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ARTICLE

Optical Properties of Vanadium Pentoxide Thin Films Prepared by Thermal Evaporation Method

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Abstract: Vanadium Pentoxide (V_2O_5) thin films were obtained using thermal evaporation technique on a glass substrate. Many films of different thicknesses were prepared. Deposition rate was controlled by using a quartz monitor connected with the system and the rate was about 5 nm per second for all films. The transmittance and reflectance of each film, in the spectral range 300 to 900 nm, were measured from which the optical constants (Refractive index, Absorption coefficient, Extinction coefficient and Energy gap) were determined. The energy gap was calculated for two films (d_1 = 320 nm and d_2 = 700 nm) and found to be 1.87 and 2.1 eV for the direct allowed transitions, respectively. All measured values were consistent with those found in other previous studies. All our films were found to have an amorphous structure as was shown by the XRD patterns of the films.
Keywords: Refractive index; Extinction coefficient; Optical constants; Absorption coefficient; Vanadium Penoxide.

Introduction

Thin films of semi-conducting materials generally have neither the same physical properties nor the same chemistry as the respective bulk material. Moreover, the preparing techniques and deposition processes used to create films dramatically change the physical properties of material such as refractive index, extinction coefficient, homogeneity, density, hardness, internal stress, adhesion to substrate and crystal structure. Therefore, the difference in physical properties between bulk and thin film material depends strongly on many factors such as the type of deposition process itself, deposition temperature, deposition rate, gas pressure, substrate geometry, preparation of the coating material and the post-deposition temperature. Vanadium pentoxide is an important material in glass and ceramic industries. Vanadium pentoxide is of big interest, since it is a good catalyst and can be used in the applications of gas sensors and other applications. Also, it is a chemical material that can be added to glass for coloration and to absorb wavelengths below 359 nm. It also can be used in ceramic resistor materials. Possible new uses include the preparation of bismuth vanadate ceramics for use in solid oxide fuel cells. Another new application is in vanadium redox batteries, a type of flow battery used for energy storage, including large power facilities such as wind farms. Many methods of preparation, physical and chemical methods, are used to prepare V_2O_5 films: chemical vapor deposition, magnetron sputtering, sol-gel technology, thermal evaporation technique and flash evaporation. The characteristics of V_2O_5 films are strongly dependent on the method of their synthesis, because V_2O_5 loses oxygen when heated in vacuum or in reductive atmosphere; this causes partial dislocation and oxygen removal from the V_2O_5 lattice, which results in the formation of defects or a reduced phase in the resulting layers [1-8].

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The electro-chromic properties of aqueous sol-gel derived vanadium oxide films with different thicknesses have been investigated [9]. Rajendra Kumar *et al*. have determined various structural parameters such as lattice constants, grain size and micro-strain and dislocation density of V_2O_5 thin films prepared by vacuum evaporation. Also, the influence of deposition temperature on the structural parameters has been discussed [10]. Pulsed laser deposition technique was used by Rajendara Kumar *et al*. to prepare V_2O_5 thin film thermistors [11]. Finally, many reports have been found about the physical properties of V_2O_5 and its compounds, especially glass and ceramic [12-15].

Theoretical Background

Many methods can be used to measure the optical constants of materials [6, 16-18], one of which is by measuring the transmittance (*T*) and reflectance (*R*) of the film. For a single absorbing layer on a transparent substrate such as vanadium pentoxide thin films on a glass substrate, it is easy to measure the reflectance from the film side and the transmittance through the film. Using these measurements, we can find the optical constants of the film material by solving the theoretical equations that give the values of transmittance and reflectance as a function of wavelength and optical constants. These relations for *T* and *R* can be approved, and have been found to be as [18, 19]:

$$T = \frac{s}{n_0}\,\frac{[(1+g_1)^2 + h_1^2][(1+g_2)^2 + h_2^2]}{Exp[2\beta] + (g_1^2 + h_1^2)(g_2^2 + h_2^2)Exp[-2\beta] + C\cos(2\gamma) + D\sin(2\gamma)} \tag{1}$$

$$R = \frac{(g_1^2 + h_1^2)\,Exp[2\beta] + (g_2^2 + h_2^2)Exp[-2\beta] + A\,Cos(2\gamma) + B\,Sin(2\gamma)}{Exp[2\beta] + (g_1^2 + h_1^2)(g_2^2 + h_2^2)\,Exp[-2\beta] + C\,Cos(2\gamma) + D\,Sin(2\gamma)} \tag{2}$$

where

$$h_1 = \frac{2n_0 k}{(n_0+n)^2 + k^2},\quad h_2 = \frac{-2sk}{(n+s)^2 + k^2},\quad g_1 = \frac{n_0^2 - n^2 - k^2}{(n_0+n)^2 + k^2},\quad g_2 = \frac{n^2 - s^2 + k^2}{(n+s)^2 + k^2}$$

$$A = 2(g_1 g_2 + h_1 h_2),\ B = 2(g_1 h_2 - g_2 h_1),\ C = 2(g_1 g_2 - h_1 h_2),\ D = 2(g_1 h_2 + g_2 h_1)$$

$$\beta = \frac{2\pi k d}{\lambda},\quad \gamma = \frac{2\pi n d}{\lambda}$$

where *d* is the film thickness, *k* is the extinction coefficient of the film, *s* is the refractive index of the substrate, *n* is the refractive index of the film material and n_o is the refractive index of air. Solving Eq. 1 and Eq. 2 by a suitable computer program (using Mathematica Package or Mat lab), *n* and *k* can be found. Then, *k* can be used to find the absorption coefficient *α* which is related to *k* by [6]:

$$\alpha = \frac{4\pi k}{\lambda} \tag{3}$$

In order to determine the fundamental absorption edge from *T* measurements, the following expression can be used:

$$\alpha(h\nu) = B(h\nu - E_g)^m \tag{4}$$

where *α* is the optical absorption coefficient, *hν* is the incident photon energy, as a constant called edge width parameter, E_g is the optical band gap of the material and *m* is the exponent, that determines the type of electronic transition causing the absorption. It can take values of (1/2) for direct allowed, (3/2) for direct forbidden, 2 for indirect allowed and 3 for indirect forbidden transitions [20].

Experimental Details

Vanadium pentoxide thin films, of different thicknesses (320, 550 and 700 nm), were prepared using thermal evaporation technique. This was achieved by using Edwards Coating System E306 A model. All samples (thin films) were deposited on glass substrates with a refractive index of about 1.52. The substrates were cleaned by the usual method of cleaning; that is: using the ultrasound cleaner filled with acetone to clean the substrates, then filled with distilled water. After this, all substrates were cleaned again with methanol and then with distilled water. Finally, hot clean air was used to dry the substrates. To prepare a certain sample with a certain thickness, the substrate was attached to a special holder in the evaporator. Then, a powder of V_2O_5 of purity 98.5% was added to the Mo boat, which was 12 cm away from the substrate, before closing the chamber to start the evacuation and evaporation process. The base pressure inside the chamber was less than 10^{-5} mbar. In each deposition process, two samples were prepared for different purposes of film characterization. After the films were deposited, they were removed from the coating chamber and a variety of characterization techniques were employed to study their various properties. The normal incidence reflectance (R) and transmittance (T) of the films were measured over the range of 300 nm to 900 nm wavelength. A spectrophotometer, Specord M500 model, was used for this purpose.

Results and Discussion

The X-ray diffraction pattern of room temperature deposited V_2O_5 films assured their amorphous nature. Fig. 1 shows a typical XRD pattern of one of the as deposited V_2O_5 thin films. Fig. 2 shows a typical curve of the transmittance in the visible region; i.e. from 300 nm to 900 nm for three films of different thicknesses (320, 500 and 700 nm). It shows that the transmittance decreases as the thickness of the film increases. Also, more peaks (interference fringes) appear when the film thickness increases. Fig. 3 shows the reflectance spectrum of the three prepared films in the same visible spectrum as for T. In order to measure the optical constants, two well prepared films of different thicknesses; i.e. d_1 = 320 nm and d_2 = 700 nm, were analyzed. As shown in Fig. 2, there are two broad peaks for the first film; namely at λ = 530 nm and 780 nm. To measure the optical constants of this film, the measured values of T and R were used with Eq. 1 and Eq. 2. The refractive index, (n), and the extinction coefficient, (k), of this film for the whole spectrum region were calculated by solving these two equations.

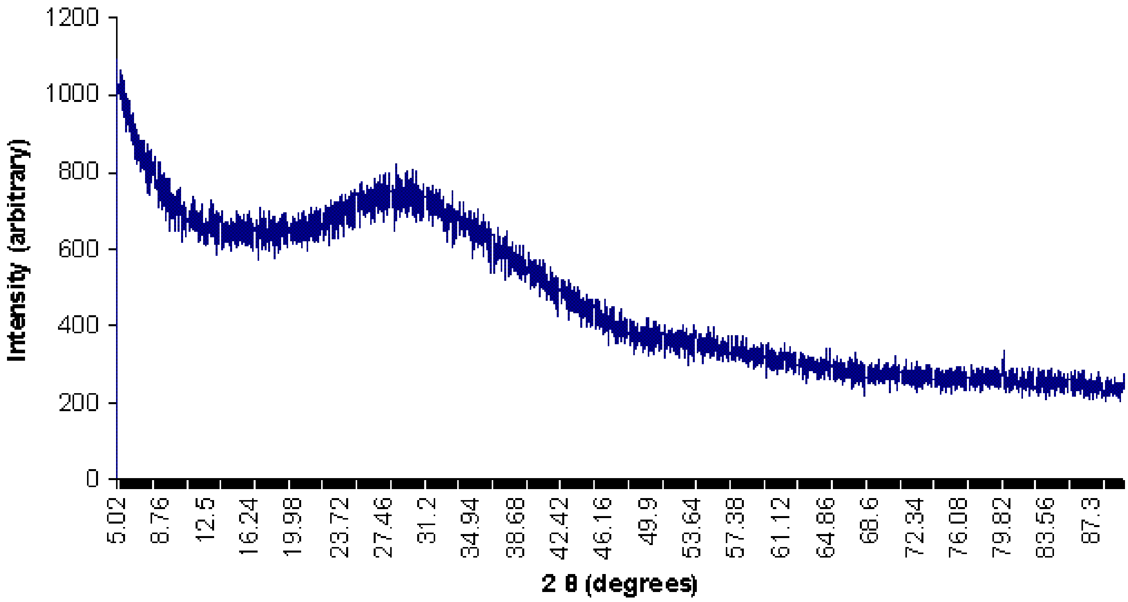

FIG. 1. X-ray diffraction pattern of an as deposited V_2O_5 thin film on a glass substrate

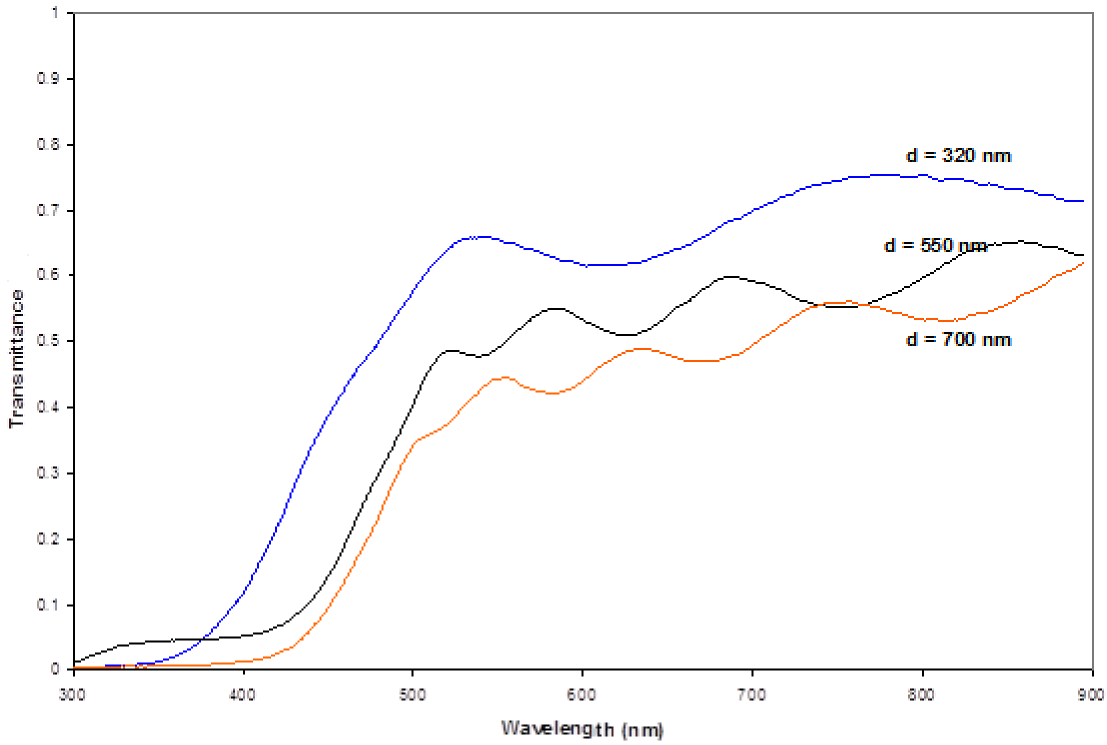

FIG. 2. The transmittance (T) curve as a function of wavelength of three V_2O_5 films (d = 320, 550 and 700 nm)

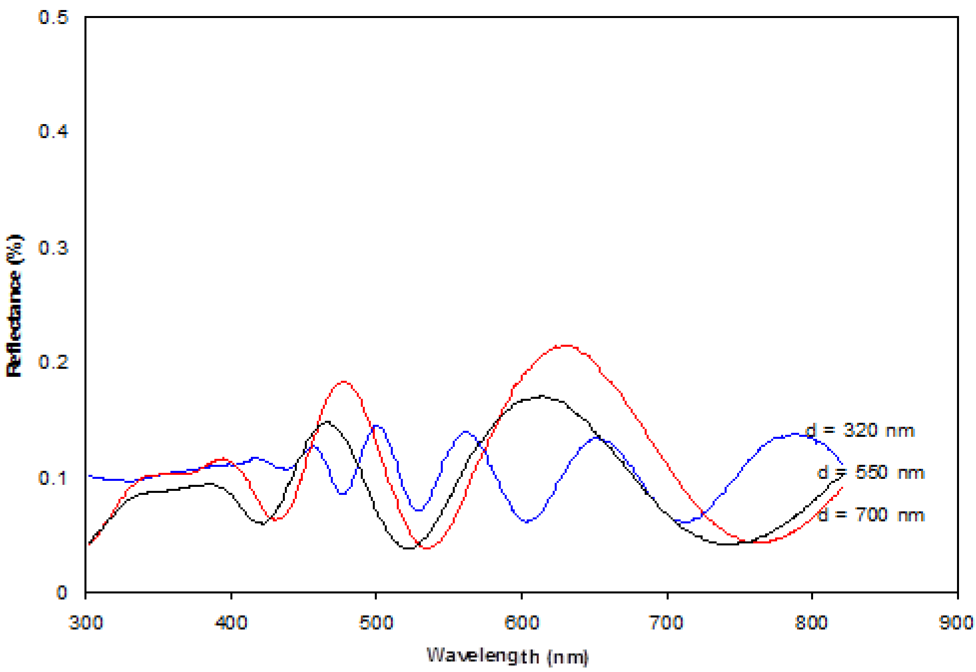

FIG. 3. The reflectance (R) curve as a function of wavelength of three V_2O_5 films (d = 320, 550 and 700 nm)

The calculated values of the refractive index as a function of wavelength are shown in Fig. 4. It appears that the refractive index of this film decreases from 1.88 to 1.73 as wavelength increases from 500 nm to 900 nm. These calculated data of refractive index were fitted to the two-term Cauchy formula. The output of this fitting process gives us a relation between the refractive index and the wavelength; that is:

$$n(\lambda) = 1.68606 + \frac{51020.2}{\lambda^2} \tag{5}$$

The full curve in Fig. 4 represents the fitted data curve according to Eq. 4. This Cauchy formula can be used to calculate the refractive index at any wavelength.

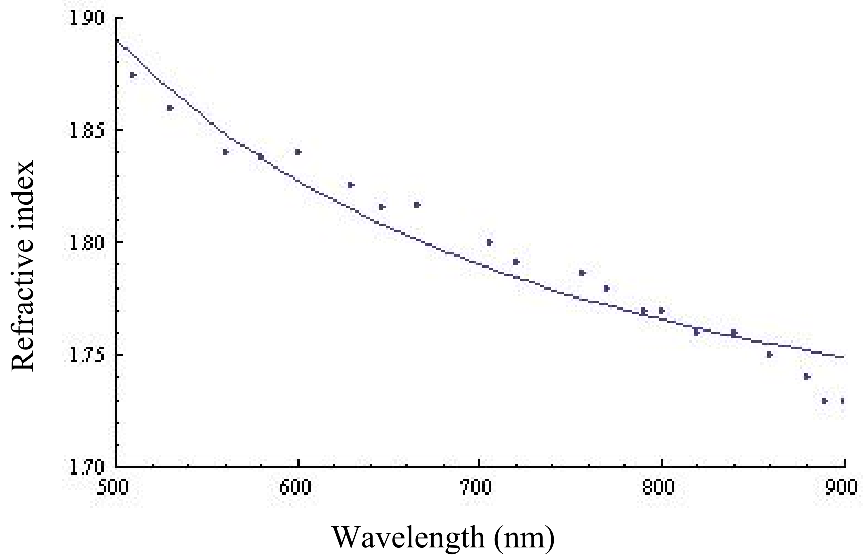

FIG. 4. Refractive index of V_2O_5 film (320 nm) versus wavelength. The points represent the calculated values and the full curve is the fitting curve according to Eq. 4

Fig. 5 shows the extinction coefficient variation versus wavelength. As indicted in the Figure, the extinction coefficient of this film decreases from 0.057 to about 0.039 as wavelength increases from 500 nm to about 620 nm, then up to 900 nm the extinction coefficient was found to be constant with the value of about 0.039. In order to calculate the absorption coefficient of the film, Equation 3 was used. Fig. 6 shows the behavior of the calculated values of the absorption coefficient as a function of wavelength. It appears that the absorption coefficient decreases from 0.0013 nm^{-1} to 0.0007 nm^{-1} in the range of 500 nm to 620 nm. After this value of wavelength, from 620 nm to 900 nm, it becomes almost constant and equal to about 0.0007 nm^{-1}. Finally, to measure the optical energy gap for this film, Eq. 4 was used. Fig. 7 shows that the energy gap for direct allowed transition in this film is about 2.1 eV. This result is reasonable and is very close to other values found in literature. However, more accurate values can be deduced for all optical constants if more efficient programs for solving these equations were used.

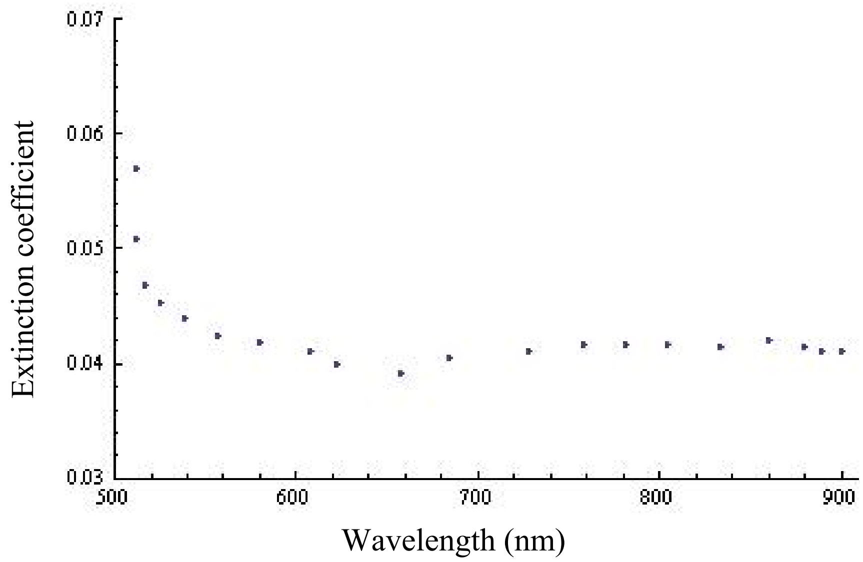

FIG. 5. Extinction coefficient of an as deposited V_2O_5 (320 nm) thin film against wavelength

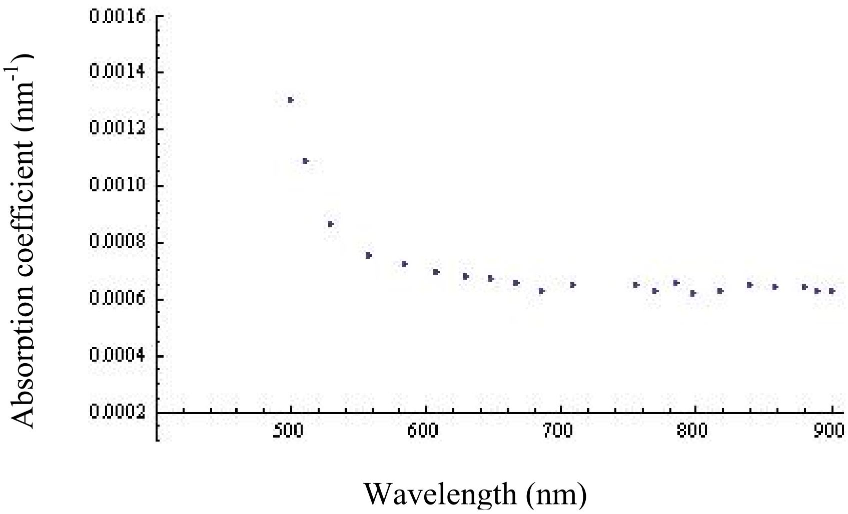

FIG. 6. Absorption coefficient of an as deposited V_2O_5 (320 nm) thin film against wavelength

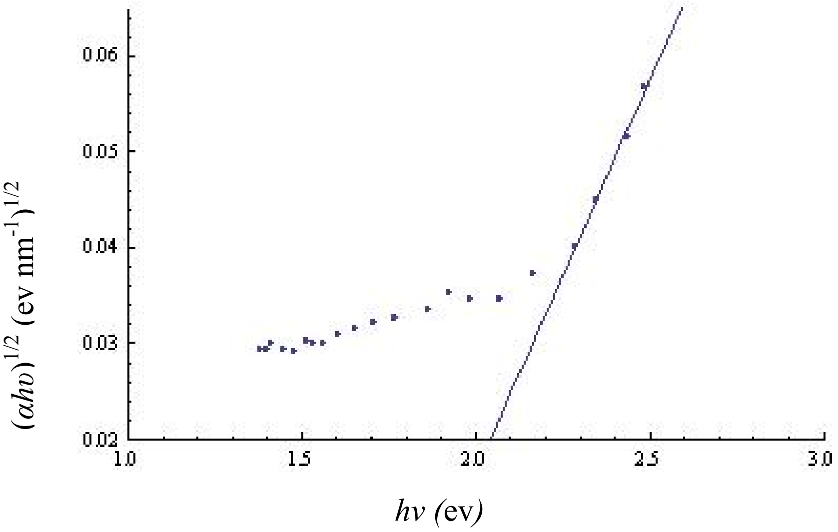

FIG. 7. $(\alpha h\upsilon)^{1/2}$ versus $(h\upsilon)$ plot for 320 nm V_2O_5 thin film

Another V_2O_5 film with a thickness of 700 nm was used to determine and compare the optical constants of a larger film thickness. Using the same procedure and equations, the optical constants of this film were calculated.

It is clear that the transmittance is less than that of the first film (thickness = 320 nm). The maximum value of T is about 62% with three maximal points (peaks) in the spectrum. Also, the transmittance falls down to almost zero value at about and less than 400 nm. Comparing with the first film; i.e. d_1 = 320 nm, there were two broad peaks and the transmittance falls down to zero at about 320 nm. As indicated in the Figure, the film shows different types of absorption. In the range of 320 to 420 nm, the film has a strong absorption, while in the region from 420 nm to 540 nm the film has a weak absorption, and a medium absorption region exists in the range from 540 nm to 900 nm.

In order to measure the optical properties, Eqs. 1 and 2 were solved. Fig. 8 shows the calculated refractive index of this film (dot points) as a function of wavelength interval of 500 nm to 900 nm. It appears that the refractive index decreases from 1.94 to 1.7 as wavelength increases from 520 nm to 900 nm. This shows higher values of n compared with lower film thickness as indicated in Fig. 4 for the 320 nm film. The full curve on Fig. 8 represents the fitted data curve where the data were fitted to the two-term Cauchy formula. The Cauchy formula that can be deduced from fitting data and can be used to calculate the refractive index at any wavelength is found to be:

$$n(\lambda) = 1.55465 + \frac{109243}{\lambda^2} \quad (6)$$

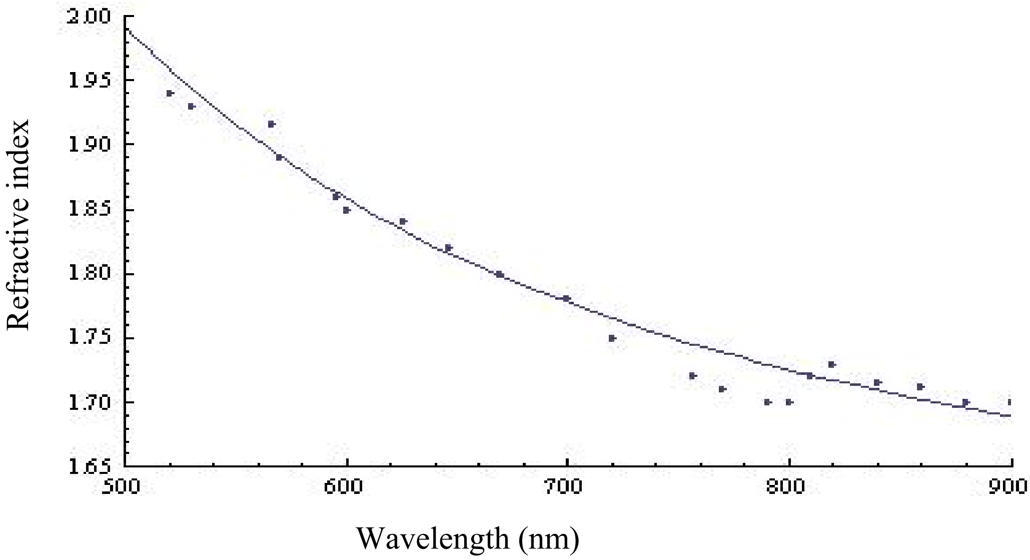

FIG. 8. Refractive index of V_2O_5 (700 nm) film versus wavelength (dot points for measured and line for fitting)

The behavior of the extinction coefficient against wavelength is shown in Fig. 9. It appears that the extinction coefficient decreases from 0.035 to 0.018 as wavelength increases from 500 nm to 900 nm. Using these data of *k*, the absorption coefficient was calculated. Fig. 10 shows the behavior of the absorption coefficient as a function of wavelength. As Fig. 10 shows, it is clear that the absorption coefficient decreases from 0.0009666 nm^{-1} to 0.00035 nm^{-1} as wavelength increases from 520 nm to 700 nm. Then it will be constant and equal to 0.00035 nm^{-1} in the interval of wavelength from 700 nm to 900 nm.

Finally, the optical band gap was calculated using Eq. 4. Using the data in Fig. 11, the optical band gap energy for direct allowed transition was found to be about 1.87 eV.

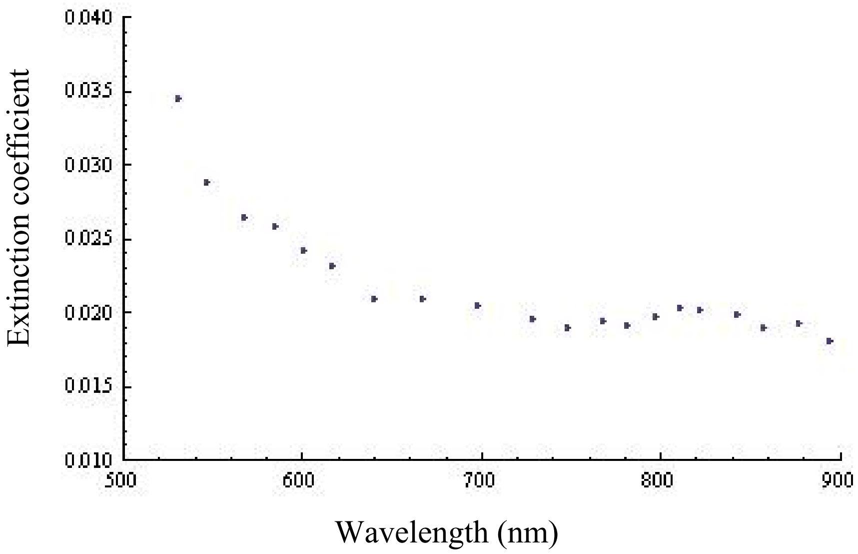

FIG. 9. Extinction coefficient of the as deposited V_2O_5 (700 nm) thin film against wavelength

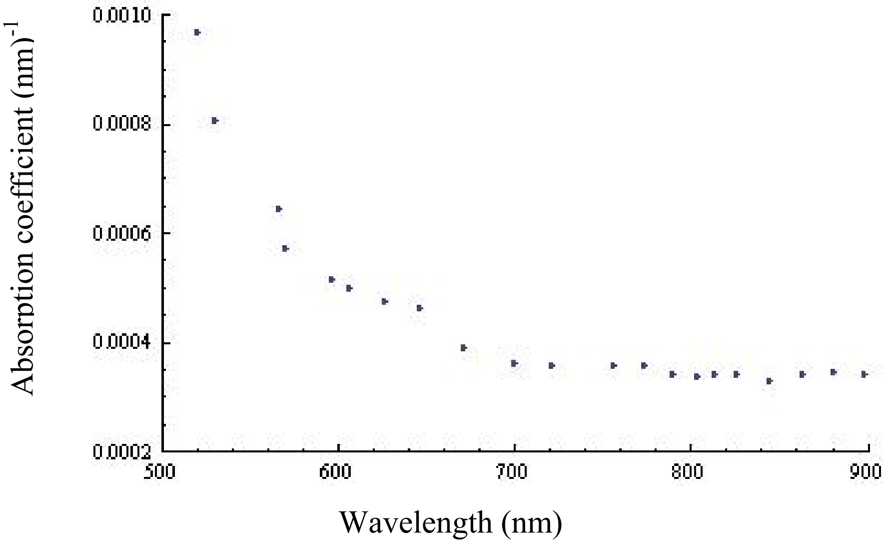

FIG. 10. Absorption coefficient of the as deposited V_2O_5 (700 nm) thin film against wavelength

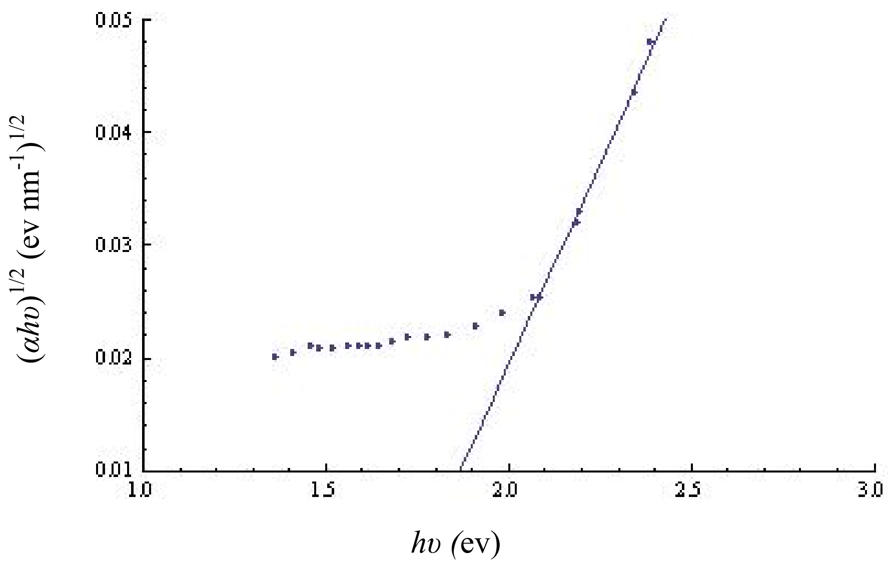

FIG. 11. $(\alpha h\upsilon)^{1/2}$ versus $(h\upsilon)$ plot for 700 nm V_2O_5 thin film

Conclusions

Thermal evaporation method was used to prepare Vanadium Pentoxide thin films. The films are deposited on a glass substrate at room temperature. X-ray analysis reveals that the V_2O_5 films are amorphous. The transmittance increased when the film thickness decreased. However, more peaks appear when the thickness increases. The refractive index was calculated and found to decrease from 1.88 to 1.73 and from 1.94 to 1.7 for the two analyzed films. Other optical constants were calculated and found to be inconsistent with other previous studies. The energy gap was found to be between 1.87 and 2.1 eV for direct allowed transition. All measured values were consistent and very close to those found in other previous studies. However, using more accurate and faster programs may give more accurate values.

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