

Deposition of SiO₂ in a SiH₄/O₂ inductively coupled plasma

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Abstract. Plasma enhanced chemical vapour deposition (PECVD) process in a SiH₄/O₂ inductively coupled plasma (ICP) is studied in this paper. The detailed chemical reactions in plasma and surface reactions on the wafer are included in the simulation using finite element method (FEM), so that the formation of bulk species of SiO₂ is examined. The study is performed for 10% SiH₄/90% O₂ gas mixtures operating at the rf frequency of 13.56 MHz and the total gas pressure of 25 mTorr with the variation of gas flow rate from 20 to 500 sccm. The gas temperature is 300 K and the input power is 700 W. It is found that the deposition rate near the rim of wafer is much lower than that in the centre. The deposited film thickness near the rim of wafer is 70% of that in the centre after the discharge of 0.2 sec. The study shows that the oxygen atom density, which directly contributes to the deposition of SiO₂, decreases when the gas flow rate increases. The deposition rate on the wafer is reduced by around one order and the deposited film thickness is reduced to 12% of the original when the gas flow rate is increased from 20 to 500 sccm.

1. Introduction

High density plasma deposition of silicon dioxide (SiO₂) is an important process in integrated circuit manufacturing [1-3]. To deposit SiO₂ on the wafer, typically a SiH₄/O₂ or SiH₄/N₂O mixture is applied [4]. SiH₄ is the precursor gas, while an oxidizing agent (e.g., O₂) is added to grow a SiO₂ film. SiO₂ can be deposited on the wafer at low temperatures of 100-300°C, using PECVD [1]. Low-pressure SiH₄/O₂ reaction in chemical vapour deposition (CVD) has been found to be a fast gas phase reaction. However, the hydroxyl reaction products could be imbedded into the growing oxide and lead to low-quality electrical properties of the film. PECVD holds the potential to overcome the limitation by the selective excitation of gas phase species to control reaction pathways [2]. The numerical study of PECVD in SiH₄/O₂ mixtures would provide us direct insights into the correlation between the deposition of films and the reaction of gas phase species.

Plasma conditions determine the film properties such as the dielectric constant and stress which in turn affect the device performance and reliability. Although many experimental researches have been carried out, model investigations are still limited to the estimation of fluxes of precursor species to the wafer and deposition rates [4,5] due to the lack of detailed data for all the surface reactions on the wafer. Recently, the investigation of SiH₄/O₂/Ar inductively coupled plasmas used for the filling of microtrenches in shallow trench isolation (STI) was reported [6], in which the plasma chemistry of SiH₄/O₂/Ar discharges as well as surface processes such as deposition were presented. An extra analytical module was used to predict changes in the composition of the surface layers.

The gas flow rate, used as an operating parameter for experiments in plasmas, has been found to affect the plasma properties in N₂/H₂/Ar and Ar/N₂ inductively coupled plasma (ICP) reactors [7-9]. It



has been indicated that electron density increases and electron temperature decreases with a rise in gas flow rate for the different Ar fractions in Ar/N₂ discharges. However, the effect of gas flow rate on surface reactions such as deposition is still not clear.

In order to estimate the deposited film thickness, the discharge time considered for PECVD will be longer than that commonly used for plasma simulation, *e.g.*, 1~10 msec. It is known that although for the regime of operation a kinetic description based on the particle scheme can provide accurate electron energy distribution, the fluid approximation can be applicable in low pressure plasma discharges [6,9]. It is noted that the calculation time can be dramatically reduced using fluid models. In this work, COMSOL Multiphysics, a finite element analysis simulation software, is used to combine the surface reactions on the wafer with the chemical reactions occurred in plasma so as to estimate the formation of bulk species of SiO₂ in a SiH₄/O₂ PECVD. The deposition rate and deposited film thickness of SiO₂ are obtained. The effect of gas flow rate on plasma properties as well as deposition of SiO₂ is investigated.

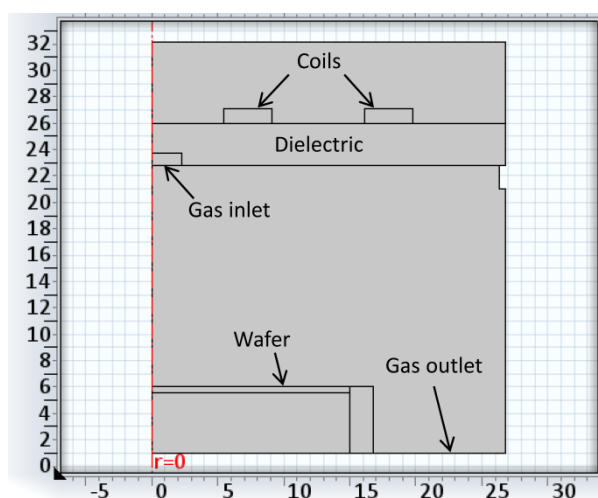


Figure 1. Model geometry of PECVD.

2. Description of the model

Figure 1 shows a model geometry used in this work, which has been described in the earlier publication [10]. The calculations are performed for the case of 10% SiH₄/90% O₂ PECVD operating at the rf frequency of 13.56 MHz and the total gas pressure of 25 mTorr. The gas temperature is assumed to be 300 K and the input power is 700 W. The gas flow rate is varied from 20 to 500 sccm.

The species taken into account include electrons, neutrals (O₂, O₂^{*}, O, O^{*}, H₂, H, H₂O, OH, SiH₂, SiH₃, SiH₄, SiHO, SiH₂O, SiH₃O, SiO, SiO₂), ions (O₂⁺, H₂⁺, SiH₂⁺, SiH₃⁺, O⁺, SiH₂⁺, SiH₃⁺), as well as surface species (Si(s), SiH(s), SiH₂(s), SiH₃(s), SiO(s), SiHO(s), SiH₂O(s), SiH₃O(s), SiO₂(b)). 88 types of chemical reactions occurred in plasma and 29 types of surface reactions appeared on the wafer are taken into account. The electron impact cross-section data and chemical reaction rates for the above-described reactions are taken from the published literature [1,5,6]. The basic equations for the plasma simulation used in this research include a pair of drift diffusion equations for the electrons, a modified Maxwell-Stefan equation for the ion and neutral species, a Poisson's equation for the space charge electric field, and an electromagnetic field equation for the induced electric field. In this work, the plasma simulations are coupled with the fluid equations, which include the continuity equation and momentum equation. The detailed information for the plasma simulation can be found in our previous work [8,9].

In this work, the surface reactions on the wafer are calculated to obtain the deposition rate and deposited film thickness, which are combined with the above-described plasma simulation. The surface rate expression for species *k* is defined as

$$R_k = \sum_{i=1}^I \nu_{ki} q_i \quad (1)$$

where $\nu_{ki} = \nu_{ki}^r - \nu_{ki}^f$ is the stoichiometric coefficient, f and r mean the forward and reverse reaction, respectively, I is the number of surface reactions, q_i is the rate of the i th reaction governed by the law of mass action

$$q_i = k_{f,i} \prod_{k=1}^K c_k^{\nu_{ki}^f} - k_{r,i} \prod_{k=1}^K c_k^{\nu_{ki}^r} \quad (2)$$

where K is the number of chemical species, c_k is the concentration of the k th species, $k_{f,i}$ and $k_{r,i}$ are the rate coefficients for the i th forward and reverse reactions, respectively. The rate coefficient $k_{f,i}$ is related to the sticking coefficient γ_i via the Motz-Wise correction [11]

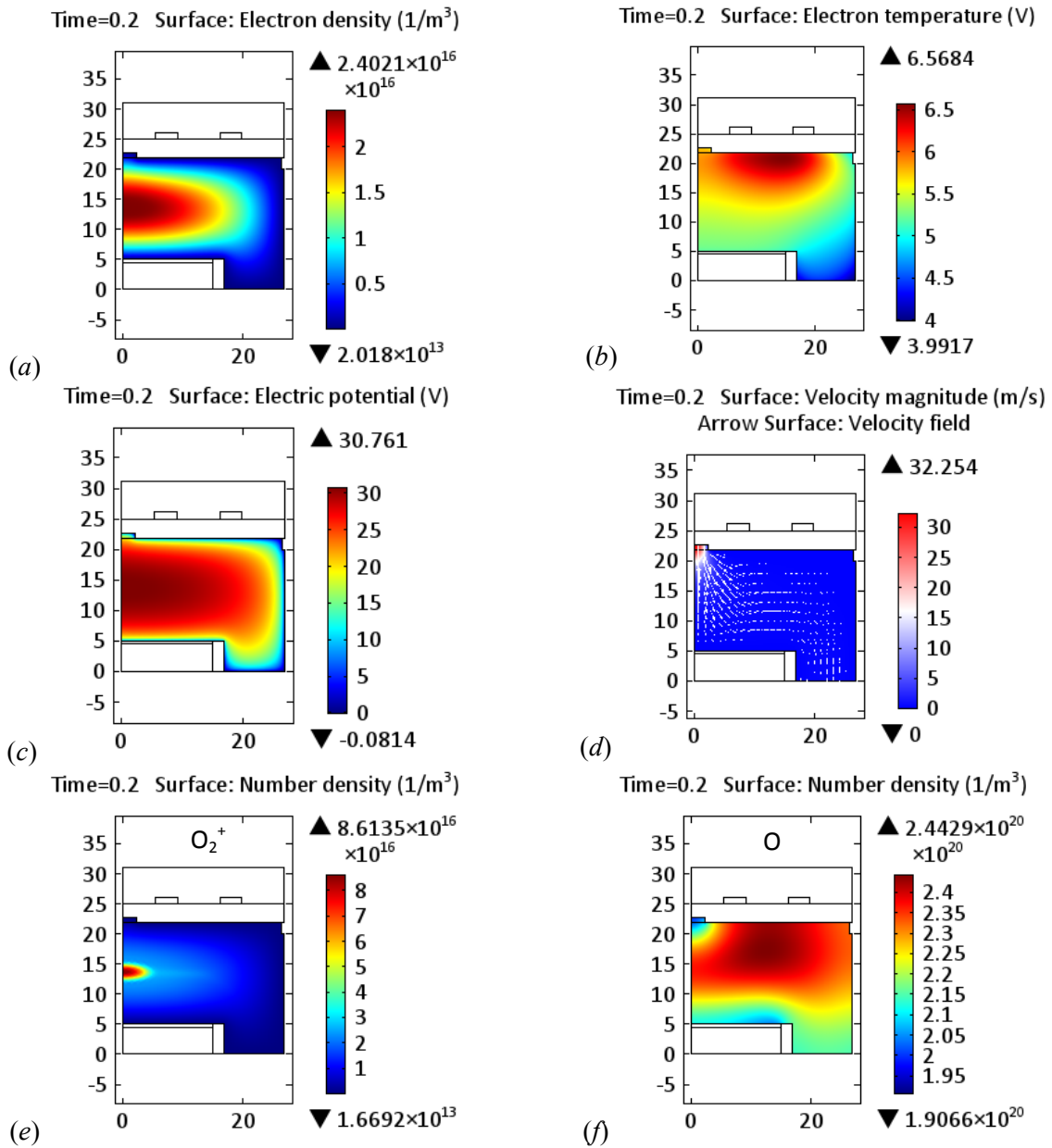


Figure 2. Discharge structure in a 10% SiH₄/90% O₂ ICP plasma ($p = 25$ mTorr, $P = 700$ W, $T = 300$ K, $Q = 50$ sccm, $t = 0.2$ sec). (a) Electron density, (b) Electron temperature, (c) Electric potential, (d) Fluid field, (e) Oxygen ion: O_2^+ density and (f) Oxygen atom density.

$$k_{f,i} = \left(\frac{\gamma_i}{1 - \gamma_i/2} \right) \frac{1}{(\Gamma_{tot})^m} \left(\frac{1}{4} \right) \sqrt{\frac{8RT}{\pi M_n}} \quad (3)$$

where Γ_{tot} is the total surface site concentration, m is the sum of all of the surface species' stoichiometric coefficients, M_n is the mean molecular weight, R is the universal gas constant, T is the temperature.

For the bulk surface species, the following equation is solved to obtain the deposited film thickness h_k

$$\frac{dh_k}{dt} = - \frac{R_k M_k}{\rho_k} \quad (4)$$

where M_k is the molecular weight, and ρ_k is the density of the bulk species.

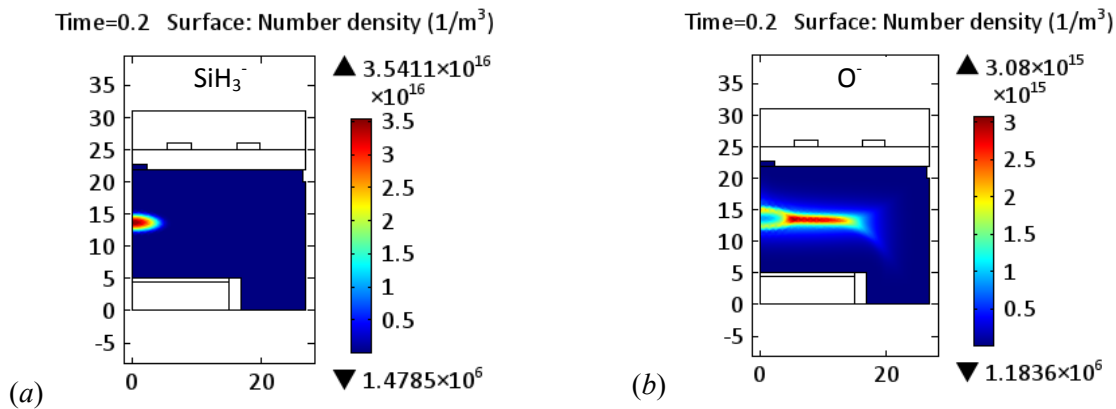


Figure 3. Negative ion density in a 10% SiH₄/90% O₂ ICP plasma ($p = 25$ mTorr, $P = 700$ W, $T = 300$ K, $Q = 50$ sccm, $t = 0.2$ sec). (a) SiH₃⁻ ion and (b) O⁻ ion.

3. Results and discussion

Figure 2 shows the calculated results for a 10% SiH₄/90 %O₂ PECVD at a gas flow rate of 50 sccm. The maximum density of electron arrives at $2.40 \times 10^{16} \text{ m}^{-3}$ and the electron temperature is in a range from 3.99 to 6.57 eV with the low electron temperature near the outlet of gas flow and the high electron temperature beneath the coil domain. The fast gas flow appears around the inlet of the gas flow and the maximum velocity reaches $32.25 \text{ m} \cdot \text{s}^{-1}$. The governing ion is O₂⁺, being concentrated in the centre of the reactor. It is known that O may react with SiO(s) on the wafer to form the bulk species of SiO₂. Figure 2 (f) shows that the density of O spreads from the high electron temperature area, which could be deduced due to electron impact collisions with O₂ in the area.

Since both SiH₄ and O₂ are electronegative gases, the plasma considered in this research is electronegative. In electronegative discharges, the negative ions occurred in discharges are held in the core of the plasma, where they can acquire energy from the high frequency electromagnetic field. The calculations show that SiH₃⁻ and SiH₂⁻ possess a similar distribution. Thus in this paper, only SiH₃⁻ and O⁻ ion densities are shown in figure 3. The densities of SiH₃⁻ and SiH₂⁻ are so high in the core of plasma that O⁻ ions are excluded from the area with high densities of SiH₃⁻ and SiH₂⁻. It should be noted that the maximum densities of SiH₃⁻ and SiH₂⁻ have reached $3.54 \times 10^{16} \text{ m}^{-3}$ and $2.62 \times 10^{16} \text{ m}^{-3}$, respectively, both being higher than electron density.

The distributions of surface species on the wafer are shown in figures 4 (a) and (b). The governing surface species is SiO. The concentration of SiO is found to be over one order of magnitude higher than the others, which is consistent with the previous research of Tinck and Bogaerts [6]. The obtained deposition rate and deposited film thickness are given in figures 4 (c) and (d). The deposition rate near

the rim of wafer is 55% of that in the centre. As a result, the deposited film thickness near the rim of wafer is 70% of that in the centre.

Results of the effect of gas flow rate on SiO₂ deposition are shown in figures 5 and 6. The density of O shows a decreasing tendency when the gas flow rate is increased. The decrement of O could be considered as a major factor to cause the reduction of deposition rate and deposited film thickness. The surface reaction of O to form SiO₂ can be simplified as [11]



where SiO(s) is the surface species of SiO on the wafer and SiO₂(b) is the bulk species of SiO₂. As seen in figure 6, the deposition rate is reduced by nearly one order when the gas flow rate is increased from 20 to 500 sccm and the deposited film thickness is reduced to 12% of the original.

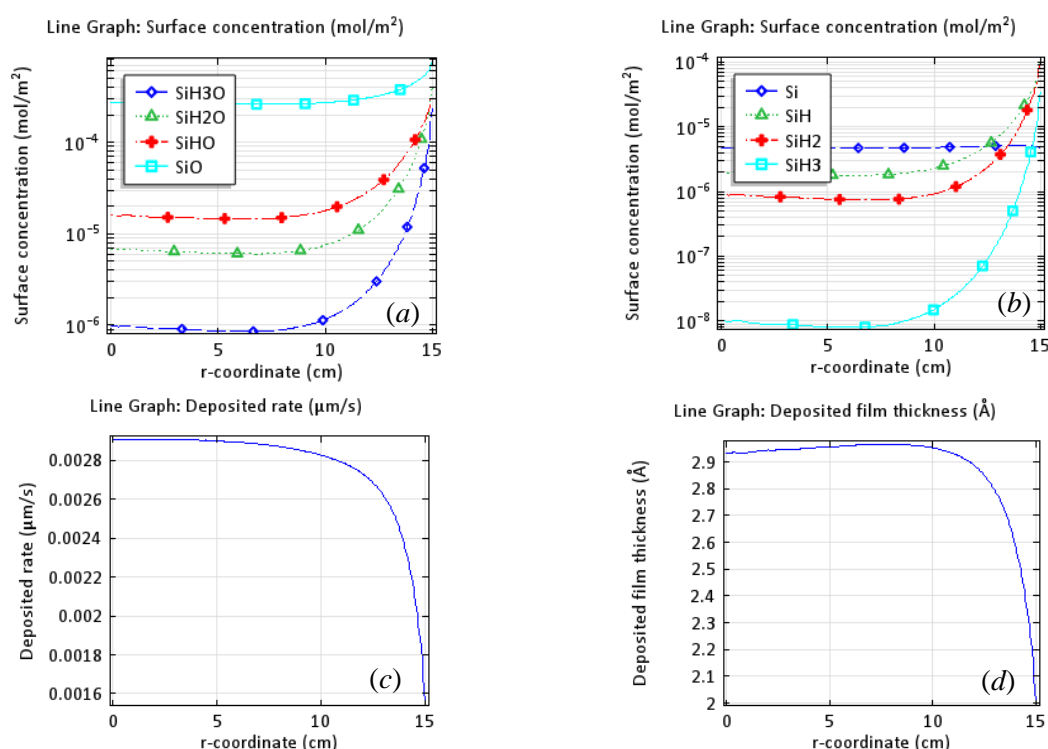


Figure 4. Concentration of surface species, deposition rate and deposited film thickness on the wafer in a 10% SiH₄/90% O₂ ICP plasma ($p = 25$ mTorr, $P = 700$ W, $T = 300$ K, $Q = 50$ sccm, $t = 0.2$ sec). (a) and (b) Concentration of surface species, (c) Deposition rate and (d) Deposited film thickness.

4. Conclusion

In this work, the deposition of SiO₂ in a SiH₄/O₂ inductively coupled plasma was investigated at the gas flow rates of 20-500 sccm. The spatiotemporal distributions of plasma species in plasma as well as on wafer surface were obtained. It was found that the deposition rate and deposited film thickness near the rim of wafer were much lower than those in the centre.

The effect of gas flow rate on SiO₂ deposition was presented. The increase of gas flow rate caused the reduction of oxygen atom density. The deposition rate on the wafer is reduced by around one order and the deposited film thickness is reduced to 12% of the original when the gas flow rate is increased from 20 to 500 sccm. The obtained results provide insight on the gas flow control in the PECVD process, which could be used to improve industrial applications.

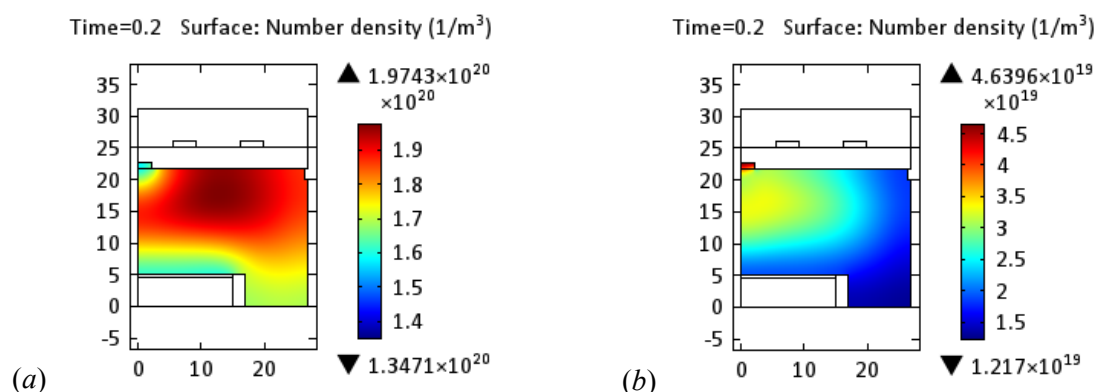


Figure 5. Oxygen atom density at the gas flow rates of (a) 100 sccm and (b) 500 sccm in a 10% SiH₄/90% O₂ ICP plasma ($p = 25$ mTorr, $P = 700$ W, $T = 300$ K, $t = 0.2$ sec).

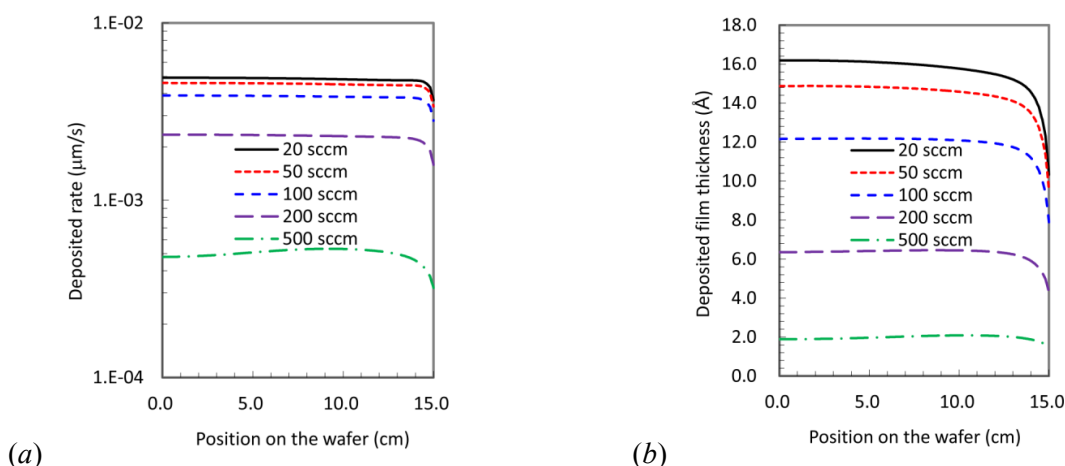


Figure 6. Deposition rate and deposited film thickness on the wafer in a 10% SiH₄/90% O₂ ICP plasma after $t = 0.5$ sec ($p = 25$ mTorr, $P = 700$ W, $T = 300$ K).

5. References

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