CHAPTER V

DEPOSITION OF SiO₂ FILMS BY ArF EXCIMER LASER PHOTOLYSIS OF SiH₄ AND N₂O ADMIXTURES
In this chapter, studies on growth of silicon dioxide thin films by ArF pulsed excimer laser induced chemical vapor deposition technique using mixtures of SiH₄ and N₂O are reported. The growth rate dependence on the substrate temperature and the [N₂O]/[SiH₄] flow ratio is investigated. The films have been characterized by infrared transmission, low angle x-ray and spectroscopic ellipsometry techniques.
Integrated electronic and optical devices require the fabrication of many different components, each with its own material and structural requirements, on one chip. To achieve optimum performance of an integrated device, each individual device component must possess the desired set of physical and chemical properties. Silicon oxide is an insulating material that is widely used in a thin film form in present day Si-based microelectronics as passivation layers for integrated circuits [1], interlevel dielectrics [2], and diffusion or photographic mask coatings [3]. Silicon oxide is a key-material for metal-oxide semiconductor (MOS) devices because of its wide band gap and its electronically perfect interface with silicon. Although various forms of silicon oxide exist, the most technologically important form is silicon dioxide, SiO$_2$. It is an excellent insulator (Resistivity $> 10^{16}$ ohm cm), can withstand very large electric fields (dielectric breakdown strength $> 10$ MV/cm), and is chemically very stable. Direct oxidation of the Si surface at elevated temperatures (1000°C) in an oxygen rich environment is the most commonly followed technique for formation of SiO$_2$. Other techniques are chemical vapour deposition by pyrolytic decomposition of SiH$_4$ in an oxygen environment, reactive sputtering etc. For chemical vapor deposition (CVD) of the dielectric material, complete decomposition of reactants require high temperature, usually above 750°C and damages the device functioning by failure of the impurity profile and metal connections in large scale integration. Therefore, there has been considerable activity in search for efficient low temperature techniques for depositing thin dielectric films in semiconductor device fabrication process. Thin film deposition of SiO$_2$ has been reported by plasma enhanced (PE) CVD [4-6], ultraviolet (UV) CVD [7,8] and laser (L) CVD [6-8] techniques. Although (UV) CVD methods using Hg-sensitization have been reported for depositing SiO$_2$ films [12], Hg should be avoided in a system in order to avoid contamination into semiconductor processing. Considerable effort to deposit oxides by remote-PECVD [13-20] and electron
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cyclotron resonance (ECR) has also been made.

Laser assisted chemical vapor deposition (LCVD) can provide another approach to address current material problems facing the integration of electronic devices. By using the LCVD approach, devices with different structural requirements can be deposited selectively and independently on the same substrate, with their locations accurately determined using a laser beam scanner. Since the substrate temperature used in this technique is fairly low, growth only occurs on the area exposed to the laser beam. The low temperature deposition offers advantages such as an abrupt doping profile, reduced interdiffusion between the heterointerfaces, and reduced outdiffusion of impurities from the substrate. Silicon oxide films are deposited from the vapor phase by providing laser energy to initiate and sustain chemical reactions.

In the present work, silicon oxide films are deposited using the ArF excimer laser photolysis for various flow ratios of [N$_2$O]/[SiH$_4$] admixture, at low substrate temperatures of 150-350°C, with slightly focused, perpendicular laser beam irradiation of the substrate. The N$_2$O/SiH$_4$ system give a better spatial confinement of the reaction and a better quality of the films with good refractive index on account of their much lower content of water or hydroxyl group.

V.2 EXPERIMENTAL DETAILS

The reaction chamber and gas manifold was designed and fabricated according to the experimental requirements for laser chemical vapor deposition of silicon dioxide films. The reaction chamber made of stainless steel consists of quartz window at the top for laser irradiation, heater-substrate manipulation arrangement, and 1/4" vessel port for admittance of gaseous reactants. The gas manifold consists of reactant reservoirs connected to electronic mass flow meters (RDM 280, Alphagaz) for SiH$_4$, N$_2$O and argon alongwith common controller (CRDM 280, Alphagaz) and mixing cylinder for homogeneous mixing of reactant gases prior to admittance into the
reaction chamber. Fig. V.1 shows the schematic of laser chemical vapor deposition setup. The gas transport lines are purged with argon before and after the deposition. The reaction chamber and gas transport lines are evacuated by turbo molecular pump (V80, Varian) to a base pressure of 4x10\(^{-5}\) Torr. Laser beam was delivered by ArF (193 nm, 20 ns) excimer laser (Lambda Physik, EMG200) at repetition rate of 10 Hz. The laser fluence of 70 mJcm\(^{-2}\) was realized at the substrate surface with slightly focused laser beam to a dimension of 120x70 mm\(^2\) after considering energy loss in the optical system. Laser beam was introduced perpendicularly through the quartz window to irradiate Si substrate (2x2 cm\(^2\)) in the reaction chamber. The controlled flows of N\(_2\)O and SiH\(_4\) admixture with different flow ratios varying from 20 sccm:3 sccm to 80 sccm:3 sccm alongwith argon as a carrier gas were admitted into the reaction chamber in different experiments. The flow rate of SiH\(_4\) and Ar was held constant at 3 sccm and 10 sccm during all the depositions. Total operating pressure was kept constant at 10 Torr for all depositions in the substrate temperature range of 150-350°C. Growth of SiO\(_2\) films was found in the laser irradiated region of the substrate. The reaction chamber was mounted on computer controlled xy motion table for substrate movement in order to generate extended pattern of the deposited film. The growth of the oxide film was studied in the mentioned substrate temperature and gas flow ratio parameter window.

The deposited oxide thickness was measured with a profilometer and refractive index of the film was determined by optical ellipsometer. The deposited oxide films were characterized by infrared spectroscopy and low angle x-ray diffraction technique.

V.3 RESULTS AND DISCUSSION

V.3.1 FILM GROWTH

The growth rate depends on many parameters, such as the substrate temperature, the nitrous oxide/silane flow ratio, the total pressure, etc. The substrate temperature...
Excimer Laser (LPX 200) ArF (193 nm)

Substrate Manipulator

45° Mirror

L1 L2 L3

Quartz window

To computer x-y translation stage

Fig V.1: Schematic view of the laser chemical vapor deposition setup.
(H: Heater, L1,L2,L3: Lenses, S: Slit)
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dependence of the deposition rate (Arrhenius plot) for laser fluence of 70 mJcm⁻² and repetition rate of 10 Hz was investigated in a substrate temperature range of 150-350°C with [N₂O]/[SiH₄] flow ratio of 40 sccm:3 sccm and total pressure of 10 Torr (Fig. V.2). The [N₂O]/[SiH₄] flow ratio was kept fixed at 40:3 for all temperature variation experiments, which is slightly larger than the optimum value (30:3) for the maximum deposition rate, but allowed a dilution of silane sufficient to keep the total pressure at a large value at the same time avoiding powder formation in the gas phase. In the studied parameter window, the deposition occurred only by irradiation of the excimer laser. No deposition was noticed by the same parameter window without laser irradiation up to 30 minutes. In the given temperature range, high deposition rate of 12 nm/min was obtained at 350°C. An activation energy of 0.055 ev (1.27 kcal/mole) for laser chemical vapor deposition of SiO₂ is estimated from the Arrhenius plot (Fig. V.2) in the studied temperature range. This value is slightly lower than that reported for the Hg photo-sensitized CVD from N₂O/SiH₃ mixtures below 300°C (0.098 ev) [25]. However, it is much smaller than that in the KrF (248 nm) induced CVD (0.18 ev) [11] in a parallel geometry and in the thermal CVD (0.61 ev) [12], both from SiH₄/O₂ mixtures, below 200°C and 300°C, respectively.

The variation of deposition rate of the oxide film with flow ratio of [N₂O]/[SiH₄] (20:3-80:3) with a fixed flow rate of SiH₄ (3 sccm) at the substrate temperature of 250°C is shown in Fig. V.3, for the same values of laser fluence and total pressure. The deposition rate of oxide increases with [N₂O]/[SiH₄] flow ratio and becomes maximum at the flow ratio of 10 and then drops rapidly at higher flow ratio. The decreasing nature of the deposition rate with increasing flow ratio after a maximum of deposition rate is related with the deposition mechanism of the SiO₂ film using N₂O and SiH₄ admixture. For 193 nm light, silane does not have single photon absorption [26], but the photon energy is sufficient for the dissociation into Si and H₂ via two photon absorption scheme [27]:
Fig. V.2: Temperature dependence of the deposition rate (Arrhenius plot) of the SiO$_2$ film. The N$_2$O flow rate: 40 sccm, SiH$_4$ flow rate: 3 sccm, total pressure: 10 Torr, and laser fluence: 70 mJcm$^{-2}$. 

ArF laser (193 nm)  
Laser fluence = 70 mJcm$^{-2}$  
N$_2$O/SiH$_4$ : 40/3  
Total pressure (10 Torr)
ArF laser (193 nm)
Laser fluence = 70 mJcm\(^{-2}\)
\(T_S = 250^\circ C\)
Total pressure (10 Torr)

Fig. V.3: Deposition rate of SiO\(_2\) film as a function of \([N_2O]/[SiH_4]\) flow ratio.
[Total pressure: 10 Torr, Substrate temperature: 250\(^\circ\)C, and laser fluence: 70 mJcm\(^{-2}\).]
Deposition of SiO\textsubscript{2} films.

\[
\text{SiH}_4 + 2\text{hv}(193 \text{ nm}) \rightarrow \text{Si} + 2\text{H}_2
\]

Whereas, nitrous oxide, having a large single photon absorption coefficient for 193 nm, dissociates into an active O(\textsuperscript{1}D) and an inactive N\textsubscript{2} atom:

\[
\text{N}_2\text{O} + \text{hv}(193 \text{ nm}) \rightarrow \text{O}(\textsuperscript{1}D) + \text{N}_2
\]

Thin SiO\textsubscript{2} films are reported to be grown by direct oxidation of silicon by an active O(\textsuperscript{1}D) atoms produced in reaction (B) \cite{28} with thickness limitation by diffusion of oxidation species across the grown film. Growth of thicker oxide films is possible to grow by LCVD from N\textsubscript{2}O and SiH\textsubscript{4} admixtures as compared to direct oxidation process.

The further reaction of O(\textsuperscript{1}D) atoms produced in reaction (B) with N\textsubscript{2}O produces O\textsubscript{2} and NO \cite{29}:

\[
\text{O}(\textsuperscript{1}D) + \text{N}_2\text{O} \rightarrow \text{O}_2 + \text{N}_2
\]

\[
\rightarrow 2\text{NO}
\]

The decrease in the deposition rate observed for [N\textsubscript{2}O]/[SiH\textsubscript{4}] flow ratio of more than 10 is probably due to decrease in O(\textsuperscript{1}D) concentration by secondary reaction (C). Also, lower deposition rate for flow ratio below 10 is probably accounted for low concentration of O(\textsuperscript{1}D) produced in reaction (B). Thus the [N\textsubscript{2}O]/[SiH\textsubscript{4}] flow ratio of 10 appears to maintain species concentration folowing above reaction mechanism which finally results into higher deposition rate. The major possible exit channel for the SiH\textsubscript{4} and O(\textsuperscript{1}D) reaction yields OH and SiH\textsubscript{3} radicals \cite{30}:

\[
\text{O}(\textsuperscript{1}D) + \text{SiH}_4 \rightarrow \text{OH} + \text{SiH}_3
\]

The other reactions among Si, O(\textsuperscript{1}D), O\textsubscript{2}, OH, SiH\textsubscript{3}, N\textsubscript{2}O and SiH\textsubscript{4} form SiO\textsubscript{x}H\textsubscript{y} as an intermediate product in the gas-surface reaction \cite{31,32}:

\[
\text{SiH}_3 + \text{(OH)}_{\text{surface}} \rightarrow \text{(O-Si=H)}_{\text{surface}} + \text{H}_2
\]

\[
\text{OH} + \text{(Si-H)}_{\text{surface}} \rightarrow \text{(Si-O)}_{\text{surface}} + \text{H}_2
\]

\[
\text{OH} + \text{(Si=H)}_{\text{surface}} \rightarrow \text{(O-Si-H)}_{\text{surface}} + \text{H}_2
\]

\[
\rightarrow \text{(Si-OH)}_{\text{surface}} + \text{H}_2
\]

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From intermediate $\mathrm{SiO_xH_y}$, the elimination of $\mathrm{H_2}$ and $\mathrm{H_2O}$ results in $\mathrm{SiO_2}$ formation. In addition to photochemical mechanism, there may be some thermal contribution to $\mathrm{SiO_2}$ growth by ArF irradiation of the surface.

**V.3.2 FILM COMPOSITION**

Silicon oxide shows three prominent IR absorption bands: 1070 cm$^{-1}$ (Si-O stretching), 800 cm$^{-1}$ (O-Si-O bending), and 450 cm$^{-1}$ (Si-O-Si rocking). The frequency, width, and relative intensities of IR spectrum reveal information about stoichiometry and structure of $\mathrm{SiO_2}$ films. Fig. V.4a-4e shows the infrared spectra (in the 200-1400 cm$^{-1}$ spectral window) of oxide films deposited at substrate temperatures of 150 to 350°C in steps of 50°C, respectively, for $[\mathrm{N_2O}]/[\mathrm{SiH_4}]$ flow ratio of 40:3 and total pressure of 10 Torr. Three characteristic absorption peaks due to $\mathrm{SiO_2}$ films are identified at the mentioned positions in all the spectra (Fig. V.4a-4e). The band due to the stretching of OH bonds in silanol groups and adsorbed water molecules (3200-3600 cm$^{-1}$) are not noticed in $[\mathrm{N_2O}]/[\mathrm{SiH_4}]$ case for actual sample scan in the range of 4000-200 cm$^{-1}$, which otherwise is observed for the $\mathrm{SiH_4/O_2}$ system [8]. The bandwidth of the Si-O stretching band (1070 cm$^{-1}$) is found to decrease with an increase in the substrate temperature. The bandwidth varies from $\sim$150 cm$^{-1}$ to $\sim$100 cm$^{-1}$ for the studied temperature range. The broadening of the Si-O stretching band of $\mathrm{SiO_2}$ films is more than that of the thermally grown $\mathrm{SiO_2}$ film ($\sim$80 cm$^{-1}$) [31]. Earlier [32], it has been proved that the Si-O stretching frequency in $\mathrm{SiO_x}$ is linearly related to the oxygen concentration x, whereas the bandwidth is mainly determined by O-Si-O bond angle variation. Thus, the IR data can be interpreted in the following way. The LCVD $\mathrm{SiO_2}$ films are stoichiometric within the accuracy of the measurements and show no oxygen deficiency. On the other hand, the broadening of the band shows an additional degree of structural disorder such as variation in bond angle with lowering of substrate temperature. The bandwidth variation [(a) 160 cm$^{-1}$, (b) 140 cm$^{-1}$] of the Si-O stretching band with $[\mathrm{N_2O}]/[\mathrm{SiH_4}]$ flow variation from (a) 20:3 to (b) 80:3,
IR spectra of SiO$_2$ films deposited at substrate temperatures of (a) 150°C, (b) 200°C, (c) 250°C, (d) 300°C, and (e) 350°C. The [N$_2$O]/[SiH$_4$] flow ratio is 40:3 at constant total pressure of 10 Torr and laser fluence of 70 mJcm$^{-2}$. 

Fig. V.4
respectively at substrate temperature of 250°C is observed as shown in Fig. V.5. This implies that, flow ratio variation away from 10 [Fig. V.4(c), 120 cm⁻¹] results in higher degree of disorder.

Fig. V.6 shows low angle x-ary diffraction pattern of the LCVD SiO₂ films deposited at substrate temperatures of 350, 250, and 150°C and a constant flow ratio of 40:3 at 10 Torr total pressure. In addition to SiO₂, some degree of SiO formation is also found to be present in the film as seen in x-ray data. However, at 150°C, the SiO₂ₓ is present. From the x-ray measurements of LCVD SiO₂ films obtained at different flow ratios [(a) 80:3, (b) 20:3] at substrate temperature of 250°C (Fig. V.7) it can be inferred that the oxide films appear to be amorphous in nature.

V.3.3 REFRACTIVE INDEX

Fig. V.8 shows the dependence of refractive index on the [N₂O]/[SiH₄] flow ratio for LCVD SiO₂ films at constant substrate temperature of 250°C. The refractive index decreases from 1.50 to 1.47 with increase in the flow ratio from 20:3 to 40:3 and then again increases to 1.55 with further increase in the flow to 80:3. The known refractive index values for Si, SiO and SiO₂ are 3.87, 2.0 and 1.47, respectively. The refractive index of the film deposited for [N₂O]/[SiH₄] flow ratio of 40:3 coincides with that of SiO₂. For flow ratio of 30:3, the refractive index of the film is 1.46 which less than the value for SiO₂, which indicates the formation of either porous film or film having comparatively large free volume. The higher refractive indices for other flow ratios are probably due to excess silicon in the deposited film. Fig. V.9 shows variation of refractive index and thickness of the SiO₂ film with photon energy for one chosen parameters set [250°C, 60 sccm:3 sccm, 10 Torr]. The refractive index and thickness of the film are seen to be almost constant in the energy range of 2.3-3 ev.
Fig. V.5: IR absorption spectra of SiO$_2$ films deposited at different [N$_2$O]/[SiH$_4$] flow ratios of (a) 20:3 and (b) 80:3. The substrate temperature: 250°C, total pressure: 10 Torr, and laser fluence: 70 mJcm$^2$. 

TRANSMITTANCE [arb. unit] 

WAVELENGTH [cm$^{-1}$]
Fig. V.6: Low angle x-ray diffraction spectra of SiO$_2$ films deposited at substrate temperatures of (a) 350°C, (b) 250°C, and (c) 150°C with constant [N$_2$O]/[SiH$_4$] flow ratio of 40:3, the total pressure of 10 Torr, and laser fluence of 70 mJcm$^{-2}$. 

![X-ray Diffraction Spectra](image-url)
Fig. V.7: Low angle x-ray diffraction spectra of SiO$_2$ films deposited at different [N$_2$O]/[SiH$_4$] flow ratios of (a) 80:3, and (b) 20:3 with constant substrate temperature of 250°C, the total pressure of 10 Torr, and laser fluence of 70 mJcm$^{-2}$. 
Fig. V.8: Refractive index of the deposited SiO$_2$ film as a function of [N$_2$O]/[SiH$_4$] flow ratio. The total pressure: 10 Torr, substrate temperature: 250$^\circ$C, and laser fluence: 70 mJcm$^{-2}$. 

Laser fluence = 70 mJcm$^{-2}$
Substrate temperature (250$^\circ$C)
Total pressure (10 Torr)
Fig V.9: Variation of the refractive index and thickness of the SiO₂ film [at substrate temperature: 250°C, \([\text{N}_2\text{O}]/[\text{SiH}_4]\) flow ratio: 60/3, total pressure: 10 Torr, and laser fluence: 70 mJ/cm²] with photon energy as obtained from ellipsometry data.
V.4 CONCLUSION

The films of SiO$_2$ have been deposited by ArF (193 nm) induced photolysis of SiH$_4$ and N$_2$O admixtures at substrate temperatures of 150-350°C. The deposition rate is influenced by substrate temperature and [N$_2$O]/[SiH$_4$] flow ratio. The activation energy of LCVD SiO$_2$ film is estimated to be 0.055 eV (1.27 kcal/mole) in the investigated temperature range. The maximum deposition rate of 22.2 nm/min is obtained for flow ratio of 10 at substrate temperature of 250°C. The broadening of the Si-O stretching band is influenced by the substrate temperature and nitrous oxide/silane flow ratio. The refractive index of the oxide film is found to be 1.47 for flow ratio of 40:3 at 250°C.
V.5 REFERENCES


