Optical Properties of vanadium pentoxide prepared by sol gel method

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Abstract

Vanadium pentoxide **(V_2O_5)** thin film were deposited using the sol-gel technique. An aqueous solution of **V_2O_5**was used for depositing the thin films on glass substrates. The structural and optical characteristics of both non-annealed and annealed**V_2O_5** thin films were examined with X-ray diffraction (XRD) and double-beam UV-visible spectrophotometry. The X-ray diffraction study of the **V_2O_5**thin films revealed a mixture of amorphous and polycrystalline nature. The dispersion of the refractive index is discussed in term of Wlemple-DiDomenico single oscillator model, many dispersion parameters such as single oscillator energy (E_o),dispersion energy (E_d), refractive index (n(0)), were discussed using Miller's rule, the optical absorption at the fundamental absorption edge dielectric constant (ε_∞), moment of the dielectric constant optical spectrum(M_{-1} ,M_{-3})and energy gap by Wimple-DiDomenico approximation (E_g^{WDD})have been calculated, non- linear optical susceptibility ($\chi^{(3)}$) has been discussed, direct energy gap by Tauc relation (E_g^T), and Urbach energy of the localized states (E_u) were also calculated. The results were found to be consistent with the data of the previous studies carried out on **V_2O_5** thin films.

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Keywords: Metal oxides, Vanadium pentoxide, sol gel, optical properties, energy gap, dispersion parameters.

الخواص البصرية لخامس أوكسيد الفناديوم المحضر بطريقة السول جل

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الخلاصة

حُضرت أغشية رقيقة من خامس أوكسيد الفناديومبطريقة–سول جل-وتم دراسة الخواص البصرية للنماذج المسخنة وغير المسخنةبمدى الاطوال الموجية -- 190-1200 نانو ميتر-- بطريقة نموذج وامبلديد منكو للمتذبذب الوحيد، أذ تم إيجاد العديد من معاملات التشتت ، كما تم إيجاد الحد الثالث اللاخطي للتأثيرية البصرية بأستخدام قاعدة ميلر،كذلك حساب حافة امتصاص الطاقة البصرية وتم حساب فجوة الطاقة وطاقة يورباخ للمستويات المقيدة.

الكلمات المفتاحية: أكاسيد المعادن, خماسي اوكسيد الفناديوم, المحلول الجيلاتيني (سول جل), الخصائص البصرية, فجوة الطاقة, معاملات التفريق.

1. Introduction:

Within the recent years, transition metal oxides have been a subject of extensive research due to their fundamental importance in technological aspects. Amongst the interesting transition metal oxides, Vanadium pentoxide **(V_2O_5)** is promising for many technological applications due to their fascinating and novel properties.

Vanadium makes many compounds with oxygen which have different structural,

optical and chemical properties. The differences between the properties of different phases of vanadium oxides like **VO**, $\mathbf{VO_2}$, $\mathbf{V_2O_3}$ and $\mathbf{V_2O_5}$ depend on their structure, which determines other properties. Like many other transition metal oxides, vanadium oxides possess useful optical, electronic, magnetic, and catalytic properties.Their chemical and physical propertiesinclude the highest oxidation state in the **V– O** system, a wide band gap, high stability and electrothermal effects.Vanadium pentoxide is a thermodynamically stable form, which exhibits electrochromic properties. $\mathbf{V_2O_5}$ thin films find applications in various field such as:cathode material for rechargeable lithium-ion batteries, sensors in electro chromic devices, in optical filters, reflectance mirrors, smart windows, surfaces with tunable emittance for temperature control, and in spintronic devices. $\mathbf{V_2O_5}$ thin films can be prepared by different methods such as, Chemical vapor deposition (CVD), Physical vapor deposition (PVD), Atmospheric pressure chemical vapor deposition (APCVD) and electrochemical deposition. These methods are commonly used to deposit vanadium oxide films. However, the most effective method for fabricating monolithic structures is the sol-gel method, a well-studied, versatile technique that has been provedto be feasible for numerous transition metal oxides. This method is feasible for device fabrication of many geometries, especially those that require high porosity or surface area [1-6].

2. Experimental details:

Sol-gel technique involves evolutions of inorganic networks through the formation of the colloidal suspension (sol) and gelation of sol to form a network in a continuous liquid phase (gel). This technique offer many advantages such as low cost, ease of fabrication and can be considered as a better alternative approach to conventional production of thin film and nano-powder[6-8].

$\mathbf{V_2O_5}$ thin films can be prepared by the dissolution of metals,**V** metal oxides, or **V**metal salts into aqueous solutions $\mathbf{H_2O_2}$.$\mathbf{V_2O_5}$ thin films prepared by this method have important electronic and ionic properties utilized in antistatic coatings, battery cathodes, and electrical components. Extensive work has been performed on the convenient synthesis of $\mathbf{V_2O_5}$ gels from $\mathbf{H_2O_2}$, including a process involving ion exchange.

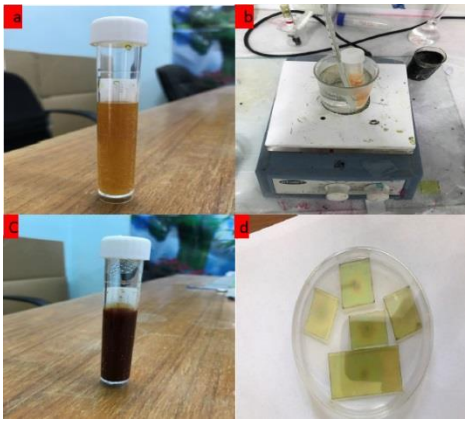


Fig 1: different processes carried out to obtain $\mathbf{V_2O_5}$ thin films.

The synthesis of vanadium pentoxide thin film was carried using powders $\mathbf{V_2O_5}$ (purities 99.9 % ‘‘Sigma-Aldrich’’). 0.05 g of $\mathbf{V_2O_5}$ powder was dissolved in 3.5 ml of $\mathbf{H_2O_2}$ (purity 99 %, ‘‘Standard’’) solution at a temperature of 273 K. Then the solution was heated at 333 K and exposed at this temperature about 1 h until peroxide complexes of vanadium fully decomposed. It should be mentioned that obtained gels are sensitive to the temperature changes, and heating above 333 K would irretrievably damage them (see Fig 1 c). Later gels were spread on a glass substrate and spin coated then left to dry in an ambient air for 24 h in order to remove chemically unbound water.Oneslide was cut into two pieces, one piece has kept aside, theother one was heated at 453 K for 1h.Fig 1 shows different processes carried out to obtain $\mathbf{V_2O_5}$ thin films. Thickness of the samples were estimated using weight-density method.

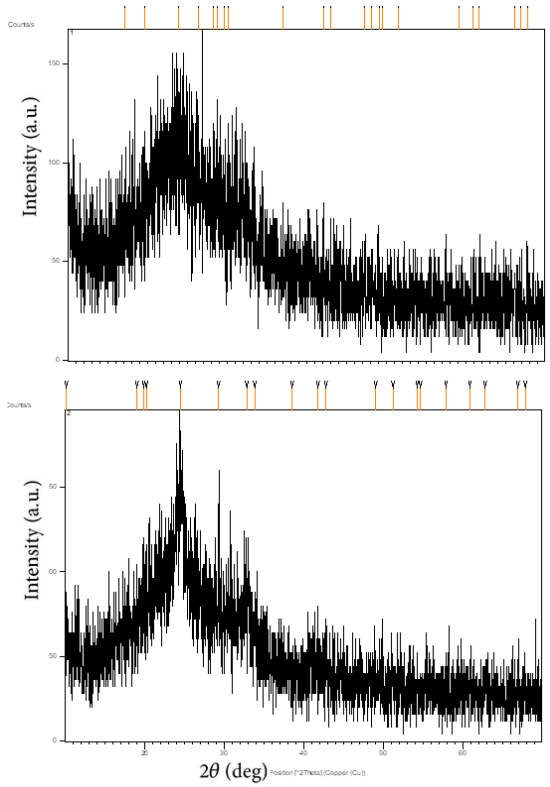


Figure 2: XRD patterns for both non-annealed (upper panel) and annealed (lower panel) V_2O_5 thin films.

X-ray diffraction for annealed and non-annealed samples were recorded with (XPert Pro MPD-Multi-Purpose analytical band- The Netherlands). By the data of X-ray diffractions, both as deposited and annealed $\mathbf{V_2O_5}$ thinfilms appeared to be mixture of amorphous and polycrystalline with small $\mathbf{V_2O_5}$ grain size (see Fig 2).
UV-VIS spectra were recorded using Shimatzu 1800 double beam spectrometer, the same piece of slides were used as a reference to subtract the absorption of glass substrate.

3. Results and discussion:

The optical properties of solids provide areliable meanfor studying energy band structure, impurity levels, excitons, localized defects, lattice vibrations, and certain magneticexcitations. The simplest method to investigate the electronic structure of a solid thin film is by studying its optical absorption as a function of the wavelength or energy. The absorption process induces an interaction between electromagnetic radiation and the material of the thin film, which can be interpreted through variations in the absorption spectra. An absorption spectrum is a fingerprint of electronic configurations of the material. UV-Vis absorption is a commonly used analytical tool for studying the interactions between electrons and radiation. On the other hand, infrared absorption is widely used to analyze the interactions between the vibration energy of bonds and electromagnetic waves [9-12].
Within this context, the absorption (A) and the transmittance(T) spectra for $\mathbf{V_2O_5}$thin films were recorded in the wavelength range of (190-1100nm) .The reflection (R) can be determined using the following relation[12] :

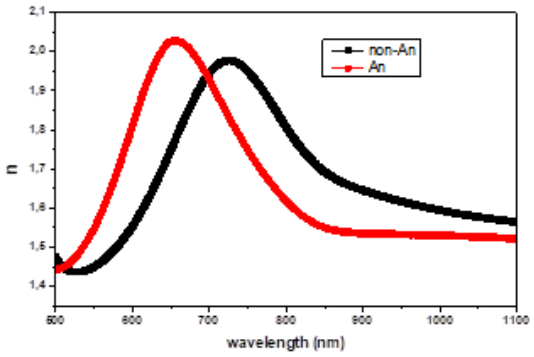
$$T = \frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad \text{..... (1)}$$

Where T is transmittance, α is the absorption coefficient, d is the thickness of the sample. From the absorption coefficient data, extinction coefficient (K) can be calculated by :

$$K = \frac{\alpha\lambda}{4\pi} \quad \text{..... (2)}$$

The refractive index (n) can be calculated using the following relation[12]:

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \quad \text{..... (3)}$$



Figure(3)The relationship between reflective index and wavelength for both annealed (red curve) and non-annealed (black curve) V_2O_5thin films.

The calculated value of refractive index versus wavelength (λ) is shown in Figure(3) . The optical properties of solids are usually described in terms of the complex dielectric function $\mathbf{\varepsilon(E)=\varepsilon_1(E)+i\varepsilon_2(E)}$ .The real part $\mathbf{\varepsilon_1}$and the

imaginary part$\varepsilon_2$of this description are both frequency dependent quantities , which include all desired response information . The quantity ε_2 is thought to contain many useful physical information about the material ,it is well known that ε_2 is considered to be superimposed from many independent contributions by interband transitions at energies **E>> Eg** , interband transition near the absorption edge , free carrier absorption and by optical phonon absorption .Namely there are four terms that contribute to the real part of dielectric constant .In transparent region ,K has very small value and is negligible and therefore all above terms result in the normal dispersion [13]. According to the single oscillator model, the only contribution to the dispersion of dielectric constant is due to interband transition and assumed that each electron behave as an oscillator [14].So the dielectric constant (ε_1) can be given as:

$$\varepsilon_1(\omega) = 1 + \frac{F}{E_o^2 - (h\omega)^2} \quad \ldots\ldots\ldots \textbf{(4)}$$

In this single-oscillator approximation , E_o and F are parameters dependent on electric dipole oscillator .In Wemple – DiDomenic model (WDD) ,the parameter F is expressed as $F=E_dE_o$, E_d is defined as dispersion energy and E_o as a single –oscillator energy. Finally, the dielectric constant for any material can be given by [15]:

$$\varepsilon_1(\omega) = n^2(\omega) - 1 = \frac{E_o E_d}{E_o - (h\omega)^2} = \frac{E_d}{E_o}[1 - \frac{(h\omega)^2}{E_o^2}]^{-1}$$

……...(5)

The dispersion energy E_d is the measure of the strength of interband optical transition and can be considered as a parameter having very close relation with the charge distribution within unit cell and therefore with the chemical bonding. The other dispersion parameter, E_o, is usually considered as an "average" energy gap (E_g^{WDD}) and is empirically related to the lowest direct Tuac energy gap (E_g^T). The dispersion parameters E_o and E_d are described by means of the r^{th} moment of the $\varepsilon_2(E)$ optical spectrum .It is known that the r^{th} moment of ε_2 (E) spectrum is defined as [14,15] :

$$M_r = \frac{2}{\pi}\int_{E_t}^{\infty} E^r \varepsilon_2(E) dE \qquad \ldots\ldots\ldots(6)$$

where E=hω and E_t is the absorption threshold energy. One can develop some relationships between the dispersion parameters and $\varepsilon_2(\omega)$ spectrum via :

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \qquad \ldots\ldots\ldots\ldots(7)$$

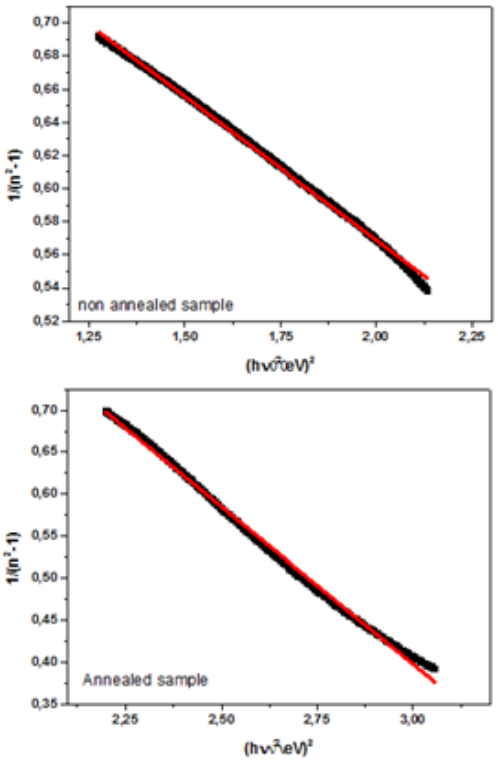
$$E_d^2 = \frac{M_{-1}^3}{M_{-3}} \qquad \ldots\ldots\ldots\ldots\ldots(8)$$

Where M_{-1},M_{-3} are moments of optical spectrum and the -1 , -3 moments are involved in computation of E_o and E_d .It is known that static dielectric constant of any substance is defined as:

$$\varepsilon_r(o) = \lim_{E \to o} n^2(E) = n_o^2 \qquad \ldots\ldots\ldots(9)$$

The static dielectric constant can be written in term of dispersion parameters simply as :

$$n_o^2 = \varepsilon_r(o) = 1 + \frac{E_d}{E_o} \qquad \ldots\ldots\ldots\ldots(10)$$



Figure(4):The relationship between $1/(n^2-1)$ and $(h\nu)^2$ for both annealed (lower panal) and non-annealed (upper panal) V_2O_5 thin films (red lines in both graphs represent the best linear fit).

By plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ and fitting a straight line as shown in Figure(4),

E_o and E_d are determined directly from the gradient $(E_oE_d)^{-1}$ and the intercept (E_o/E_d) on the vertical axis .The value of E_o,E_d, M_{-1} ,M_{-3}, n(o)and ε(∞) are listed in table (I). E_o is interpreted as a measure of a separation between the centers of valance and the conduction bands, the calculated value of E_g^{WDD} byWemple-Didomenico approximation is listed in table (II).

Optical constant	Non-An. sample	An. sample
E_o(eV)	2.2	2.0
E_d(eV)	2.5	1.33
n(o)	2.13	1.665
ε∞	1.46	1.29
M_{-1}	1.1	0.67
M_{-3}(eV)$^{-2}$	0.217	0.046

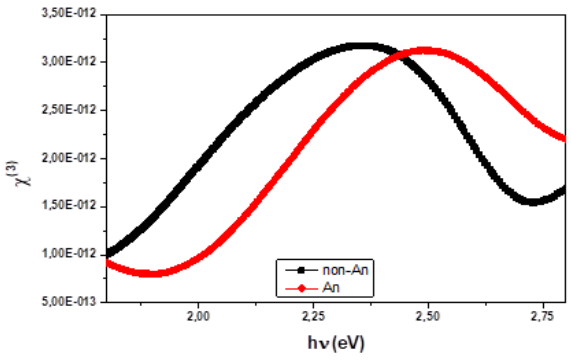
Table (I): The estimated values of the oscillator parameters for both V_2O_5 thin films.

According to Wagner et al. [10]the Muller rule is very convenient for visible and nonliner and near infrared frequancies,which equalize the third order nonliner polarizability parameter $(\chi^{(3)})$ through the equation[16]:

$$\chi^{(3)} = A(\chi^{(1)})^4 = A[E_oE_d / 4\pi(E_o^2 - (h\nu)^2]^4 = \frac{A}{(4\pi)^4(n^2-1)^4} \quad \ldots\ldots(11)$$

where A =1.7x10^{-10}

The third order nonlinear optical susceptibilities for both $\mathbf{V_2O_5}$ thin films calculated from equation (11) are depicted in Figure (5).



Figure(5): Variations of the third order nonlinear optical susceptibility and photon energy for both annealed (red curve) and non-annealed (black curve) V_2O_5thin films.

The most direct and perhaps simplest method for probing the band structure of semiconducting materials is to measure it's optical absorption spectrum, by studying the change in the transmitted optical intensity as a function of wavelength, one can investigate some possible quantum mechanical transition that the semiconductor electrons can make and learn much about the distribution of allowed electronic energy levels [17].In the strong absorption region (there is linear increase in α with increasing incident photon energy), the relationship between the absorption coefficient and the photon energy is given by Tauc relation [18]:

$$\alpha h\nu = B(h\nu - E_g^T)^r \quad \ldots\ldots\ldots(12)$$

Where B is constant, E_g^T is Tauc energy gap, r is the index that characterizes the absorption process. In ($\mathbf{V_2O_5}$ thin solid film analysis of experimental results showed that for r=3/2 .plot of $(\alpha h\nu)^{1/r}$ against hν shows one linear relation is most fitted for equation (12), this indicates that the indirect transition is responsible for interband transition in $\mathbf{V_2O_5}$ thin films, the value of E_g^T is obtained by plotting $(\alpha h\nu)^2$ against (hν) in Figure(6) followed by extrapolating the linear region of the plot (αhν =0),the optical Tauc band gap for $\mathbf{V_2O_5}$ thin films.

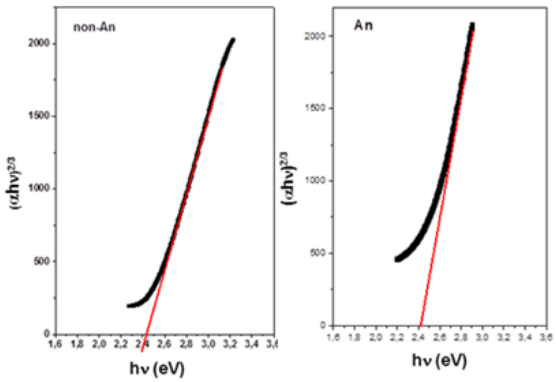


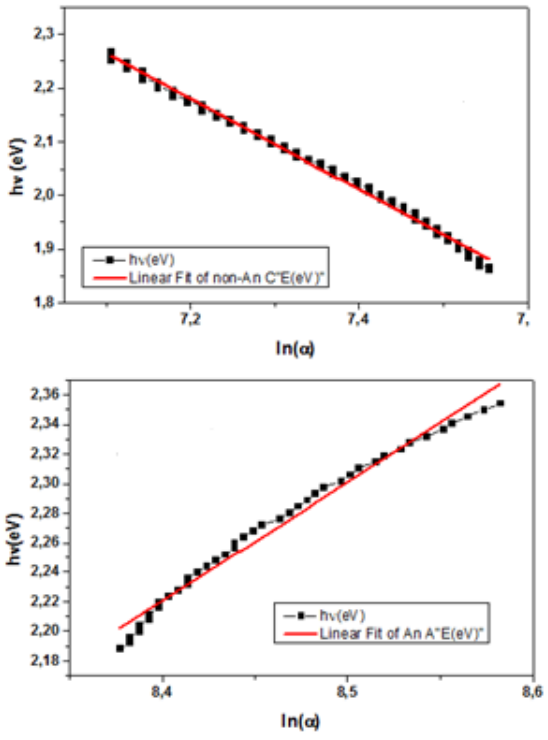
Figure (6):The relationship between $(\alpha h\nu)^2$ and photon energy for both annealed and non-annealed) V_2O_5 thin films (red lines in both graphs represent the best intercept).

Quite commonly in direct gap semiconducduing materials, disorder due to impurity and temperature effect will

cause exponential band tails of electronic states to extend into the forbidden gap.Then near the absorption edge,optical transitions from a parabolic band to an exponential band-tail states are manifested by an exponentially varying absorption coefficient [19],the absorption coefficient then is given by :

$$\alpha = \alpha_o e^{\frac{h\nu}{E_u}} \quad \text{.....(13)}$$

E_u is Urbach energy corresponding to the width of the band tails. Figure(7) represents the linear dependence of ($\ln\alpha/\alpha_o$) with photon energy ($h\nu$) for both **V_2O_5** thin films, the slope of the line gives the magnitude of E_u which listed in table (II). It is well known that unsaturated bond are responsible for the formation of some defects in the film, such defects produce localized states or tail states in the forbidden gap of amorphous solids.The presence of high concentration of localized states in the band structure is responsible for the low value of the optical gap (E_g).



Figure(7): Variation of lnα and photon energy for both V_2O_5 thin films (red lines are the best linear fit)

Band energy	Non-An. sample	An. sample
$E_g^{WDD}(eV)$	2.257	2.203
$E_g^{T}(eV)$	2.41	1.41
$E_u(meV)$	-0.84	0.805

Table(II): The calculated values of energy gap V_2O_5 thin films,by Wemple-DiDomenico approximation, by Tauc relation, and the calculated values of Urbach tails energy respectively.

4. Conclusions:

V_2O_5 thin films have been prepared by sol gel technique, the dispersion of the refractive index in the film follows the single oscillator model. Using this method the values of the oscillator parameters were obtained, the value of the direct energy gap (E_g^{WDD}) was calculated using Wemple-DiDomenico approximation, the value of the third ordernonlinear optical susceptibility was estimated using Miller's rule. The optical band is discussed using absorption spectrum direct energy gap were calculated by using different methods, localized tail states were also discussed and Urbach energy was calculated using absorption spectrum. The calculated values of energy gap (E_g^{WDD}, E_g^{T}) by different approaches, listed in table (II) the results of the calculations by different approacheswere found to be consistent with the data of the literatures. The value of nonlinear optical susceptibility ($\chi^{(3)}$) indicated that **V_2O_5** can be used widely in many photonic applications.

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