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Study the Effect of PH Variation on the Particle Size of Sio_2 Thin Films

Mohamed K. Dhahir and **Hasan. A. Khyoon**

Institute of laser for postgraduate studies, university of Baghdad, Baghdad,

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Abstract: In this paper, SiO_2 nanoparticles thin films were synthesised at different PH values of solution by sol gel method at fixed temperature (25^oC) and molar ratio (R $=H_2O$/precursor) of (Tetra Ethyl Ortho Silicate) TEOS as precursor at (R=1). The structure and optical properties of the thin films have been investigated. All thin films were tested by using X-RAY diffraction. All X-RAY spectrum can be indexed as monoclinic structure with strong crystalline (110) plane. The morphological properties of the prepared films were studied by SEM. The results indicate that all films are in nano scale and the particle size around (19-62) nm .The size of silica particles increases with increasing PH value of solution where both the rate of hydrolysis and condensation become faster and affect on the solubility of intermediate [Si (OC2H5)4-X(OH)X] and hence affect on the supersaturation of the nucleation process . Also the UV-visible study indicates that the absorption is minimum and transmittance is maximum at the visible range of the spectrum. Accordingly, the sample is suitable for antireflection coating such as solar cells.

Introduction

Silicon is present in the environment in several forms. It is not only found in nascent form, but it is also present as a joint with oxygen (as in silica) or with hydroxides (As in silicic acid). 78% of earth's crust consists of silicon and oxygen compounds, both crystalline amorphous and compounds for example quartz, opal, flint, silicates etc. Silicon is also present in the oceans as silicic acid. Also silica is found in living organisms like sponges, algae, and grasses (for example, diatoms) [1-4].

The sol-gel technique is very attractive and versatile method that can be relatively easily be applied to a range of materials. It can be used to fabricate ceramic coatings from solutions by chemical means. Sol-gel technique has also been used to improve the mechanical properties of the coatings as a result of the nano-crystalline grain structure produced [5]. This technique is a chemical process to synthesize the metal oxide materials. In this process, the product may be in amorphous or crystalline phase [6]. It used for synthesis nanomaterial, bulk materials in addition to nano, thick, thin films depositing on substrates at lower temperatures[7] .

There are some specific parameters that influence the hydrolysis and condensation reactions of sol-gel process, such as the PH value. When this value is less than 2, as H^+ concentration increases, the polymerization speed will increase; contrarily, when pH value is higher than 2, as OH^- concentration increases, speed of polymerization will be faster, while, when PH equals 2 is a point of zero charge, which is a stable area, and the gelation time will become longer. Under acidic environment, the hydrolysis reaction rate will be faster than that of condensation reaction rate, hence, the formed particles are small and are of linear and neat structure; to the contrary, under caustic environment, condensation reaction rate will be faster than that of hydrolysis, larger size and particulate shape particle could easily be formed, as shown in figure (1)[9], as well as the dependence of the reaction rate with PH is different for acid and base catalyzed systems as it shown in figure (2)[10] .

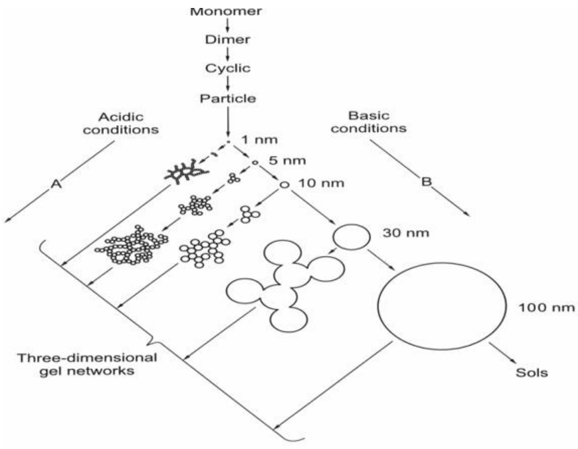

Fig. (1): Polymerization situation of SiO2 under different pH values[9]

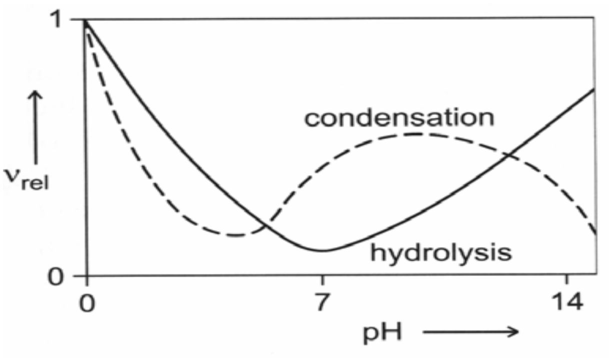

Fig. (2): The dependency of the relative rates of hydrolysis and condensation reactions of $Si(OR)_4$ on the PH[10].

In this work we chose the sol-gel technique. It is one of the Chemical deposition methods. Highly transparent and conductive SiO_2thin films were prepared by this technique. The results of the preparation SiO_2 thin films and the effect of PH variation of the solution on the particle size were reported, with fixed experimental conditions .

Experimental work

At first (2ml) of (TEOS) Tetra Ethyl Ortho Silicate which has the chemical form of [Si $(OC_2H_5)_4$] (99.99% Sigma- Aldrich) were mixed with one ml of ethanol (99.9 Scharlab S.L Spain) in glass beaker. This solution is denoted as (SOL- A) (Silica solution). Separately 2 ml of deionized water (acidified to 0.15M HCl, PH=2) was added to 2 ml of ethanol. The solution was refluxed for 15 minutes. The final solution is denoted as (Sol- B)(catalyst solution). Then the catalyst solution was added slowly to silica solution with stirring. The final solution was TEOS: H_2O : ETOH = 2: 2 : 3 with a molar ratio R of (H_2O/Si). This final mixed solution was poured in glass beaker 25ml and left for aging for 24 hours. All the steps above were repeated with PH =7 and PH=9.

The nanostructure SiO_2 thin film is formed by spin coating on glass substrate at room temperature and a constant revolution speed of about 2000 rpm. Square glass sheets of 1mm thickness and 2.5×2.5 cm^2 area were used as a substrate. Clean glasses sheets were placed on the disk of spin coating device, and the preparing solution was dropped on the glass sheet. Figure (3) shows the preparation steps of SiO_2 thin film.

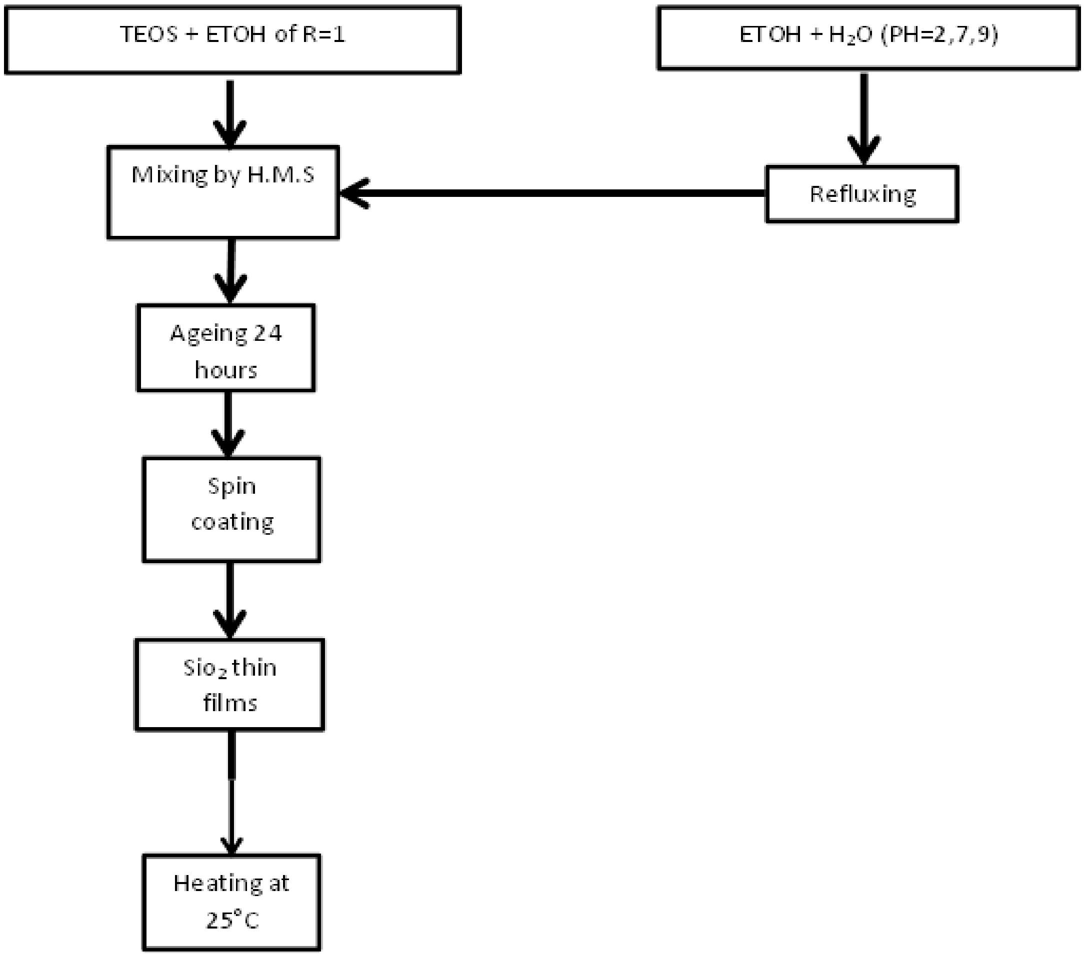

Fig.(3): schematic diagram of the SiO_2 thin film preparation stages

Result and Discussion
X-Ray Diffraction

Figure (4) shows the XRD pattern of SiO_2 thin films deposited at a certain PH=2, R=1 and drying temperature T=25^{o}C. It is seen from the XRD pattern that the film was polycrystalline in nature, with narrow peaks indicating large grain size. According to (ASTM) cards, the structure of thin films showed a polycrystalline monoclinic structure. The analysis is demonstrated the reflection surfaces (001),(110), (11ī),(020) and (20ī)which corresponding to 2θ = (14.2746) ,(17.1443),(18.6000), (21.8000) and (25.7661) respectively. The film is crystallized with a strong peak at (110) directions which corresponds to 2θ = (18.6000), which means typical SiO_2 with lattice constant of a=6.9979 Å b=8.2122 Å c=6.5106 Å β=114.930 º. That means this plane is suitable for crystal growth. Table (1) lists the experimental and standard d-values for SiO_2 thin film. The observed d-values match the standard values for the monoclinic structure for (ASTM).

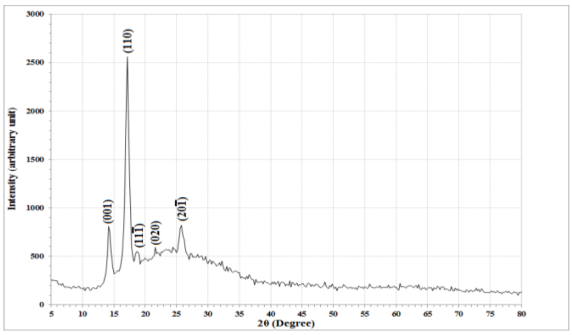

Fig. (4): X-ray diffraction pattern of SiO_2 thin film having 750 nm thicknesses.

Table (1): X-ray diffraction data for SiO_2 thin films.

2θ (Deg.)	FWHM (Deg.)	Intensity (%)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	Hkl
14.2746	0.715	26	6.1997	11.2	5.9040	(001)
17.1443	0.721	100	5.1679	11.1	5.0214	(110)
18.6000	1.106	10	4.7666	7.3	4.6702	(11$\bar{1}$)
21.8000	0.520	7	4.0736	15.6	4.1061	(020)
25.7661	1.043	18	3.4549	7.8	3.4707	(20$\bar{1}$)

Scanning Electron Microscopy Measurements (SEM):

SEM images were taken to monitor, and calculate the size and distinguish the shape of SiO_2 particles at different values of PH with fixed value of molar ratio (R=1) and drying temperature (T=25°C).
It was found that the shape of SiO_2 particles was similar to spherical shape also the SiO_2 particles is in nanoscale. Figure (5) shows the SEM image of SiO_2 Particles at different PH values and R=1, and drying temperature (T) =25°C.

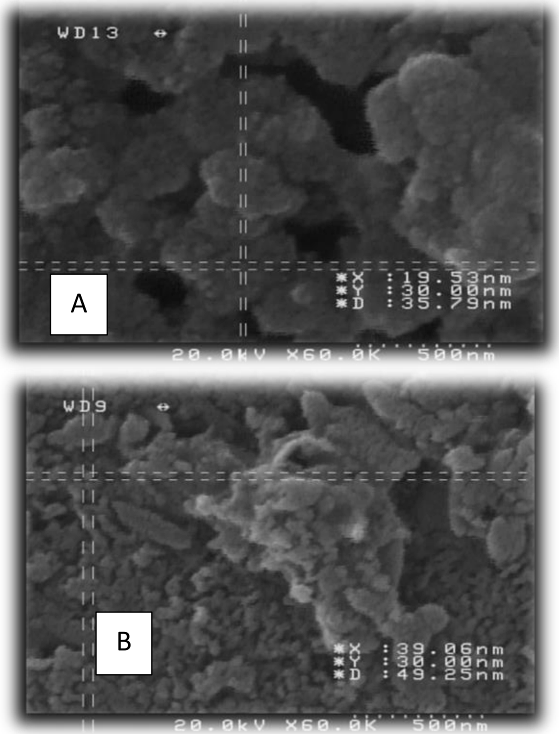

Fig. (5a, b) :SEM images of SiO_2 thin films of thickness 750nm at molar ratio R=1 and drying temperature T=25°C at (A- PH=2) (B - PH=7)

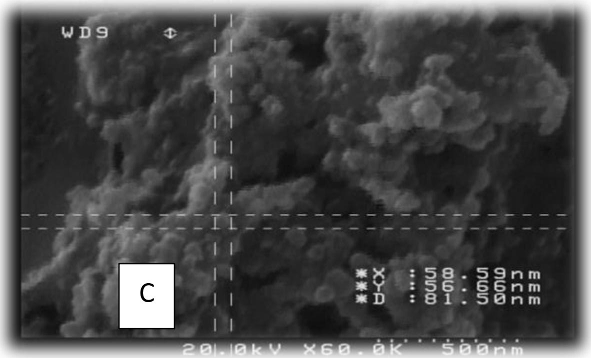

Fig. (5c): SEM images of SiO_2 thin films of thickness 750nm at molar ratio R=1 and drying temperature T=25°C at PH=9 .

Figure 3 shows that the prepared silica particles are similar to a spherical shape. The particle size increases with increasing of the PH value for the rang from PH=2 to PH=9 for fixed value with fxed values for each of TEOS and water concentrations (R=1/1). When PH increases the rate of hydrolysis and condensation became faster[9], and the formation of intermediate compound [Si (OC2H5)4-X (OH)X] increases rapidly due to the high hydrolysis reaction. When it reaches the supersaturation region, the consumption rate of intermediate compound through condensation reaction becomes relatively fast[10], which probably shortens the nucleation period. So, the total number of nuclei formed will decrease, and the final particle size of synthetic silica colloids will be relatively larger [11].

The Optical Properties of SiO_2 nano Films

The optical properties of the deposited SiO_2 nano films on glass substrate at room temperature and with different thickness have been investigated UV-Visible spectrum.

The Absorption Spectra

Fig. (6) shows the absorbance spectra of the nanostructures of (SiO_2) thin films at different values of PH as a function of wavelength in the range of (300-1100) and at constant molar ratio R=1 and drying temperature T=25°C. It can be observed that when the PH of the film increases; the absorption value decreases, since in the case of high PH film, more porous structure are present in the film , where the particulates may have a high solubility in the sol, due to the pH affects the dissolution and precipitation of silica. While in PH value dense structure, fine porous networks are obtained due to low dissolution precipitation rate so more states will be available for the photons to be absorbed. At visible light region, the strong photo-absorption is presented in the range of (440-460 nm) and for all PH values. At the visible spectrum, the absorption is minimum, so it can be considered as suitable antireflection coating. At high λ the incident photons do not have enough energy to interact with atoms, so the photon will be transmitted when wavelength (λ) increases (photon energy decrease).

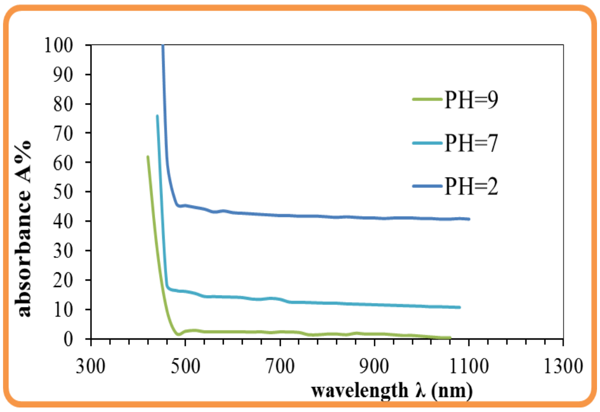

Fig. (6): Absorbance spectra of nanostructure SiO_2 thin films at R=5,T=25 °C and different values of PH.

Reflectance Spectrum (R):

Reflectance is calculated from the spectra of absorbance and transmittance for all prepared thin films. It can be observed from Fig. (7) that the reflectance increases by decreasing the wavelength. Also, Fig. (7) shows that the reflectance has low value where decreased with increasing wavelength for all films, and this is attributed to decrease in the absorption coefficient.

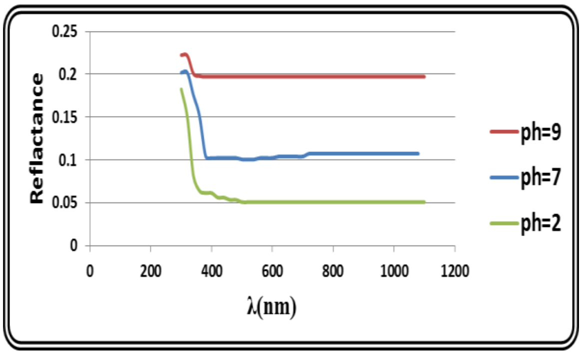

Fig. (7): Reflectance spectra of nanostructure SiO_2 thin films at different PH values.

Absorption Coefficient (α):

Figure (8) shows the variation of (α) with photon energy (hν) for (SiO_2) thin films for different PH values. From this figure, it can be seen that the absorption coefficient (α) increases with increasing photon energy for investigated thin films. It can clearly be seeing that absorption coefficient having values ($\alpha > 10^4 cm^{-1}$) leads to an increase in the probability of occurrence of direct transition. whereas the absorption coefficient increases with decreasing PH value the. This can be linked with the formation stage and with increase in grain size and density of thin film and it may be attributed to the light scattering effect for its high surface roughness.

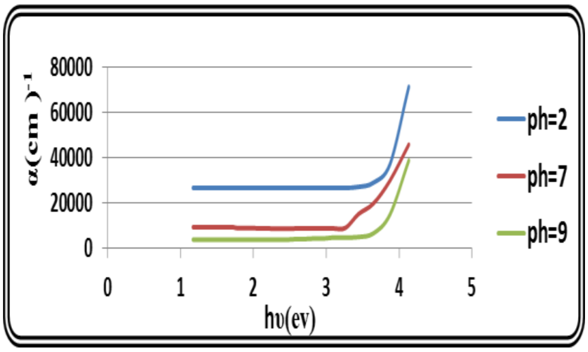

Fig. (8): Absorption coefficient as function of energy photon for different PH values of nanostructure SiO_2 thin films.

The Optical Energy Gap (E_g):

The optical energy gap values (Eg) for nanostructure SiO_2 thin films have been determined. The plot shown in Fig.(9) is linear indicating the direct band gap nature of the films. The Extrapolation of each line to the *hv* axis gives the band gap. The energy gap increased with increasing the nanostructure SiO_2 thin films PH values (E_g =2.7, 3, 3.6ev) for

PH=2, 7, 9 respectively. This is due to the decreasing of the density of localized states in the Eg which cause a shift to higher values as shown in figure (9).

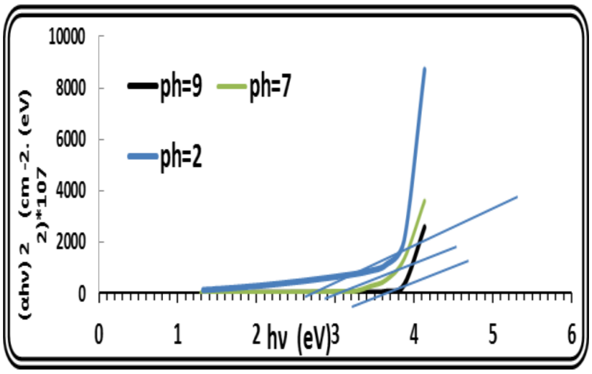

Fig. (9): $(\alpha h\nu)^2$ as function of energy photon for different PH values of nanostructure SiO_2 thin films.

Optical Constants

Extinction Coefficient (K)

Figure (10) illustrates the variation of (K) as a function of the wavelength for SiO_2 thin films. As shown in this figure the variation of K versus films PH values are not systematic. The rise and fall in the extinction coefficient are due to the variation of the absorbance, with increasing PH values.

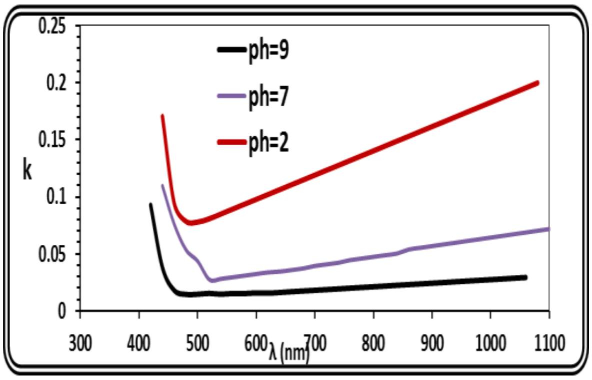

Fig.(10): Extinction coefficient (k) as wavelength for different PH values of nanostructure SiO_2 thin films.

Refractive Index (n) :

Refractive index is calculated by using the following relation

$$n = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$

The variation of n as a function of wavelength for nanostructure SiO_2 thin films at different PH value is shown in figure (11). From this figure it can be observed that the refractive index increases with PH increasing. The increase may be attributed to higher packing density and the change in crystalline structure, this increase due to the enhancement of growth crystalline.

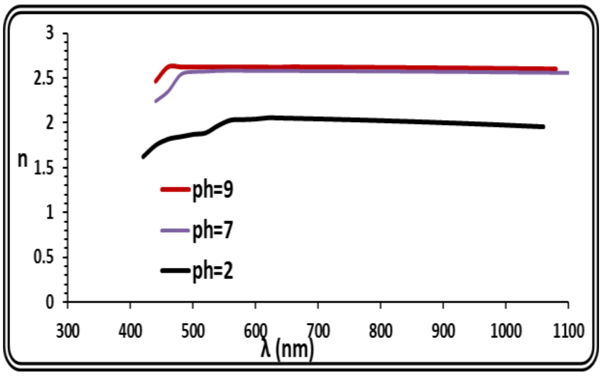

Fig. (11): Refractive index as function of wavelength for different PH values of nanostructure SiO_2 thin films.

The Dielectric Constant:

The dielectric constant (ε) consists of real part (ε_r) and imaginary part (ε_i) depend on the frequency of the electromagnetic wave. The variation of ε_r and ε_i versus wavelength in the range (400-1100) nm at different PH values are shown in Figure (12) and (13). The variation of ε_r and ε_i with the increase of the wavelength of the incident radiation is due to the change of reflectance and absorbance. The behavior of ε_r is similar to that of the refractive index because of the smaller value of k^2 compared with n^2, while ε_i mainly depends on the k value, which are related to the variation of absorption coefficient. ε_i represent the absorption of radiation by free carriers. It is observed that ε_r increases with increasing PH values, and this is attributed to the same reason mentioned previously for the refractive index, while ε_i decreases with increasing of PH values and this is due to the similar interpretation discussed previously for the extinction coefficient.

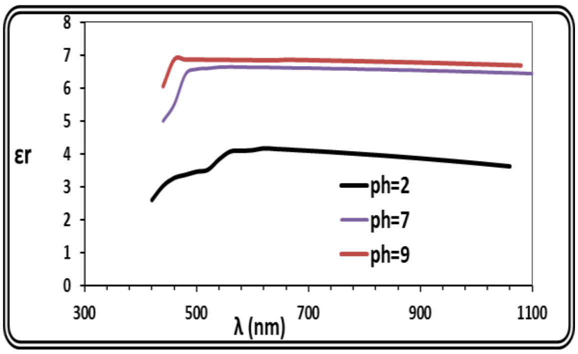

Fig. (12): Real dielectric constant (ε_r) of nanostructure SiO_2 thin films for different PH values.

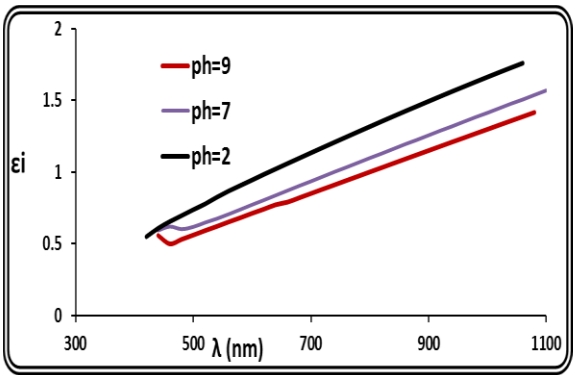

Fig. (13): Imaginary dielectric constant (ε_i) of nanostructure SiO_2 thin films for different PH values.

Conclusion

Herein, we have studied the effects of PH of solution (catalyst) on the resulting particle size of silica thin films which prepared by sol gel method. Our results are discussed in terms of relative contribution from nucleation, growth processes and the effect of PH variation on the reducing particle size. Where, increase of the rate of hydrolysis, tend to produce fewer nuclei during the nucleation process and therefore a larger particle size in the end. The effect of PH of solution on optical properties of thin films was studied too. It has been found that the increasing of PH value lead to decrease the absorption of thin film and increase reflectance, the absorption coefficient (α) and energy gap. In addition to that the variation of K versus films PH values is not systematic, and the refractive index increases with PH increasing. Finally it has been observed It is observed that ε_r increases with increasing PH values, while ε_i decreases with increasing of PH values.

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دراسة تأثير معامل PH على حجم الجزيئات الغشاء الرقيق لمركب SiO_2

محمد كريم ظاهر   حسن علوان خيون

معهد الليزر للدراسات العليا ، جامعة بغداد ، بغداد ، العراق

الخلاصة: في هذا العمل تم تصنيع اغشية ثنائي اوكسيد السليكون SiO_2 بطريقة السول جل عند درجات مختلفة للرقم الهيدروجيني PH مع ضبط درجة الحرارة عند 25 درجة مئوية وعند نسبة مولارية (تركيزمادة التيترا اثيل اورثو سليكاتTEOS)R=1 . تم فحص الخواص البصرية والتركيبية للاغشية الرقيقة ، حيث فحصت جميع الافلام باستخدام حيود الاشعة السينية(XRD) ووجد بانها ذات تركيب بلوري يندرج تحت الطور الاحادي مع هيمنة الاتجاه (110) .درست الخصائص التشكيلية بواسطة المجهر الالكتروني الماسح SEM ووجد بان جميع الافلام ذات مقياس نانوي حوالي (19-60) نانومتر . حجم الجسيمات النانوية يزداد بزيادة الرقم الهيدروجيني للمحلول حيث يصبح معدل كلا من التحلل والتكاثف اسرع ويؤثر على ذوبانية المركب الوسيط [Si (OC2H5)4-X(OH)X] وبالتالي يؤثر على التشبع لعملية التنوي ، استخدمت مطيافية الاشعة المرئية وفوق البنفسجية لدراسة الخواص البصرية ووجد بان الامتصاص يكون اقل ما يمكن والنفاذية اكبر ما يمكن عند الطيف المرئي . يعتبرالنموذج استنادا الى كل الفحوصات اعلاه مناسب لتطبيقات الطلاءات المضادة للانعكاس مثل الخلايا الشمسية .