Optical characteristics of NiO thin film on glass formed by Chemical spray pyrolysis

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Abstract

Electochromic material came to public attention around 30 years ago, nickel oxide(NiO) thin film(which is one of the inorganic electrochromic material) has grown on cleaned glass substrate at 498 ^{o}K temperature using spray pyrolysis deposition technique of thickness(1451.8A^{0}).UV.-VIS. spectra of the film was studied by using the optical absorbance measurements which were taken in the spectral region from 300nm to 1100nm. The transmittance and reflectance spectra of the film in the UV.-VIS. region were also studied. Optical Constants such as optical allowed and forbidden energy band gap of direct transition, absorption coefficient, extinction coefficient, refractive index and optical conductivity, were evaluated from these spectra. The film was found to exhibit high transmittance(~55-87%) and high absorbance values at ultraviolet region which they decrease rapidly in the visible / near infrared region. Optical allowed band energy for direct transition was (3.694eV) and the forbidden one was(3.653eV).

الخصائص البصرية لأغشية NiO المحضرة على الزجاج بطريقة الرش الكيميائي الحراري

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الخلاصة

جرى اهتمام كبير بالمواد الكهروكروماتيه خلال الثلاثين سنه الماضية،اوكسيد النيكل(NiO) هو أحد المواد الكهروكروماتيه اللاعضويه حيث تم تحضير غشاء اوكسيد النيكل NiO على قواعد زجاجيه نظيفة مسخنه بدرجة حرارة 498^{0}K وبسمك (1451.8A^{0}) بطريقة الرش الكيميائي الحراري.أطياف الأشعة المرئية – فوق البنفسجية للأغشية درست باستخدام حسابات الامتصاص البصري والتي أخذت من المنطقة الطيفية من 300nm إلى 1100nm. كما درست أيضا أطياف النفاذيه والانعكاسية للأغشية في المنطقة المرئية – فوق البنفسجية،UV.-VIS. ومن هذه الأطياف تم حساب الثوابت البصرية مثل فجوة الطاقة البصرية للانتقال المباشر المسموح والممنوع ومعامل الامتصاص ومعامل الخمود ومعامل الانكسار والتوصيلية الضوئية. أظهر الغشاء نفاذيه عاليه بحدود(%87_55~)، وقيم امتصاص عاليه في المنطقة فوق البنفسجية التي سوف تنخفض بسرعة في المنطقة المرئية/تحت الحمراء. قيم فجوة الطاقة البصرية للانتقال المباشر المسموح 3.694eV وللانتقال المباشر الممنوع 3.653eV.

1.Introduction

Nickel oxide thin film (NiO) is an attractive material due to its excellent chemical stability as well as optical ,electrical and magnetic properties [1].NiO is a group VIII-VI semiconductor which has a polycrystalline of cubic structure.

It is a functional layer material for chemical sensors and it considered to be a model semiconductor with p-type conductivity films due to its wide band-gap energy from (3.6-4)eV. [2,3,4].Furthermore, it is used as a electrochromic(EC) material which can change its optical properties under an applied electric field[5].

Development was more successful in the case of electrochromic automatically dimming rear -view mirrors, which are now generally available for cars and trucks and for smart windows [5].Among inorganic (EC) material ,nickel oxide considered to be a good anodic candidate because it has low material cost and an excellent contrast[6]. Usually ,nickel oxide is used as a counter – electrode in complementary (EC) devices assembled with a cathodic (EC) electrode , such as tungsten oxide [6] . Nickel oxide thin films have been fabricated by various physical and chemical vapor deposition techniques , which include spray pyrolysis [7] , plasma enhanced chemical vapor deposition [8] and reactive sputtering [3] .

Spray pyrolysis technique is basically a chemical deposition technique in which the fine droplets of the solution containing the desired species are sprayed on a preheated substrate.

The thermal decomposition takes place on the hot substrate giving rise to a continuous film [9]. We used this method in this study because of its preeminent features of deposition are large area , deposition with uniformity , low fabrication cost , simplicity , fast ,non– vacuum system and low deposition temperature [10,11] .

The optical properties of thin films are markedly different from these of the bulk speci-mens and are dependent on many parameters such as film thickness, film structure and substrate temperature [12,13]

2. Experimental Details

The NiO thin films were prepared by spraying aqueous solution of nickel nitrate Ni $(NO_3)_2$.$6H_2O$ which prepared with 0.05M by dissolving 1.81756gm of Ni $(NO_3)_2$. $6H_2O$ in (250 ml) of distilled water, then the resulting solution was sprayed on preheated glass substrates to 498 ^oK; When the solution is sprayed the following reaction takes place at the surface of the heated substrate.

$$2Ni(NO_3)_2 \rightarrow 2NiO + 4NO_2 + O_2$$

The resulting films were transparent, gray in color, stable, free from pinholes and have a good adhesive properties. NiO thin films were prepared with different thickness, the selected thickness was (1451.8)A^0 .The absorbance and transmittance of prepared thin film was measured using Shimadzu 157 UV.-VIS. spectrophotometer in the wave length range (200-1100)nm.

3. Results and Discussion

Fig.(1) shows the optical transmission spectra of NiO thin films .This film shows more than 55% transmission for wave lengths longer than 400 nm, this behavior is similar to the behavior in the transmission spectra of NiO films prepared by RF magnetron sputtering process [1].

The absorbance spectra of NiO film is shown in fig.(2). We can notice a high absorbance at ultraviolet region, then it decrease rapidly in the visible /near infrared region.

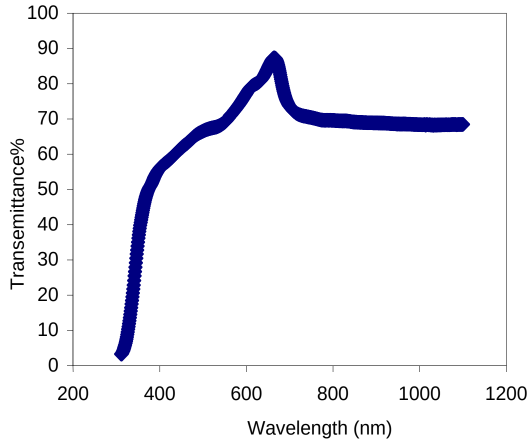

Fig.(1) Transmission spectra of NiO thin film.

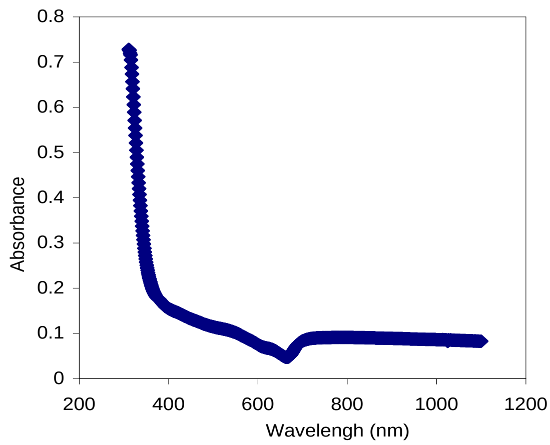

Fig.(2) Absorbance spectra of NiO thin film.

3.1 Absorption Coefficient

From the absorbance data, the absorption coefficient α was calculated in the fundamental absorption region using Lambert law[9]:

$$Ln\left(\frac{I_0}{I}\right) = 2.303A = \alpha d$$

$$\alpha = 2.303A/d..............(1)$$

Where Io and I are the intensity of incident and transmitted light respectively ,A the optical absorbance and d the film thickness . Fig.(3) shows the variation of absorption coefficient with photon energy for NiO thin film ,the fig. also shows the variation of absorption coefficient in the low energy range then its value increase rapidly beyond absorption edge region .We can evidently see that NiO thin film has high value of absorption coefficient $(\alpha > 10^4 cm^{-1})$ which be conducive to increasing the probability of occurrence direct transitions. .

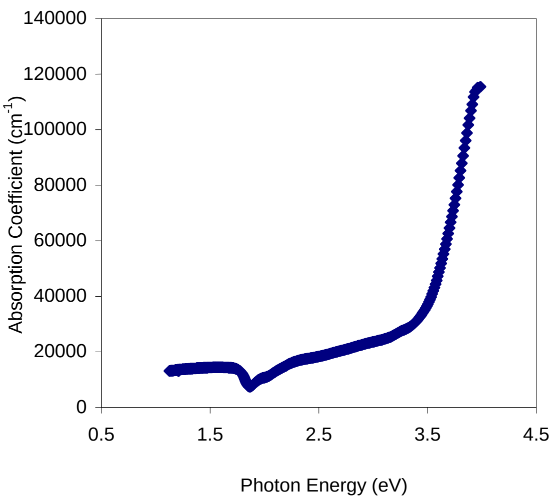

Fig.(3) Absorption coefficient vs. photon energy of NiO thin film.

3.2 Extinction Coefficient

Extinction coefficient (k) of prepared films was calculated by using the relation [10,11]:

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

Where λ is the wavelength of the incident photon. Variation of extinction coefficient as a function of photon energy is shown in fig.(4),the extinction coefficient of prepared film has values in the range (0.3951 - 2 .8296). The rise and fall in the extinction coefficient are directly related to the absorption of light. In the case of polycrystalline films, extra absorption of light occurs at the grain boundaries[9]. This leads to non-zero value of k for photon energies smaller than the fundamental absorption edge.

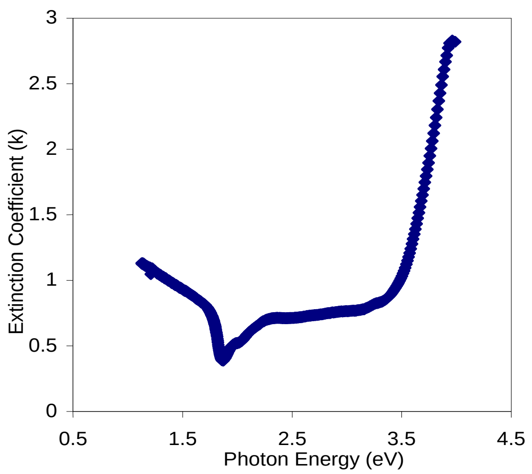

Fig.(4) Extinction coefficient vs. photon energy of NiO thin film.

3.3 Reflectance

Fig.(5) shows the optical reflectance spectra for NiO thin film. The reflectance has been found by using the relationship:

$$R+T+A=1$$

The figure also shows that the film reflectance increases rapidly at the low energies and then makes peaks at the energies which are corresponding to the energy gap of the film, then the reflectance decreases at the photon energy which is larger than the energy band gap which are attributed to the very low absorbance of the film at the photon energies less than the forbidden energy gap, and when it becomes larger or equal to the energy band gap a clear value of absorbance appears and increases because the material electrons interaction with the incident photon which has enough energy to make the electronic transitions take place[9,10].

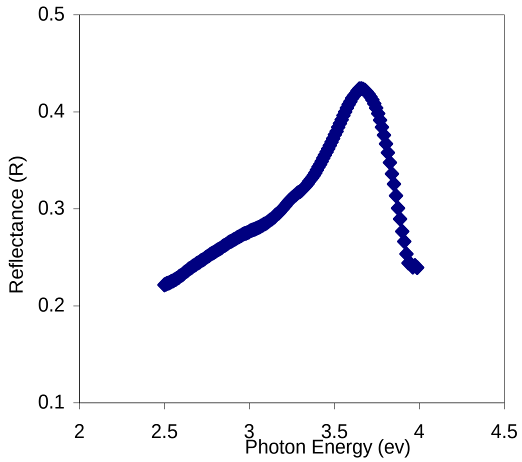

Fig.(5) Reflectance vs. photon energy of NiO thin film.

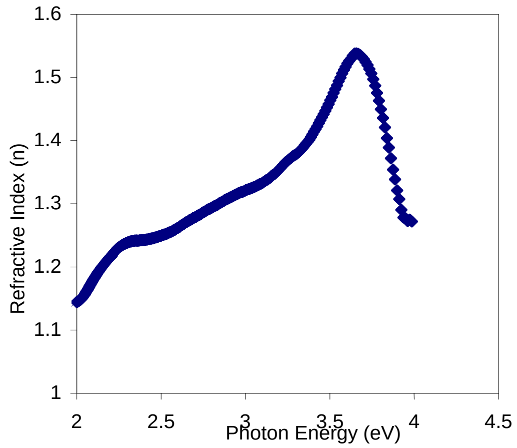

Fig.(6) Refractive index vs. photon energy of NiO thin film.

3.4 Refractive Index

From the reflectance data, the refractive index (n) was calculated by using the following relationship [14]:

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}} \text{..........(3)}$$

Fig.(6) shows the variation of refractive index with photon energy of NiO thin film. The behavior of this fig. is similar to the behavior of reflectance spectra in fig(5), because of the strong dependence calculation of the refractive index values on the reflectance values as above relationship, where the refractive index increases rapidly at the low energies and then make peak at the energies which is corresponding to the energy gap of the film. Then (n) decreases at the photon energy which is larger than the energy band gap because of the increasing the direct electronic transitions at that energies. The results show that the refractive index values of prepared film have values in the range(1.144-1.538)eV. It can be also said that at every lowest value of refractive index there is highest value for extinction coefficient [10].

3.5 Optical Conductivity

From the below relation we can calculate the optical conductivityσ [14,15]:

$$\sigma = \frac{\alpha n c}{4\pi} \text{...............(4)}$$

Where c is the velocity of light. The optical conductivity versus photon energy curve is shown in fig.(7). It can be noticed from the fig. the slow variation of optical conductivity in the low energy range then its value increases rapidly beyond absorption edge region, because of the high increase of the absorbance in this region.

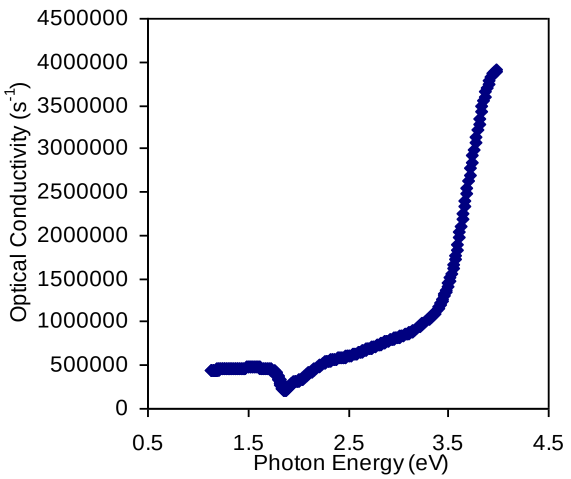

Fig.(7) Optical conductivity vs. photon energy for NiO thin film.

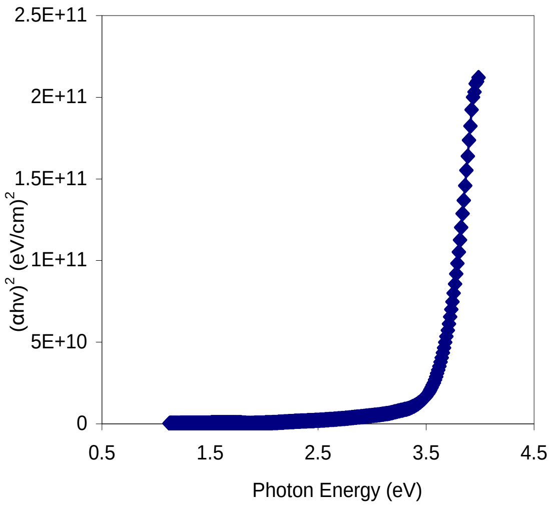

Fig.(8) Variation of $(\alpha h\upsilon)^2$ with photon energy for NiO thin film.

3.6 Energy Gap

Study of material by means of optical absorption provides a simple method for explaining some features concerning the band structure of material. In the present investigation, optical absorption(fig.2) in NiO film was studied in the wave length (300-1100)nm. The nature of transition(direct or indirect) is determined by using the relation[11]:

$$\alpha hv = A(hv - E_g)^n \,.................(4)$$

Where hυ is the photon energy, E_g the band gap energy, A and n are constants. For allowed direct transition, n=1/2 and for forbidden direct transition, n=3/2. The plot of $(\alpha h\upsilon)^2$ vs. hυ is shown in fig.(8), for NiO film. The linear nature of the plot indicates the existence of direct transitions. In fig.(8) from the straight line obtained at high photon energy the direct allowed energy gap could be determined which was equal(3.69 4eV). Fig.(9) shows that the forbidden direct transition was equal(3.653eV).These results were in good agreement with the results in reference [4],which was from (3.6-4)eV.

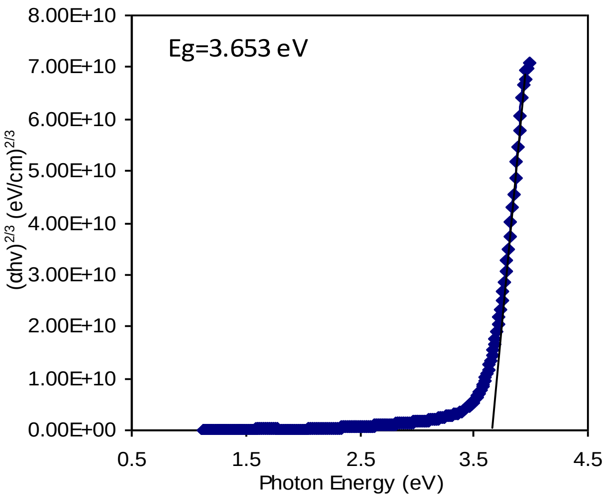

Fig.(9) Variation of $(\alpha h\upsilon)^{2/3}$ with photon energy for NiO thin film.

Conclusion

NiO films wa prepsared by a spray pyrolysis technique using a solution of nickel nitrate. The film was deposited on to glass substrate at temperature(498°K).NiO thin film of thickness(1451.8A^0)has been characterized by using optical measurements to obtain optical properties as the T-R-A spectra, optical band gap energy ,refractive index, optical conductivity, absorption and extinction coefficients. The variations of these parameter with incident photon energy wave length have been studied. The film exhibits high transmittance(~55-87%) and high absorbance values at ultraviolet region which they decrease rapidly in the visible / near infrared region. The film shows a direct transition which was (3.694eV) for allowed energy gap and (3.653eV) for forbidden one. In conclusion, spray pyrolysis method for the production of thin solid films is a good method for the preparation of thin films which are suitable for scientific studies and for many applications in technology and industry.

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