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The bonding modes and optical characteristics of annealed silicon oxide thin films prepared by plasma enhanced CVD

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ABSTRACT Silicon oxide (SiO_x, $0 < x < 2$) thin films have been prepared by the plasma enhanced CVD of gaseous silane and nitrous oxide (flow rate ratio 2/1) onto quartz and silicon wafer substrates at 250°C. The samples were then annealed in ambient oxygen at 100 to 600°C at intervals of 100 degrees. The Si-O-Si bending and stretching, Si-H stretching and Si-OH stretching modes were identified from the infrared spectra. The annealing process resulted in an excess of tetrahedral SiO_4 units and the generation of dangling bonds.

ABSTRAK Filem nipis silikon oksida (SiO_x, $0 < x < 2$) telah disediakan dengan kaedah CVD terbantu plasma dari campuran gas silane dan nitrous oksida (nisbah kadar aliran 2/1) keatas substrat kuartza dan wafer silikon pada suhu 250°C. Sampel kemudiannya disepuh-lindap di dalam oksigen ambien pada suhu 100 hingga 600° dengan sela 100 darjah. Mod-mod bengkokan dan regangan Si-O-Si, regangan Si-H dan regangan Si-OH dikenalpasti dari spektra inframerah. Proses sepuh-lindap menghasilkan lebih banyak unit tetrahedra SiO_4 dan menjana juntaian ikatan-ikatan.

(silicon oxide thin films)

The nature of SiO_x ($0 < x < 2$) thin films is much less understood than that of a-Si ($x = 0$) and stoichiometric SiO_2 ($x = 2$) thin films, which are intensively researched for use in the fabrication of microelectronic devices. Silicon oxide films find application in various masking procedures in metal oxide semiconductor (MOS) integrated circuit fabrication technology[1]. The oxide has also been used as tunnelling insulator in the metal-insulator-semiconductor (MIS) tunnel diode[2] and in heterojunction photodiodes for lensless contact-type image sensors[3,4]. SiO_x thin films deposited by evaporation, sputtering and chemical vapour deposition (CVD) techniques[1-9] possess characteristics that are dependent on the magnitude of x[9,10], and are composed of $Si(Si_yO_{4y})$ tetrahedra (y = 0 to 4)[11]. This paper discusses some of the physical properties of SiO_x films deposited by the plasma enhanced CVD (PECVD) of silane and nitrous oxide gases, together with the results on the low temperature annealing of SiO_x in O_2 and N_2 atmospheres.

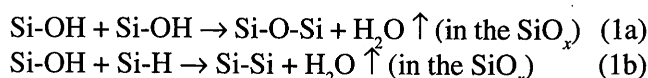
EXPERIMENTAL

The SiO_x thin films were deposited by using the PECVD of SiH_4 and N_2O gases[12]. A dc voltage of 500 V was applied across two parallel electrodes 12 cm apart to generate a plasma discharge that allowed an 8 mA current to flow across the electrodes at a chamber pressure of 0.3 mbar. Two substrates, p-type silicon wafer and quartz slide, both heated to 250 °C were used for the deposition. Samples were thermally annealed in an O_2 ambient in a carbolite furnace at between 100 to 600 °C, at intervals of 100 °C. Each annealed sample was cooled down gradually to room temperature in the presence of O_2 gas. Infrared spectra were recorded on a Perkin Elmer M 1600 FT-IR spectrophotometer. A double beam ratio-recording Shimadzu W-3101 PC UV/VIS/NIR spectrophotometer was used to record UV/VIS spectra in the 300 to 3200 nm range.

RESULTS AND DISCUSSION

The FT-IR transmission spectra of as-prepared and annealed samples showed four major vibrational modes, identified as Si-O-Si bending and stretching, Si-H stretching and Si-OH stretching(Table 1, Fig. 1)[13,14]. The Si-O-Si bending frequency did not change upon varying the annealing temperature, T_a, unlike the case for the Si-O-Si stretching vibration. The latter was shifted from 971 cm^{-1} (for as-prepared) to 981 cm^{-1} (T_a = 600 °C), corresponding to an increase in the value of x from 0.46 to 0.61 (Fig. 2).

The wavenumber increases with annealing temperature for the Si-H and Si-OH stretches (Table 1). For both these stretching modes, the reduction in the absorbance as T_a is increased indicates a fragmented loss of hydrogen as shown in the reactions (1a) through (1d)[15,16]:


$$\text{Si-OH} + \text{Si-OH} \rightarrow \text{Si-O-Si} + H_2O \uparrow \text{ (in the } SiO_x\text{)} \quad (1a)$$

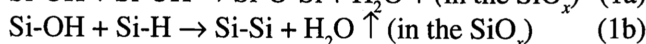
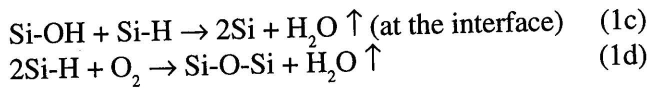

$$\text{Si-OH} + \text{Si-H} \rightarrow \text{Si-Si} + H_2O \uparrow \text{ (in the } SiO_x\text{)} \quad (1b)$$

Table 1. The FTIR vibrational modes of annealed SiO_x samples.

T_a	Si-O-Si bending ν / cm^{-1}	Si-O-Si stretching ν / cm^{-1} (x; SiO_x)	Si-H stretching ν / cm^{-1}	Si-OH stretching ν / cm^{-1}
as-prepared	865	971 (0.46)	2202	3343
100°C	865	971 (0.46)	2203	3343
200°C	865	973 (0.49)	2204	3343
300°C	865	974 (0.50)	2206	3343
400°C	865	975 (0.52)	2213	3366
600°C	865	981 (0.61)	2229	-



$$\text{Si-OH} + \text{Si-H} \rightarrow 2\text{Si} + H_2O \uparrow \text{ (at the interface)} \quad (1c)$$
$$2\text{Si-H} + O_2 \rightarrow \text{Si-O-Si} + H_2O \uparrow \quad (1d)$$

Reaction (la) gives rise to a network structure having tetrahedrally bonded SiO_4[11,17]. In the reaction (1d), the oxygen molecules from the ambient dissociate and react with Si-H to give more SiO_4 tetrahedra. Both reactions enhance the magnitude of x.

In the 200 - 3200 nm region, the transmission spectra of the samples exhibit interference patterns that are used to determine the sample thickness and refractive index $n(\lambda)$[18,19]. The sample thickness, d, is estimated to be about 150 nm and is independent of T_a. At the long wavelength limit where the absorption is negligible and the average transmission T_{av} is about 90%, $n(\lambda)$ is constant at n_o. At the short wavelength limit, $n(\lambda)$ satisfies the Cauchy dispersion relations (equation 1)

$$n(\lambda) = \frac{A}{\lambda^2} + B \quad (1)$$

This equation was used to obtain the value of n in the high absorbing region, below the optical band gap where interference pattern cannot be observed[21]. The absorption coefficient $\alpha(\lambda)$ of the sample is calculated using equation 2:

$$\alpha(\lambda) = \frac{1}{d} \ln\left[\frac{1}{T_{av}(\lambda)} (1-R(\lambda))^2\right] \quad (2)$$

where

$$R(\lambda) = \frac{[n(\lambda)-1]^2}{[n(\lambda)+1]^2}$$

is the reflectivity of the sample.

Structural studies using X-ray powder diffractometry indicate that the annealed and as-prepared samples are amorphous[21]. This finding for $x \sim 0.46$-0.61 is con-

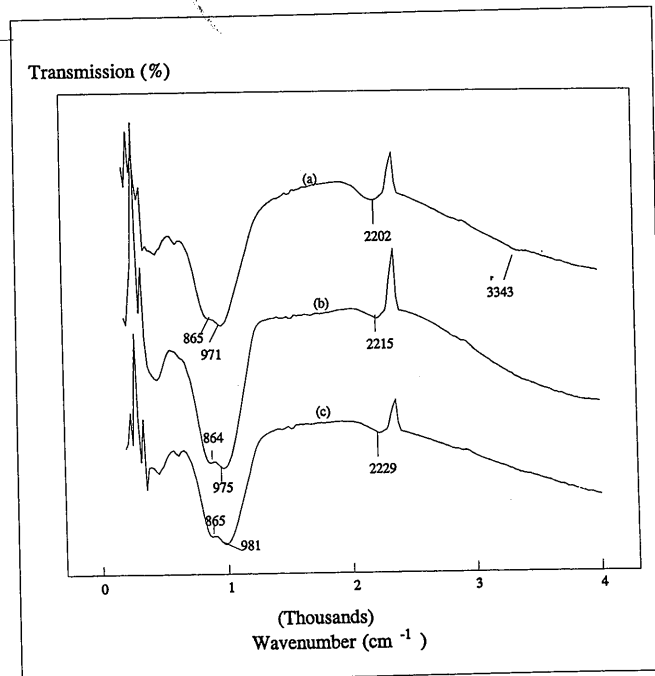


Figure 1. Vibrational modes of FT-IR transmission spectra for as-prepared and annealed SiO_x samples; a) as-prepared, b) 600 °C in N_2 and c) 600 °C in O_2.

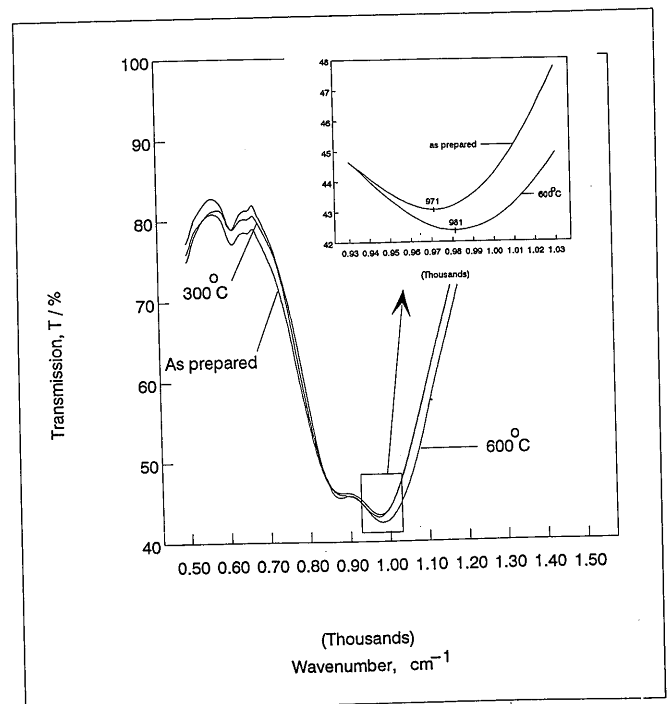


Figure 2. Si-O-Si stretching vibrational mode of the FT-IR transmission spectra for the SiO_x sample annealed in O_2.

sistent with earlier observations[22-24] that SiO_x films with $x > 0.4$ are completely amorphous. The absorption edge of the amorphous film used in this work satisfies the Simple Power Law[25] where for photon energy above 2.8 eV the absorption edge can be described[25-27] by equation 3:

$$\alpha h\nu = C(h\nu - E_T)^2 \qquad (3)$$

where E_T and $h\nu$ are the Tauc energy gap and the photon energy respectively; C is a constant. Figure 3 depicts the Tauc plot of the absorption edge. Below 2.8 eV, the absorption edge obeys the exponential Urbach relation[25-27] (equation 4),

$$\alpha = \alpha_0 \exp[\frac{h\nu}{\Delta E}] \qquad (4)$$

as expected for an amorphous material, where ΔE is the width of electronic band tail that extends into the forbidden gap. The values of E_T and ΔE as well as n_o are tabulated in Table 2.

The decrease in E_T and the concomitant increase in ΔE with T_a arise from two competing processes that take place during the annealing. SiO_4 tetrahedra are created through reactions (1a) and (1d) during annealing which serve to increase the value of E_T. Annealing also generates dangling bonds and this creates localised electronic states that extend into the forbidden energy gap. The extent of these states is measured by the width of the band tail ΔE[25,27]. Here, the creation of the localised states is more dominant than the formation of tetrahedrally bonded SiO_4; this leads to an increase in ΔE but a decrease in E_T with increasing T_a.

The oscillator strength, E_o, the dispersion energy E_d and the plasma energy E_p were estimated[28] from the value of x in SiO_x samples. The values of E_o, E_d and E_p are listed in Table 2. For purposes of comparison, results on the SiO_x samples annealed in nitrogen ambient at 600 °C are also presented in Table 3. The results show that E_T is generally smaller for samples

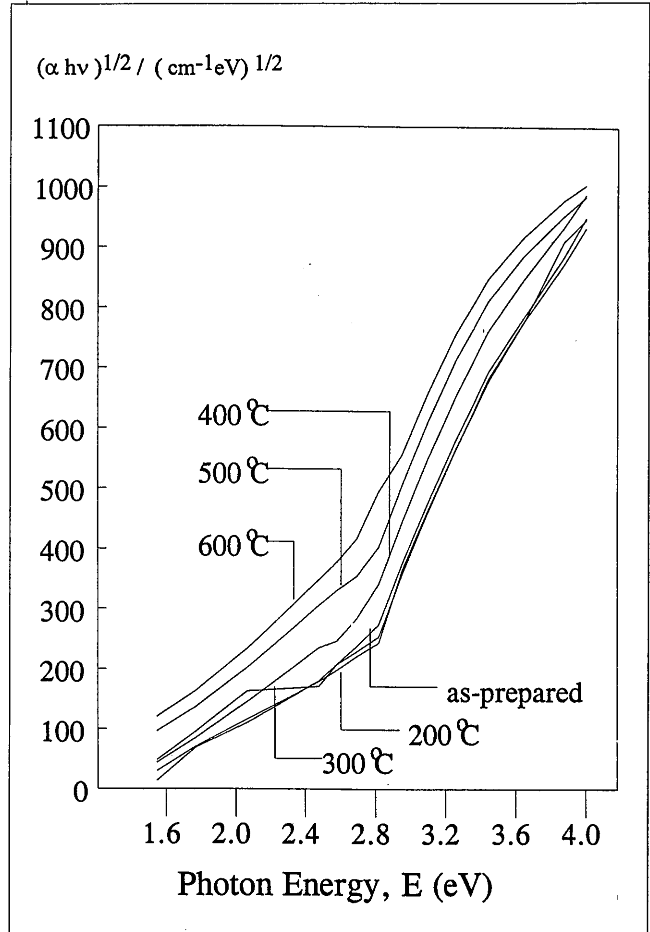


Figure 3. Tauc plot of the absorption edge of SiO_x sample annealed in O_2 ambient.

Table 2. The characteristic energies and refractive index of annealed SiO_x samples.

T_a	E_T / eV	ΔE / eV	n_o	E_o / eV	E_d / eV	E_p / eV
as-prepared	2.43	0.43	1.9	5.9	33.1	14.0
100°C	2.43	0.46	1.9	5.9	33.1	14.0
200°C	2.40	0.44	1.9	6.1	32.7	14.1
300°C	2.41	0.50	1.9	6.1	32.6	14.1
400°C	2.33	0.45	1.9	6.2	32.4	14.2
500°C	2.27	0.55	2.1	6.4	31.9	14.3
600°C	2.11	0.53	2.0	6.6	31.3	14.4

Table 3. Comparison of the vibrational modes, the Tauc gap and the band tail width of SiO_x samples annealed in O_2 and N_2 ambients.

Sample	Si-O-Si stretching (cm^{-1})	Si-H stretching (cm^{-1})	Si-OH stretching (cm^{-1})	E_T (eV)	ΔE (eV)
as-prepared	971	2202	3343	2.43	0.43
T_a = 600 °C (O_2)	981	2229	-	2.11	0.53
T_a = 600 °C (N_2)	975	2215	-	1.92	0.56

annealed in N_2 than for samples annealed in O_2 whereas ΔE is wider for samples annealed in N_2 than for samples annealed in O_2.

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