflectance *R*) were performed using a Jasco V–570 UV–VIS–NIR spectrophotometer in the wavelength range from 200 to 2500 nm at normal incidence. The simple two-probe contacts method was used to measure the electrical resistivity using a Keithley 614 electrometer. The measurements were performed at room temperature. Electrical contacts were made by applying silver paste over the surface of the films with a separation of 3 mm.

## 3. Results and discussion

Fig. 1 shows the scanning electron microscope (SEM) topographs of as-deposited $V_2O_5$ films that prepared at sintering temperature of 400 $^oC$, 500 $^oC$, and 600 $^oC$. It is evident that the surface of as-deposited films seams to be smooth and contains few small grains. By increasing the temperature of sintering the grain size starts to increase particularly at sintering temperature value of 600 $^oC$. This behavior confirms the nearly amorphous nature of as-deposited films [17].

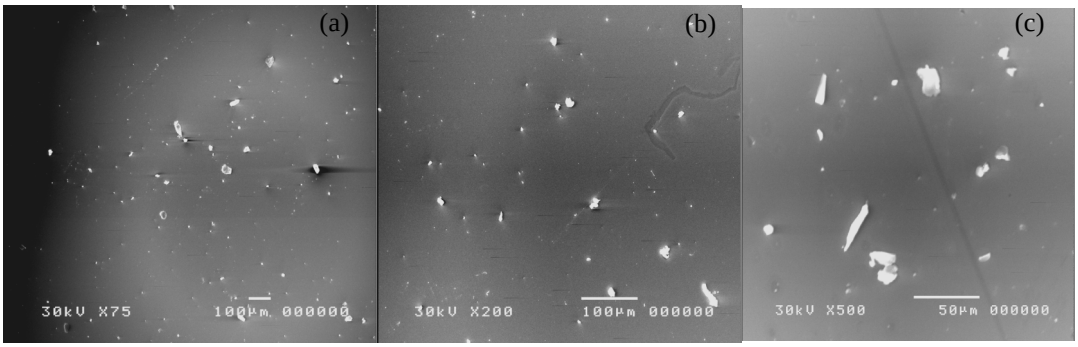


*Fig. 1. SEM of as-deposited $V_2O_5$ films prepared at different sintering temperatures (a) 400 $^oC$, (b) 500 $^oC$ and (c) 600 $^oC$.*

The effect of the annealing temperature on the $V_2O_5$ morphology at temperature of 250 $^oC$ and 400 $^oC$ is shown in Figs. 2, 3 respectively. It is clear that, with increasing the annealing temperature the grain size increase significantly and the largest grain size can be observed at annealing temperature 400 $^oC$ and sintering temperature 600 $^oC$. The grain size growth at increasing the sintering temperature indicates an improvement of $V_2O_5$ film crystallinity. Since, the sintering process is often associated with the formation of new bonds, densification and may be grain growth [14].

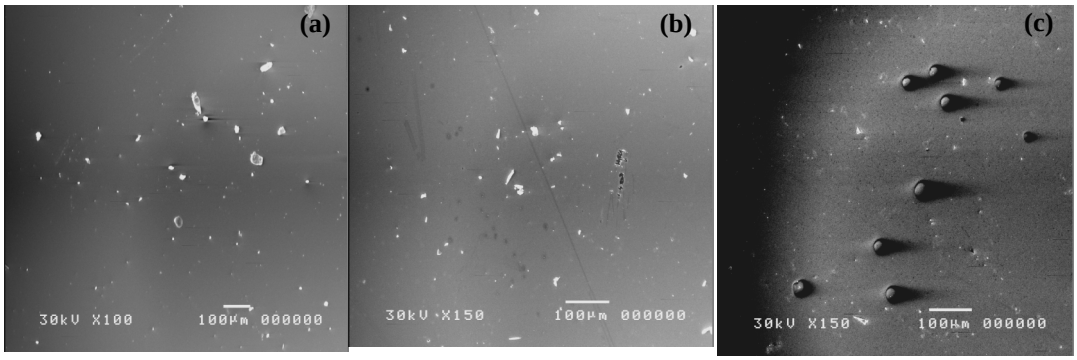


*Fig. 2. SEM of annealed $V_2O_5$ films at 250 $^oC$ which are prepared at different sintering temperatures (a) 400 $^oC$, (b) 500 $^oC$ and (c) 600 $^oC$.*

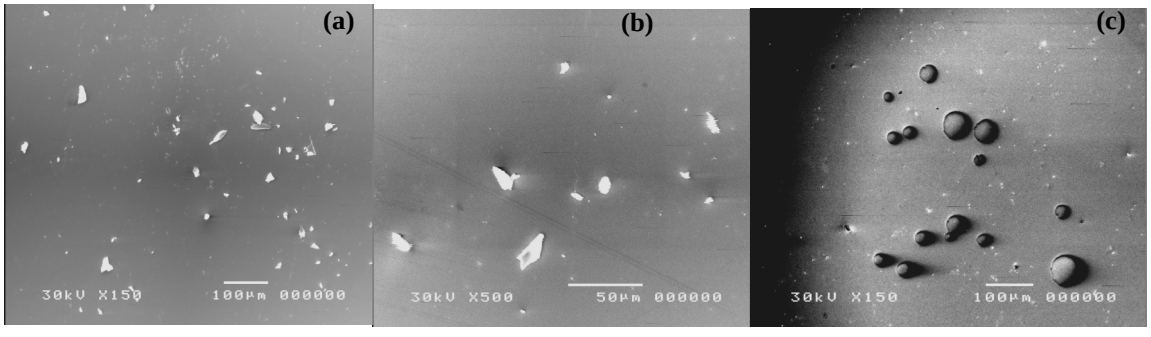


*Fig. 3. SEM of annealed $V_2O_5$ films at 400 $^oC$ which are prepared at different sintering temperatures (a) 400 $^oC$, (b) 500 $^oC$ and (c) 600 $^oC$.*

Fig. 4 (a-c) shows the UV–VS–NIR transmittance spectra of as-deposited and annealed $V_2O_5$ films that prepared at three different sintering temperatures of 400 $^oC$, 500 $^oC$, and 600 $^oC$. Fig. 4 (d) shows the transmittance at wavelength 550 nm as a function of annealing temperature at different values of sintering temperature. It could be clearly seen that, the transmittance decreases as the annealing temperature increases for all samples. Besides, the films that sintered at temperature of 500 $^oC$ show the highest value of transmittance ~ 85 % in the visible region. This may be due to the increase in energy gap resulting from the grain growth. On the other hand, the transmittance in NIR of the last films is considered low comparing to the films sintered at 400 $^oC$ and 600 $^oC$. This may be due to the free carrier concentration. Since the films that sintered at temperature of 500 $^oC$ show the high value of carriers which led to increase the free carrier absorption and hence decrease the transmittance. The decrease in transmittance with annealing temperature particularly at sintering temperature of 600 $^oC$ may be due to the increase in the surface roughness. From Fig. 3, it can be noted that the samples surface become more rough since the rough surface could resulting in a scattering light loss and then a low transmittance. Recently, H.-N. Cui et al obtained a similar results when they used dc reactive magnetron sputtering system to prepare vanadium oxide films [18].

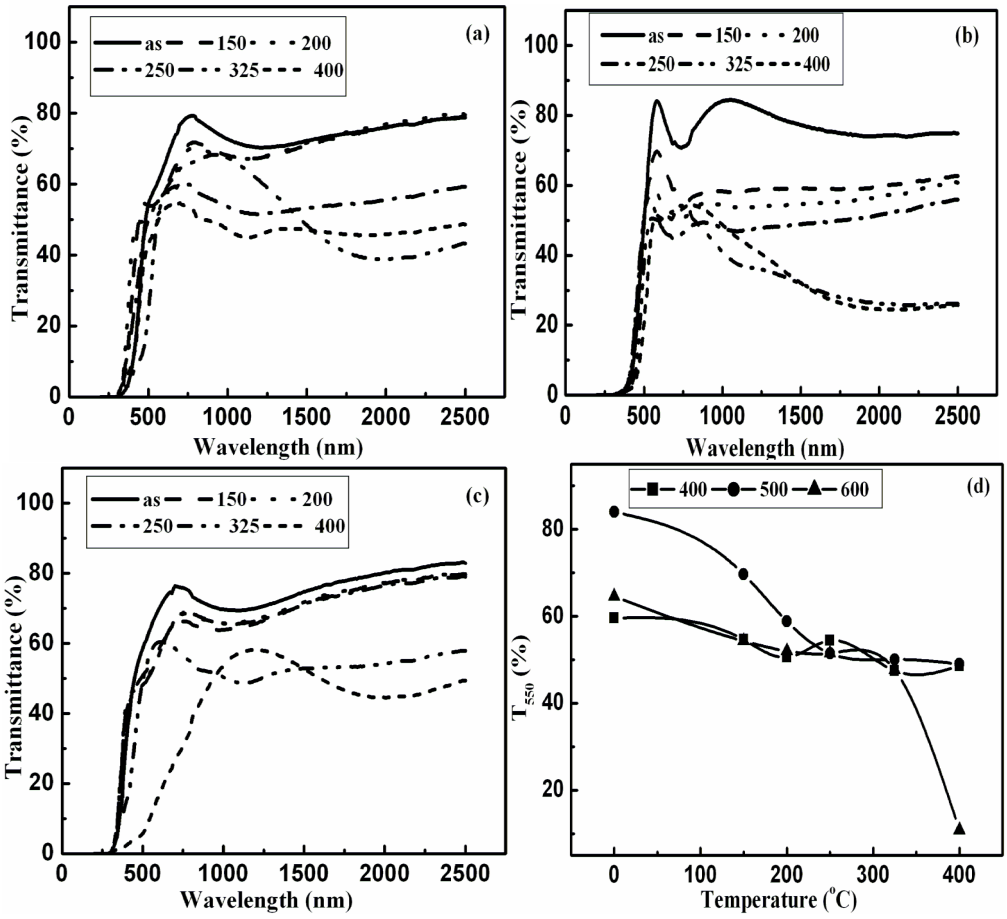


*Fig. 4. The typical transmission spectra of as-deposited and annealed $V_2O_5$ films that are prepared at sintering temperature of 400 $^oC$ (a), 500 $^oC$ (b), 600 $^oC$ (c), and the transmittance at wavelength 550 nm at different values of sintering temperatures (d).*

The typical reflection spectra of as-deposited and annealed $V_2O_5$ films that are prepared at sintering temperature of 400 $^oC$ , 500 $^oC$, and 600 $^oC$ are shown in Fig. 5 (a), (b), and (c), respectively. Fig. 5 (d) shows the average reflection in the visible region as a function of annealing temperature at different values of sintering temperature . It is clear that the reflection spectra of the sample that sintered at temperature of 500 $^oC$ differs from other samples. Since its reflection increase with increasing the annealing temperature in both visible and near infrared regions as shown from Fig. 5 (d). In addition, the reflection of as-deposited films sintered at temperature of 500 $^oC$ represents the lowest value (~ 10 %) comparing with those samples sintered at other temperatures (~ 19 %). These values of reflection confirm that the samples which are sintered at temperature 500 $^oC$ show the

maximum transmittance of as-deposited films as shown in Fig. 4. This behavior of reflection spectra will play a major role in understanding the behavior of refractive index and optical free carrier concentration.

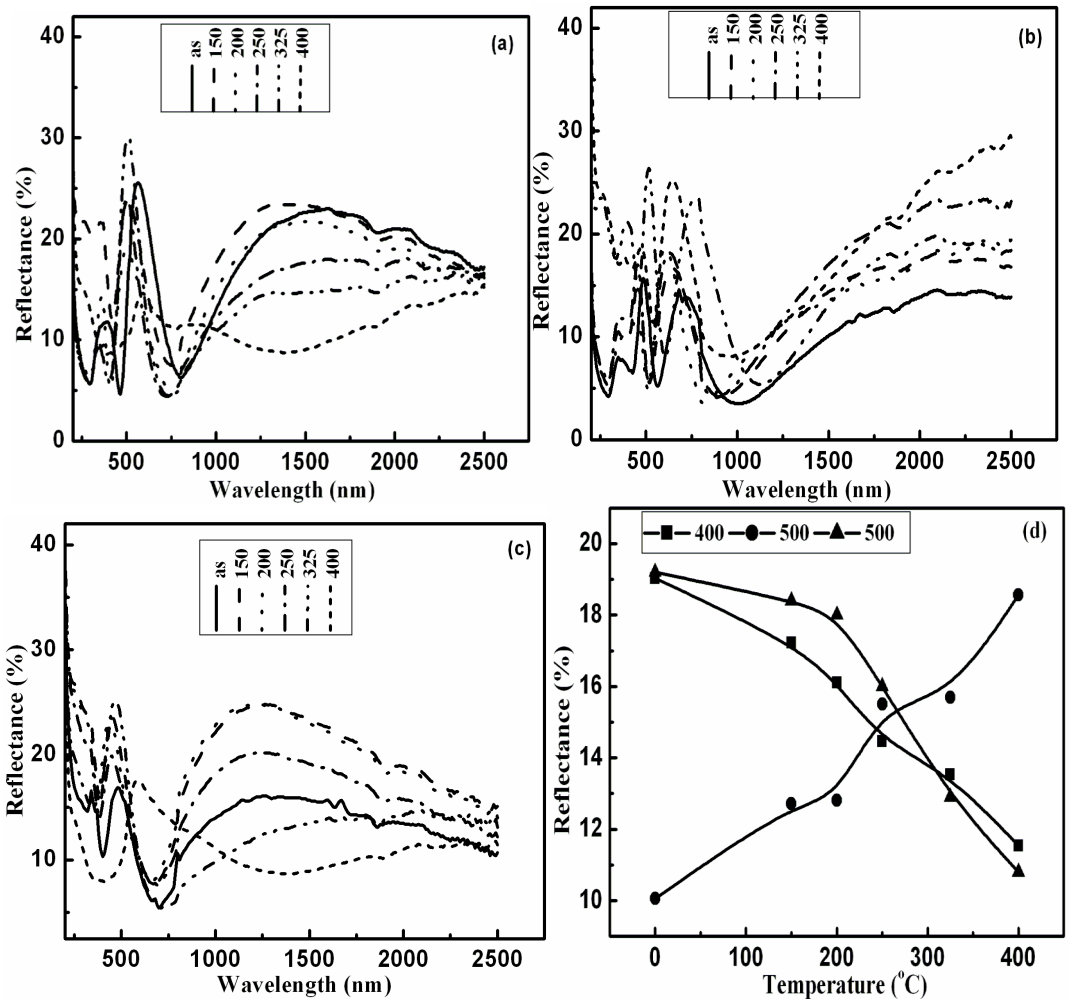


*Fig. 5. The typical reflection spectra of as-deposited and annealed $V_2O_5$ films that are prepared at sintering temperature of 400 °C (a), 500 °C (b), 600 °C (c), and the average reflectance in the visible region at different values of sintering temperatures (d).*

The absorption depth which is given by 1/α, where α is the absorption coefficient, is used to distinguish between direct and indirect optical energy gap. When the absorption depth lies in the range $10^2 – 10^3$ nm this mean a direct transition. While in the indirect optical transition case this quantity can be as large as $10^4$ nm [19]. The calculated absorption depth for as-deposited and annealed $V_2O_5$ films at sintering temperature of 500 °C is shown in Fig. 6 (a). It is evident that, the films exhibit the direct transition. The samples sintered at temperature of 400 °C and 600 °C represented the same behavior (not plotted in this work). Besides the absorption depth method, one can use another graphical method to estimate the optical energy gap and determine the type of the optical transition.

The details of this method were discussed in many references [15, 20-22]. The obtained results from the second method confirm that the as-deposited and annealed $V_2O_5$ films have direct transition at different values of sintering temperature. The calculated direct energy gap of these films as a function of temperature at different values of sintering (400 °C, 500 °C, 600 °C) is shown in Fig. 6 (b). It is clear that, the sintering process has a significant effect on the energy gap. Since, the films that sintered at temperature of 500 °C show the maximum energy gap of 3.25 eV. A sharp decrease in optical energy gap is observed at a temperature above 250 °C. It was reported [4, 23] that, thermally evaporated vanadium oxide films transform from semiconductor to metal phase at 257°C.

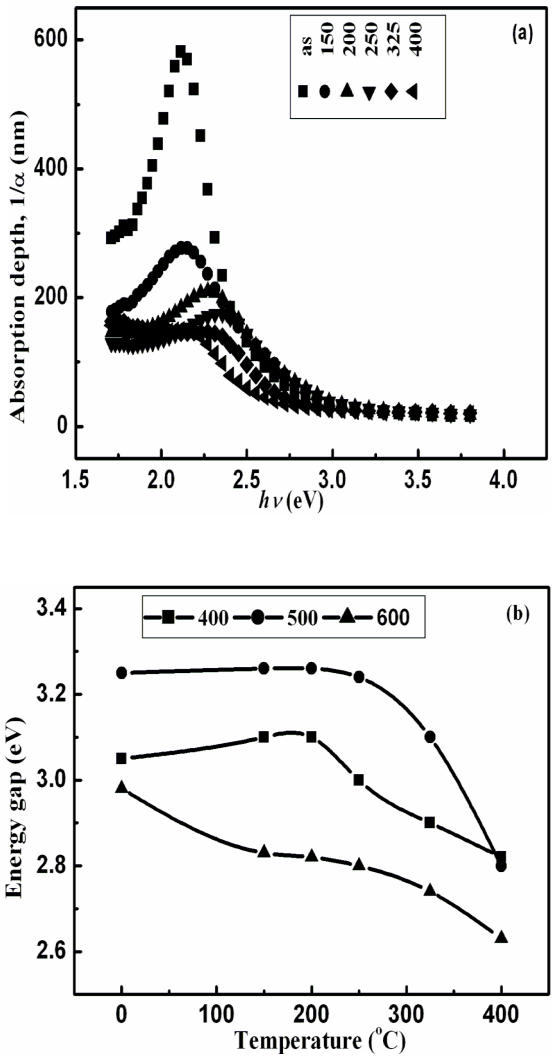


*Fig. 6. The absorption depth as a function of photon energy (hv) of as-deposited and annealed $V_2O_5$ films that are prepared at sintering temperature of 500 °C (a), and the calculated energy gap as a function of temperature at different values of sintering temperatures (400, 500, 600 °C) (b).*

The refractive index $n$ was determined from the reflection (R) and transmission (T) data using the following equation [24]:

$$n=\frac{1+R}{1-R}\pm\left[\left(\frac{R+1}{R-1}\right)^2-\left(1+k^2\right)\right]^{1/2} \quad (1)$$

where $k=\frac{\alpha\lambda}{4\pi}$ is the extinction coefficient and $\alpha$ is the absorption coefficient. The average values of the refractive index in the visible region, $n_{vis}$, derived using the above method are plotted in Fig. 7 as a function of annealing temperature at different values of sintering temperature. It can be observed that, the refractive index of the films that sintered at temperature 400 °C and 600 °C decreases upon annealing. And an opposite manner can be seen for the films that sintered at temperature 500 °C. Since the refractive index of these films increase with annealing temperature. This behavior can be attributed to the reflectance as shown in Fig. 5 (d). The refractive index of the as-deposited V2O5 films that sintered at temperature 500 °C is 1.97. This value is in the same range of other refrences. Since the refractive indices of vanadium oxide films, measured at λ=550 nm, were reported to be 1.9, 2.12 and 2.18 for films prepared by evaporation from V-boat [25], electron beam evaporation [26], and r. f. sputtering [27], respectively. Besides, in reference 4, the refractive index of $V_2O_5$ films increased with increasing the annealing temperature which agrees with the present work (for films sintered at temperature of 500 °C).

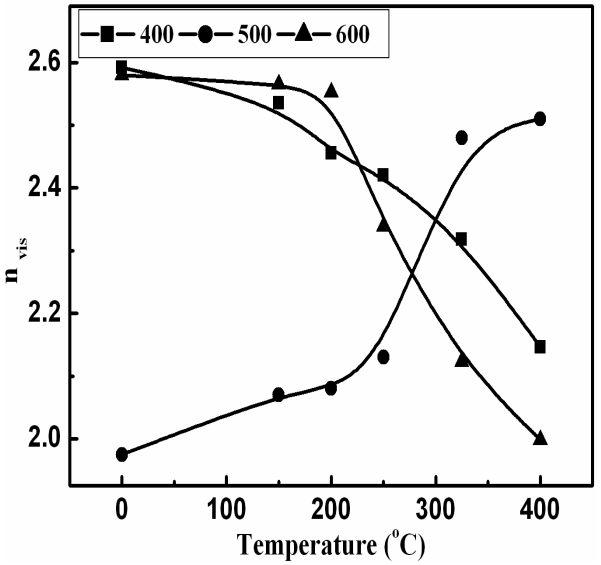


*Fig. 7. The average refractive index in the visible region ($n_{vis}$) as a function of temperature of $V_2O_5$ films that are prepared at different values of sintering temperatures .*

As shown in Fig. 8, plots of the optical dielectric constant $\varepsilon'$ versus the square of wavelength ($\lambda^2$ ) are liner verifying the following equation [28 ],

$$\varepsilon' = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{4\pi^2 c^2 \varepsilon_0}\left(\frac{N}{m^*}\right)\lambda^2 \quad (2)$$

where $n$ is the refractive index, $k$ is the extinction coefficient, $\varepsilon_\infty$ is the high frequency permittivity, $e$ is the electron charge, $c$ is the light velocity, $\varepsilon_0$ is the permittivity of free space and $m^*$ is the effective mass. Values of $N$ determined from slopes are plotted in Fig. 9 for as-deposited and annealed $V_2O_5$ film that sintered at various temperatures. It is clear that, the optical free carrier concentration of the films that sintered at temperature 500 °C varied between 1.3 – 1.8×$10^{20}$ $cm^{-3}$ in the temperature range of annealing (0 – 400 °C). But the films that sintered at temperature of 400 °C and 600 °C are significantly varied with annealing. Since, their values decrease by one order of magnitude upon annealing.

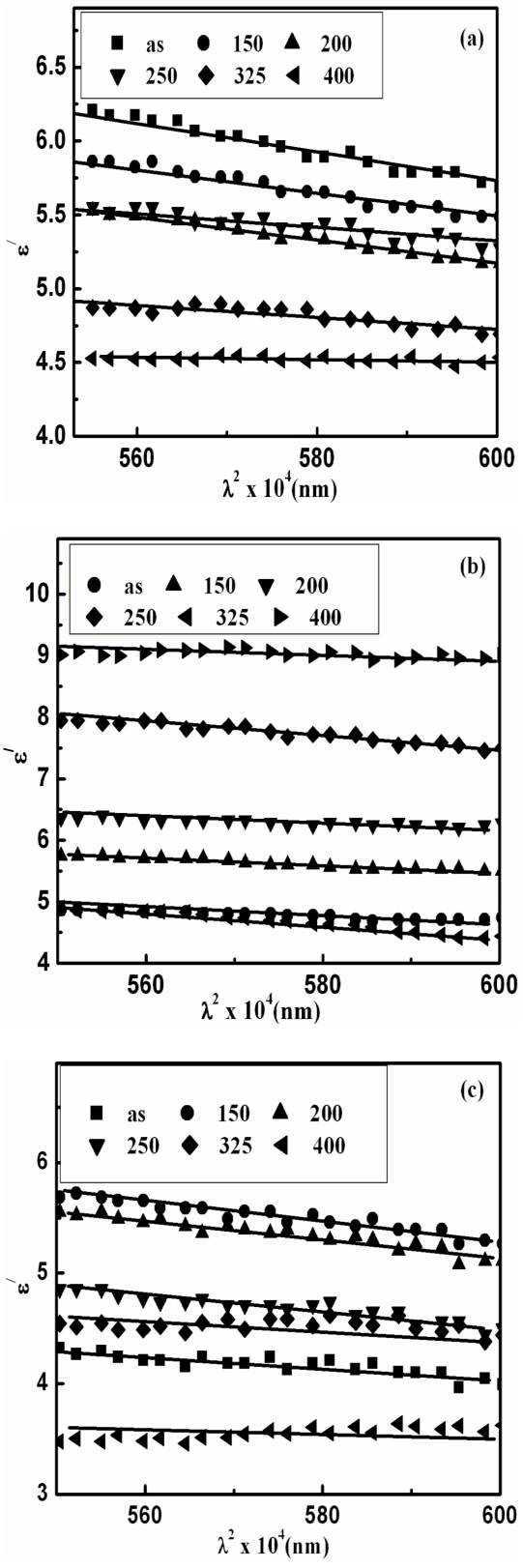


*Fig. 8. Plot of the real part of the dielectric constant ($\varepsilon^{/}$) as a function of wavelength ($\lambda$) of as-deposited and annealed $V_2O_5$ films that are prepared at sintering temperature of 400 °C (a), 500 °C (b), and 600 °C (c).*

The electrical resistivity of $V_2O_5$ films that measured using the two-probe contacts method is shown in Fig. 10 as a function of annealing temperature at various values of sintering temperature. It is clear that, the films sintered at temperature of 500 °C show the lowest value of resistivity about 9 Ω cm at annealing temperature above 200 °C. A sudden decrease in resistivity was observed above the temperature of 200 °C of the samples sintered at temperature 400 °C and 600 °C.

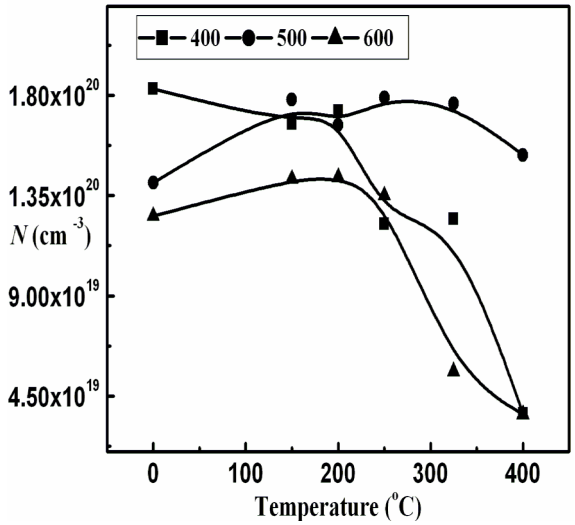


*Fig. 9. Variation of the free carrier concentrations (N) with the temperature of $V_2O_5$ films that are prepared at different values of sintering temperatures.*

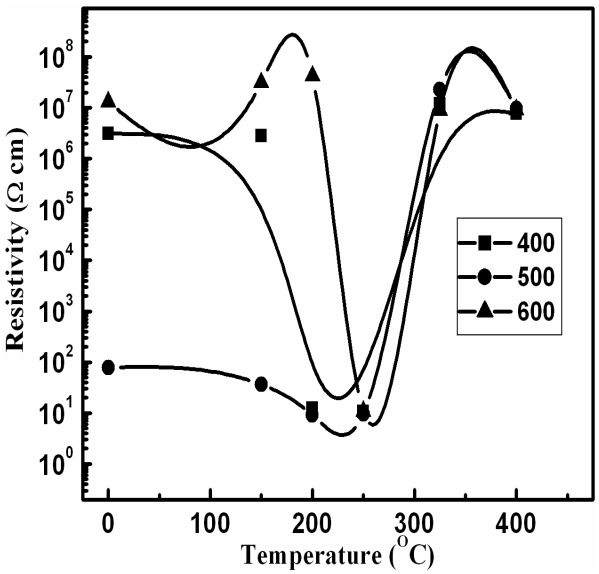


*Fig. 10. The dependence of electrical resistivity on the temperature of $V_2O_5$ films that are prepared at different values of sintering temperatures.*

Since, their resistivity decrease from $10^7$ to 10 Ω cm indicating these films undergo a semiconductor-to-metal phase transition as reported in some references [4, 23]. On the other hand, the electrical resistivity of all samples is significantly increase upon annealing at high temperature

(350 – 400 $^oC$). This behavior which is observed in some oxides such as ZnO-In [29], ITO [15], and ZnO-CdO [30] may be due to the oxygen is chemisorbed on the film surface and acts as an acceptor of electrons. Fig. 9 confirms this discussion since the free carrier concentrations decrease at high value of annealing temperature.

## 4. Conclusions

The effect of sintering process on the morphology, optical and electrical properties of as-deposited and annealed $V_2O_5$ films have been studied. It was found that, the grain size increases with increasing the temperature of sintering particularly at high values of annealing temperature. The optical measurements indicate that the $V_2O_5$ films have direct optical energy gap. The films that sintered at temperature of 500 $^oC$ exhibit the maximum value of energy gap (3.25 eV) and hence the highest transmittance. The sudden decrease in both energy gap and conductivity at temperature above 200 $^oC$ shows that these films undergo a semiconductor-metal transition. The values of other optical parameters such as; reflectance, refractive index, absorption depth, dielectric constant and free carrier concentration are strongly dependent on the sintering process and annealing temperature.

## References


[1] J. Haber, M. Witko, R. Tokarz, Appl. Catalysis A General **157**, 3 (1997).

[2] C. Julien, G. A. Nazri, in: Solids-State Batteries: Materials Design and Optimization, edited by Kluwer Academic Publishers, 1994.

[3] R. J. Cotton, A. M. Guzman, J. W. Rabalais, J. Appl. Phys. **49**, 409 (1978).

[4] M. F. Al-Kuhaili, E. E. Khawaja, D. C. Ingram, S. M. A. Durrani, Thin Solid Films **460**, 30 (2004).

[5] A. Rougier, C. Marcel, I. Bouessay, A. Blyr, N. Naghavi, L. Dupont, J. B. Leriche, J. M. Tarascon, in: Proceedings of the J. Electrochem. Soc., ECS, San Francisco, Battery session, 2001.

[6] J. M. McGraw, J. D. Perkins, F. Hasson, P. A. Parilla, C. Warmsingh, D. S. Ginley, J. Mater. Res. **15**, 2249 (2000).

[7] D. Wruck, S. Ramamurthi, M. Rubin, Thin Solid Films **182**, 79 (1989).

[8] C. R. Aita, L.-J. Liou, C.-K. Kwok, R. C. Lee, E. Kolawa, Thin Solid Films **193–194**, 18 (1990).

[9] L. Ottaviano, A. Pennisi, F. Simone, A. M. Salvi, Optical Materials **27**, 307 (2004).

[10] L. Murawski, C. Gledel, C. Sanchez, J. Livage, J. P. Audiers, J. Non-Cryst. Solids **89**, 98 (1987).

[11] L. Murawski, C. Sanchez, J. Livage, J. P. Audiers, J. Non-Cryst. Solids **124**, 71 (1990).

[12] T. Yoshino, N. Baba, Y. Kouda, Jpn. J. Appl. Phys. **26**, 782 (1987).

[13] A. Cremonesi, D. Bersani, P. P. Lottici, Y. Djaoued, R. Brüning, Thin Solid Films **515**, 1500 (2006).

[14] W. D. Kingery, in: W. Kingery (Ed), Kinetics of High Temperature Process, MIT Press, Cambridge, MA, 187, 1959.

[15] H. A. Mohamed, J. Phys. D: Appl. Phys. **40**, 4234 (2007).

[16] E. Kh. Shokr, M. M. Wakkad, H. A. Abd El-Ghanny, H. M. Ali, Eur. Phys. J. AP **8**, 215 (1999).

[17] E. Kh. Shokr, M. M. Wakkad, H. A. Abd El-Ghanny, H. M. Ali, J. of Physics and Chemistry of Solids **61**, 75 (2000).

[18] H.-N. Cui, V. Teixeira, L.-J. Meng, R. Wang, J.-Y. Gao, E. Fortunato, Thin Solid Films **516**, 1484 (2008).

[19] H. R. Fallah, M. Ghasemi, A. Hassanzadeh, H. Steki, Physica B **373**, 274 (2006).

[20] H. M. Ali, H. A. Mohamed, S. H. Mohamed, Eur.Phys. J. Appl. Phys. **31**, 87 (2005).

[21] B. Saha, R. Thapa, K. K. Chattopadhyay, Solid State Communications **145**, 33 (2008).

[22] H. A. Mohamed, H. M. Ali, Sci. Technol. Adv. Mater. **9**, 025016 (2008).

[23] G. S. Nadkarni, V. S. Shirodkar, Thin Solid Films **105**, 115 (1983).

[24] J. Tauc, in: J. Tauc (Ed.), Amorphous and Liquid Semiconductors, Plenum Press, New York, 159, 1979.

[25] L. Michailovits, I. Hevesi, L. Phan, Z. S. Varga, Thin Solid Films **102**, 71 (1983).

[26] C. V. Ramana, O. M. Hussain, S. Uthanna, B. S. Naidu, Opt. Mater. **10**, 101 (1998).

[27] M. Benmoussa, E. Ibnouelghazi, A. Benmouna, E. Ameziane, Thin Solid Films **265**, 22 (1995).

[28] I. Saadeddin , B. Pecquenard , J. P. Manaud , R. Decourta, C. Labrugère, T. Buffeteau, G. Campet, Applied Surface Science **253**, 5240 (2007).

[29] S. H. Mohamed, H. M. Ali, H. A. Mohamed, Eur. Phys. J. Appl. Phys. **31**, 95 (2005).

[30] H. A. Mohamed, H. M. Ali, S. H. Mohamed, M. M. Abd El-Raheem, Eur. Phys. J. Appl. Phys. **34**, 7 (2006).


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