

Si nanocrystal-containing SiO_x ($x < 2$) produced by thermal annealing of PECVD realized thin films

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Abstract

This paper is focused on the description of relationship between deposition parameters (flow rates of SiH_4 and N_2O precursor gases) and properties of SiO_x films. The silicon-rich silicon oxide thin films deposited using plasma enhanced chemical vapour deposition (PECVD) in silane-nitrous oxide-helium discharges were thermally annealed at 1273 K for 1 h. Fourier transform infrared (FTIR) spectroscopy indicated that the chemical composition was dominated by silicon suboxide containing silicon-nitride and silicon-hydrogen bonds. For the as-deposited films and for the annealed films, Raman spectra show a band approximately at 480 cm^{-1} , related to amorphous silicon and a band at 520 cm^{-1} , related to nanocrystallite silicon, respectively. Transmission electron microscopy analysis demonstrated that silicon nanocrystals (Si nc), having a mean radius ranging between 3 and 6 nm were present in the annealed films. Using spectroscopic ellipsometry (SE) in the $0.2\text{--}0.88\text{ }\mu\text{m}$ spectral range, the values of layer thickness, optical indices and component volume fractions were determined using the Fourouhi–Bloomer (FB) model for the as-deposited films and the Bruggeman effective medium approximation (BEMA) for the annealed ones.

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1. Introduction

Recently, considerable research effort was directed to study the silicon-rich silicon oxide films in view of their important role in device manufacturing technology such as memory devices [1]. The main advantage of Si– SiO_2 composites is their robustness and the surface stability in comparison with porous silicon [2]. In the field of nanocrystalline materials, significant effort has been dedicated to the formation and characterization of silicon nanocrystals (Si nc) embedded in SiO_2 matrix. A variety of methods such as co-sputtering [3], ion implantation [1] and chemical vapour deposition [4] have been used for producing silicon nanocrystals embedded in SiO_2 . In this work, we used high temperature annealing of substoichiometric SiO_x ($0 < x < 2$) thin films deposited by plasma enhanced chemical vapour deposition (PECVD). This technology is very promising because of good control of film quality, its easy integration in current micro-electronic technologies as well as low cost, high efficiency and reproducibility.

This work has been devoted to study the properties of silicon suboxide thin films. In particular, the possibility of varying their composition with the operating process conditions is of great interest for the control of Si nanocrystals formation. Thin silicon-rich SiO_x films within a large range of composition were produced by PECVD using SiH_4 and N_2O as precursor gases. The formation of silicon clusters embedded in a dielectric silicon oxide matrix was investigated. The properties of as-deposited as well as of annealed films were studied by various physico-chemical techniques such as fourier transform infrared (FTIR) spectroscopy, Raman spectroscopy, high resolution transmission electron microscopy (HRTEM) and spectroscopic ellipsometry (SE). We found that, by varying the flow ratio of the gaseous precursors, it was possible to change the properties of the film. The main is to observe the effect of deposition parameters in order to highlight the relationship with Si nc formation in effect of annealing.

2. Experimental details

Silicon-rich silicon oxide (SiO_x) thin films were prepared by using a PECVD reactor [5] consisting of a vacuum bell jar ($133 \times 10^{-7}\text{ Pa}$) and a 13.56 MHz RF generator connected

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through a matching LC box to the excited electrode. The silicon substrates were placed on the bottom grounded electrode. The SiO_x films were grown on intrinsic silicon and silica substrates. All deposition processes were performed at 653 K, under a pressure of 66.5 Pa and a RF power of 5 W. The source gases used were SiH_4 , N_2O and He, the N_2O gas flow rate was kept constant at 40 sccm for all samples. After deposition, the SiO_x films were annealed for 1 h at 1273 K in nitrogen atmosphere.

The SiO_x film composition ($0 < x < 2$) was controlled by varying the $\text{SiH}_4/\text{N}_2\text{O}$ flow rate ratio ($\gamma = Q_{\text{SiH}_4}/[Q_{\text{N}_2\text{O}} + Q_{\text{SiH}_4}]$). Physicochemical, structural and optical absorption properties of SiO_x films, as-deposited and subjected to thermal annealing, were investigated by FTIR spectroscopy, Raman spectroscopy, HRTEM and SE. FTIR spectroscopy was used as a non-destructive technique to obtain further information on the structural and compositional properties of films and the types of chemical bond present. The infrared analyses were performed by means of a BIORAD QS 300 FTIR spectrometer. The IR absorbance spectra of the silicon oxide films were compared in the range of $400\text{--}4000\text{ cm}^{-1}$ ($1.3\text{--}12.3\text{ }\mu\text{m}$) with a resolution of about 4 cm^{-1} . The Raman measurements were carried out with a Dilor UV spectrometer equipped with a charge-coupled device multichannel detection system and a microprobe focused on the sample. The incident beam at 363 nm line of argon laser was used for the excitation. Dark-field plan-view HRTEM analyses were carried out with a CM30 Philips microscope to determine the nanocrystal size distribution. In order to study silicon-based films, optical techniques are particularly suitable, rather easy to use, and non-destructive [6]. Most of the studies aimed at determining the optical properties of nc-Si were performed either by the use of a mixture of known materials [7] or by a direct inversion of the optical parameters of thin films [8], or else by a theoretical calculation [9]. Therefore, ellipsometry provided significant information on the dielectric function, the volume fraction of constituents and cristallinity of the layers. Particular attention was devoted to the modifications of these properties caused by the effect of the incorporation of nc-Si in thin SiO_xN_y films. Up to now, ex situ spectroscopic ellipsometry measurements were performed in order to determine the thickness, composition and optical properties of the films. The SE experiment is based on the measurement of the ellipsometric parameters defined by Ψ and Δ . They are related to the complex reflectance ratio ρ by $\rho = r_p/r_s = \tan(\Psi)\exp(i\Delta)$ where r_p and r_s are the complex reflection coefficients for a plane wave polarized parallel/perpendicular to the plane of incidence, respectively. Ellipsometric functions $\tan(\Psi)$ and $\cos(\Delta)$ are the modulus of ρ and the phase shift between r_p and r_s , respectively. They are measured in the spectral range of $200\text{--}880\text{ nm}$ at 75° angle of incidence, using a rotating polarizer spectroscopic ellipsometer SOPRA GES-5 with tracking analyzer.

3. Results and discussion

The spectral positions of the infrared absorption bands correspond to the vibrational frequencies of the chemical groups present in the layer. As a matter of fact, a lot of works [10–12] were carried out to ascribe the position of the infrared bands

present in amorphous SiO_x and SiO_xN_y . A particular attention was paid to the dependence of the stretching Si–O–Si, Si–H and Si–N frequencies on the composition of SiO_x and SiO_xN_y films. Fig. 1(a) shows the typical FTIR results of the as-deposited films for two different flow rate ratios, γ , and Fig. 1(b) shows the results after annealing in N_2 at 1273 K for 1 h. The main feature of the as-deposited sample spectra is the position of the stretching Si–O–Si bands around $1020\text{--}1030\text{ cm}^{-1}$. This frequency decreases with increasing the γ flow rate ratio. This shift is due to the substitution of O atoms by Si atoms in the network of the substoichiometric films [13]. In addition, all the samples show a subsidiary band located between 810 and 820 cm^{-1} corresponding to the Si–O–Si bending mode [12] and the Si–O–Si rocking in the range $440\text{--}460\text{ cm}^{-1}$ [12]. Several other IR spectral features are present. There are weak absorptions due to the Si–H bending in the range of $640\text{--}660\text{ cm}^{-1}$ which is correlated to the Si–H stretching between 2100 and 2260 cm^{-1} [14]. Besides, the IR spectrum appears to be noticeably influenced by the presence of nitrogen in the as-deposited films; indeed, the absorption region at about $860\text{--}880\text{ cm}^{-1}$ is due to the stretching vibration of the Si–N bonds [15], while a weak peak of the N–H stretching 3385 cm^{-1} [13] is observable only for the sample with $\gamma = 0.15$ (Fig. 1(a)).

Compared to the film with the lowest γ values ($\gamma = 0.15$, Fig. 1(a)), the sample with $\gamma = 0.43$ (Fig. 1(a)) contains a significant percentage of Si–N bonding ($860\text{--}880\text{ cm}^{-1}$) with respect to the Si–O stretching band in the spectra. Besides, the IR spectrum of the as-deposited films is characterized by other relevant absorption bands at around $2100\text{--}2127$ and $640\text{--}660\text{ cm}^{-1}$ which suggest the presence of Si–H groups in the layers [10].

The infrared spectra of the annealed samples reveal two most relevant changes; first, as γ values vary from 0.15 to 0.43, the Si–O–Si stretching absorption bands shift towards higher frequencies in the range of $1050\text{--}1075\text{ cm}^{-1}$. The heat treatment induces an evolution of the amorphous phase present in the as-deposited SiO_x films towards a Si/SiO₂ mixture. Another interesting effect is the disappearance of the Si–N bonds and the Si–H bonds. This behavior of the spectrum is due to the partial conversion of the Si–N and Si–O phases to a mixed Si–O–N phase and the effective elimination of hydrogen from the films after the annealing treatment. These last observations could explain the unusual broadening of the band at 1070 cm^{-1} after annealing due to a residual SiO_x network resolved into two different components, Si–O–N and Si–Si bonds.

Raman spectroscopy, a sensitive probe to the local atomic arrangements and Si–Si vibrations, was used to detect the presence and to study the structure of silicon particles in the deposited layers. It allows for a differentiation between amorphous and crystalline phases [16]. Fig. 2 shows typical Raman spectra of SiO_x films, as-deposited and annealed at 1273 K for 1 h, on silica substrate with two different flow rate ratios, $\gamma = 0.43$ in Fig. 2(a) and $\gamma = 1$ in Fig. 2(b). The as-deposited sample shows a broad Raman band typical for amorphous silicon [17,18] and centered at around 490 cm^{-1} (Fig. 2(a) and (b), dot spectra) indicating that as-deposited films are amorphous. After annealing, the amorphous band remains present and the spectra exhibit sharp components at 513 and 520 cm^{-1} with $\gamma = 0.43$ (Fig. 2(a),

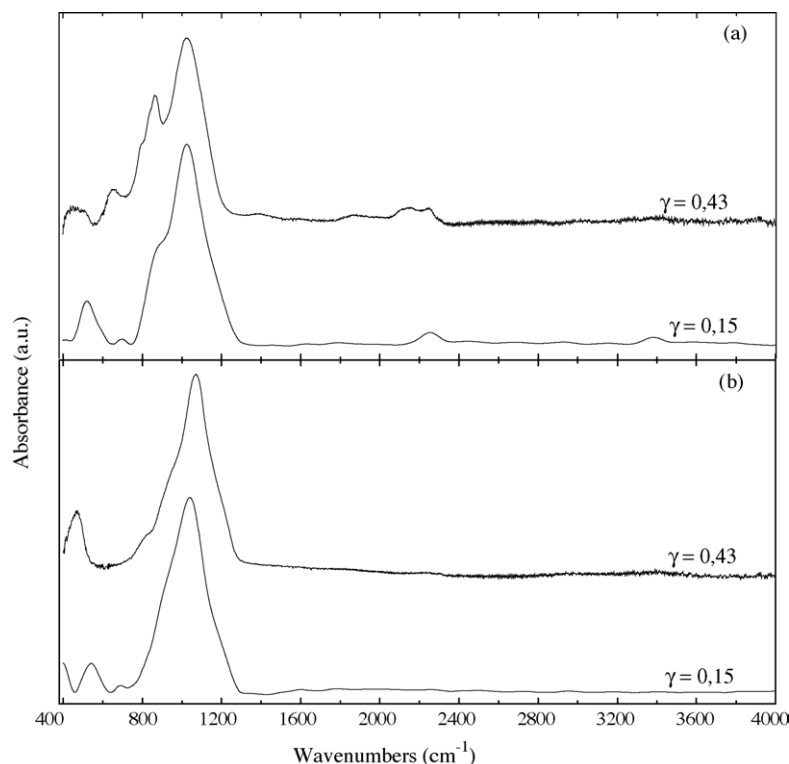


Fig. 1. Transmission infrared spectra of SiO_x films obtained at two different flow rate ratios γ , as-deposited (a) and annealed at 1273 K for 1 h in N_2 atmosphere (b).

solid spectra) and $\gamma = 1$ (Fig. 2(b), solid spectra), respectively. As a matter of fact, one can also find in the literature [17,18] that the band at 520 cm^{-1} is related to the crystalline silicon while the Raman peak located around 513 cm^{-1} can be attributed to the incorporation of nanosilicon in the SiO_x films. When the flow rate ratio decreased from $\gamma = 1$ to 0.43, the nanocrystalline silicon peak shifted down by approximately 7 cm^{-1} . It suggested a decrease in the silicon nanocrystallite size by a few nanometers, after annealing. The band-shape modification of the Raman peak has been used by many theoretical models [19,20] to evaluate quantitatively the average size of nc-Si. According to the Zi et al.'s confinement model [19] and Viera et al.'s studies [20], the

crystallite size is about 2 nm–3.6 nm, respectively. The Raman results appear to indicate that the SiO_x films obtained by PECVD exhibit an amorphous state of the as-deposited samples and a mixture of two phases in the annealed samples, an amorphous matrix and ordered silicon domains or nanocrystallites. In order to confirm the Raman measurements and to map the location of Si nanocrystals embedded in the SiO_x layers after the annealing process, we used HRTEM. Fig. 3 shows a HRTEM image relative to SiO_x film obtained with a flow rate ratio $\gamma = 0.43$, after 1 h annealing at 1273 K. Let us the deposit was the same as when the sample was characterized by Raman spectroscopy (Fig. 2(a)). The analysis of the HRTEM image showed clearly

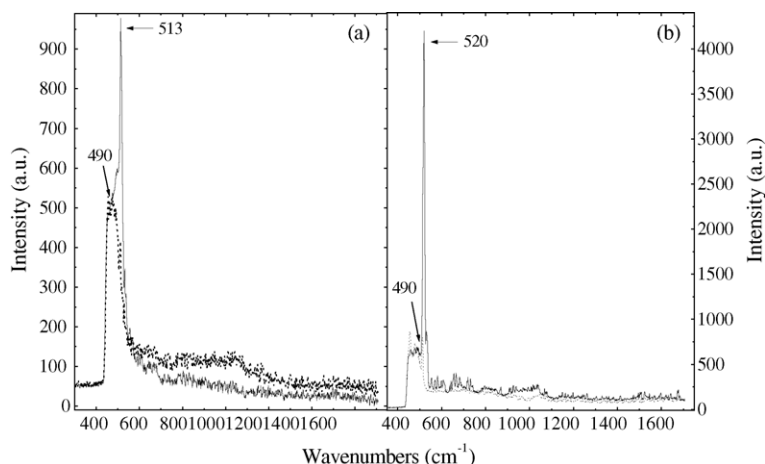


Fig. 2. Raman spectra of SiO_x films obtained for $\gamma = 0.43$ (a) and $\gamma = 1$ (b), as-deposited (dot spectra) and annealed at 1273 K for 1 h in N_2 atmosphere (solid spectra).

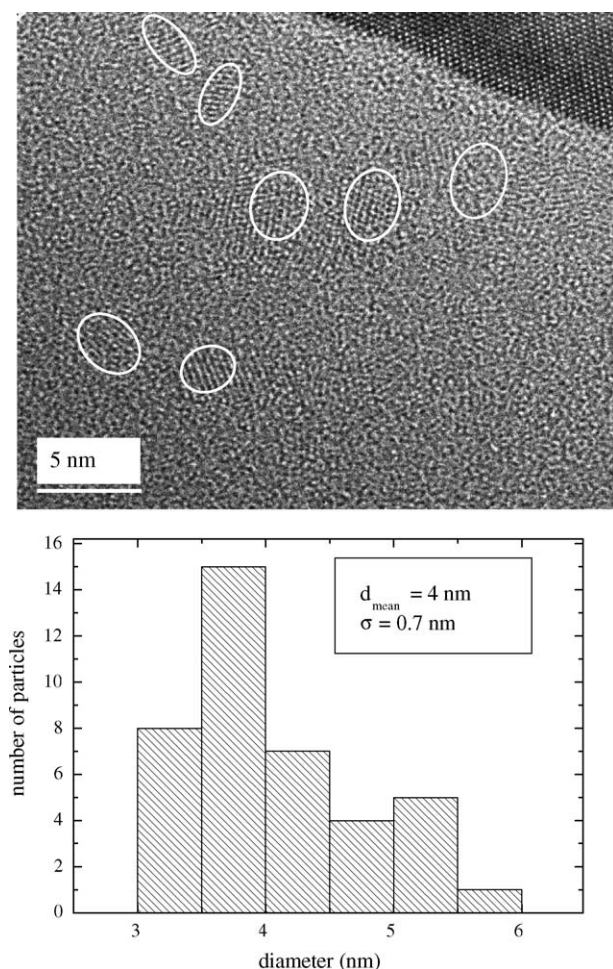


Fig. 3. HRTEM micrograph and relative Si nc size distribution of a SiO_x film prepared with a flow rate ratio $\gamma = 0.43$ and annealed at 1273 K for 1 h in nitrogen atmosphere.

that the amorphous SiO_x contained a high density of small clusters uniformly distributed in the matrix which was identified as Si nanocrystals. On the other hand, the statistical analysis of the crystal size distribution (histogram reported in Fig. 3) obtained from the HRTEM pictures showed a distribution of crystal size ranging from 3 to 6 nm with a mean radius of 4 nm, in good agreement with the particle size calculated from the Raman measurements with the Viera et al.'s model [20]. The distribution had a standard deviation σ of 0.7 nm, accounting for all the different crystal sizes detected in the HRTEM micrograph.

In this paper, the complex optical index N defined as $N = n - ik$ (where n is the refractive index and k the extinction coefficient) is obtained by fitting spectroscopic ellipsometry measurements with an appropriate model in the wavelength range of 200–880 nm. The determination of the physical parameters depends on the choice of the optical model adopted to derive n and k from $\tan(\Psi)$ and $\cos(\Delta)$ experimental data. According to our previous infrared and Raman spectra analyses, the ellipsometric spectra show that the as-deposited films consist of amorphous layers whereas the annealed films can be modelled as mixtures of poly-silicon crystals, amorphous silicon compounds and SiO_2 . Indeed, two suitable classes of models were

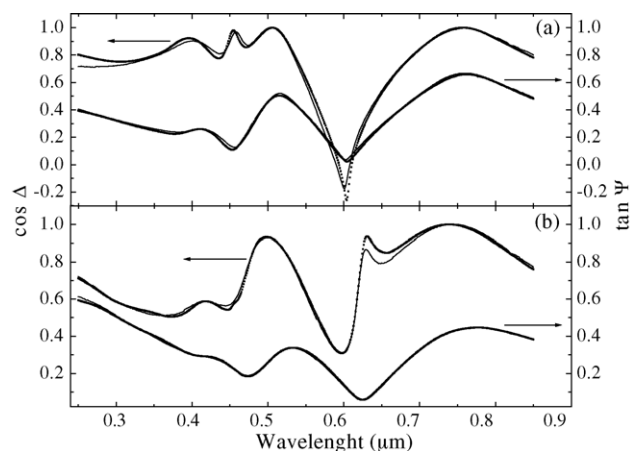


Fig. 4. Experimental (solid curve) and calculated (square data) ellipsometric spectra of SiO_x films obtained for $\gamma = 0.43$, as-deposited (a) and annealed at 1273 K for 1 h in nitrogen atmosphere (b). The square curves are obtained on the basis of the FB and BEMA models for the as-deposited and annealed films, respectively.

selected and tested to describe the sample optical properties. One class used the Fourouhi–Bloomer dispersion model [21]. In this, we assumed that the films were homogenous and the as-deposited films could be based on this model. Another model used Bruggeman effective medium approximation (BEMA) [22] which could be utilized to describe the optical properties of the annealed films. In this case, the fit parameters were the layer thickness and the volume fraction of different materials constituting the effective medium. Therefore, the complete physical model should take into account the surface roughness and possible surface oxidation. Thus, a two-layer model plus a topmost layer with a void fraction are required to reproduce the optical data of the as-deposited and annealed films. As an example, the $\tan(\Psi)$ and $\cos(\Delta)$ experimental spectra of as-deposited and annealed sample obtained at $\gamma = 0.43$ are reported in Fig. 4(a) and (b), respectively. In the same figure, we have also included the fits (solid lines) obtained with the different models discussed in the above. The agreement between the experimental data and the theoretical values is very good, as confirmed by the very low standard deviation of the fit ($\sigma = 0.000637$ and 0.000323 for the FB and BEMA models, respectively) indicates that the assumed as-deposited and annealed model is appropriate and the obtained results are reliable.

Fig. 5 shows the optical constants n and k calculated with the FB and BEMA fits. Two different samples obtained under the same operating conditions at different flow rate ratios, as-deposited and annealed, were optically characterized. The refractive index n (Fig. 5(a)) and the extinction coefficient k (Fig. 5(b)) increase from $\gamma = 0.15$ to 0.43, as the film compactness and the silicon content increase. These trends hold for both as-deposited and annealed layers. In agreement with our previous FTIR and Raman observations, the refractive index curves of as-deposited films are a smooth and structureless spectra hump [7], confirming an amorphous state. The effects of the annealing treatments on the optical function n and k of each sample reveal more information. The annealed films are conveniently simulated by BEMA model involving appropriate mixtures of

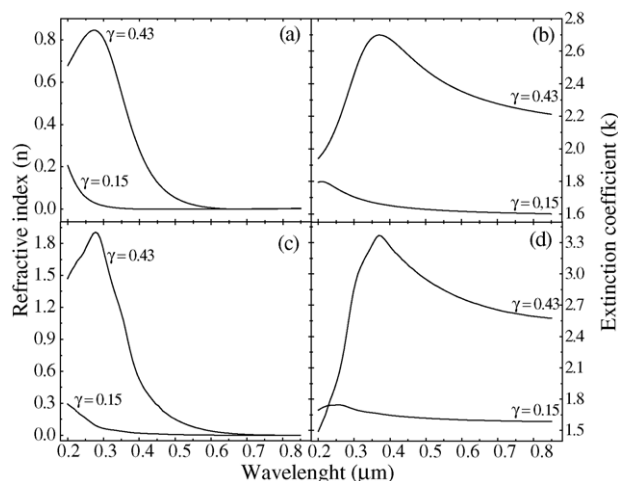


Fig. 5. Refractive index n (a, c) and extinction coefficient k (b, d) as a function of wavelength for the SiO_x films obtained for two different flow rate ratios γ , as-deposited (a, b) and annealed at 1273 K for 1 h in N_2 atmosphere (c, d).

SiO_2 , a- SiO_x and poly-Si. The BEMA modeling results show an increasing contribution of poly-Si and a decreasing contribution of SiO_2 with increasing γ (see Table 1). This behavior may be attributed to the phase separation between SiO_2 and silicon after thermal annealing process. Besides, in each case, a small amount of residual amorphous phase (a- SiO_x) remains present which explains the unusual broadening of the FTIR band at 1070 cm^{-1} (Fig. 1). According to the above observations it is obvious that the mixture assumed in the BEMA model represents favorably the true fraction of the individual components in the layer. From this discussion, we can conclude that the annealed films converge from a structure dominated by the SiO_2 for the lowest γ applied at deposition to a structure dominated by the polysilicon crystals for the highest γ .

It is known that the variations of the optical properties are due to the size reduction of nanocrystals [23]. In order to clarify this assumption, we have reported in Table 1 the optical band gap of several samples. The optical gap E_g is determined using the absorption coefficient α , and an intercept on the energy axis of $\sqrt{\alpha \times E}$ versus E plot. Before annealing, the optical gap decreased as γ increased. This expected phenomenon could be explained by the size and distribution change in the particles

Table 1
Fit values for the SiO_x films obtained at different flow rate ratios, γ , as-deposited (1) and annealed (2) at 1273 K for 1 h in N_2 atmosphere

γ	sl-t (nm)		l-t (nm)		E_g (eV)		BEMA mixture (%)		
	(1)	(2)	(1)	(2)	(1)	(2)	SiO_2	a- SiO_x	poly-Si
0.11	2.2	0.5	252	266	—	3.79	99	1	0
0.15	2.3	4.3	265	249	2.58	1.67	91.3	2.6	6.1
0.20	1.2	16.0	363	314	2.38	1.60	78.9	5.5	15.6
0.33	2.4	7.1	331	282	2.02	1.56	57.0	17.2	25.8
0.43	4.6	15.0	280	226	1.84	1.50	44.1	17.6	38.3
0.50	5.8	10.5	293	244	1.82	1.49	38.4	17.7	43.9
0.66	3.6	11.0	247	217	1.78	1.48	29.1	17.4	52.5
1.00	1.8	5.7	173	143	1.10	1.34	0	0	100

sl-t: top-layer thickness; l-t: layer thickness; E_g : optical band gap.

formed. Other studies [4,9] attribute this behavior to the quantum confinement effect, i.e., the gap energy is conditioned on the size of the nanocrystals.

4. Conclusion

SiO_x layers were grown by PECVD technique by varying the flow rates of SiH_4 precursor gases and keeping N_2O constant at 40 sccm. Using Infrared and Raman spectroscopy, transmission electron microscopy and spectroscopic ellipsometry, the films were found to consist of an amorphous state in their as-deposited form and of very small crystals (3–6 nm) covered by a native oxide in addition to an amorphous residual formed after a high-temperature annealing. In particular, it has been established that the value of γ , flow rate ratio, strongly affects both physicochemical and optical properties of the SiO_x films.

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