

Influence of Small Amounts of Oxygen on Xenon Resonance Lamp Photo-CVD

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This paper reports the influence of small amounts of oxygen on the deposition of silicon films when xenon resonance lamp photo-CVD using monosilane diluted with krypton and xenon is employed. When monosilane diluted with krypton was used, photo-excited oxygen molecules dissociated to oxygen atoms, which react with monosilane molecules to form SiOx. Monosilane diluted with xenon leads to deposition of silicon films along with the SiOx formation. Therefore, xenon photo-sensitization realizes oxygen-free, mercury-free silicon films.

1. INTRODUCTION

Photo chemical vapor deposition (photo-CVD) has been the subject of several investigations into its potential for use as a low-temperature, damage-free and low-contamination process technology for the fabrication of ULSIs¹⁾. In such photo-assisted processes, ultraviolet light having wavelengths below 300nm has been extensively used to achieve photo-excitation of the reactant gases¹⁾.

Most of the experiments regarding deposition of silicon layers from monosilane use mercury photo-sensitized reaction²⁾. In this case, mercury contamination should influence the film properties as well as destruct the environment. Therefore, direct photo-excitation technology of monosilane needs to be developed which requires less than a 150nm wavelength V.U.V light where the absorption cross-section of monosilane increases up to 10^{-17} cm^2 ³⁾. However, apparent oxygen contamination of the photo-CVD films has been observed²⁾. This is due to photo-excitation of oxygen which remains in the reaction chamber, because oxygen molecules have almost the same absorption cross-section as monosilane molecules below the 150nm wavelength⁴⁾.

The present paper describes the influence of small amounts of oxygen on photo-CVD silicon film deposition by monosilane decomposition using a xenon resonance lamp ($\lambda=147\text{nm}$). Photo-CVD films were deposited under conditions of intentional

oxygen leakage. Oxygen content and deposition rate dependences on the oxygen leakage rate were examined. Based on the experimental results, an oxygen incorporation mechanism was discussed. A look was also taken at the effect of xenon photo-sensitization on the deposition of silicon films, which should enable oxygen-free, mercury-free silicon film deposition.

2. EXPERIMENTAL PROCEDURES

The experimental apparatus is schematically shown in Fig. 1. A xenon resonance lamp was directly mounted in a reaction chamber to make it possible to avoid absorption of V.U.V. light in the atmosphere. Ten-percent monosilane diluted with krypton ($\text{SiH}_4(\text{Kr})$) or with xenon ($\text{SiH}_4(\text{Xe})$) were used as source gases. The monosilane partial pressure was kept constant at 5.3Pa. Silicon wafers were kept at room temperature and vertically irradiated with V.U.V light. A variable leakage valve was employed to let small amounts of oxygen into the chamber. The oxygen leakage rate, Q_L ($\text{Pa m}^3/\text{sec}$), was controlled by the variable leakage valve to keep it at a certain value between 10^{-5} and $10^{-3} \text{ Pa m}^3/\text{sec}$. Under these experimental conditions, oxygen partial pressure was less than 10^{-1} Pa .

Deposited film compositions were analyzed by Auger electron spectroscopy and infra-red absorption spectroscopy. All Auger spectra were measured after sputter-cleaned the possible

natural oxide layers by about 10nm with 3.5-keV argon ions. Oxygen content in the films was represented by the peak-to-peak intensity of the oxygen Auger spectra (520eV). Concentrations of Si-O bonds in those films were measured by infra-red absorption spectra (1060cm^{-1}). The deposited film thickness was measured with a Dek-Tak, with an accuracy of about 1%.

3. RESULTS

Fig. 2 shows Auger electron spectra of photo-CVD films deposited under the same oxygen leakage rates, compared with that of thermal silicon dioxide film. Oxygen Auger intensity of photo-CVD film from $\text{SiH}_4(\text{Kr})$ is weaker than that of thermal silicon dioxide film, but stronger than that of film deposited from $\text{SiH}_4(\text{Xe})$. These results were ascertained by infra-red absorption spectroscopy, as shown in Fig. 3. Both types of photo-CVD films indicate that oxygen atoms were taken into photo-CVD films in the form of Si-O bonds.

Oxygen leakage rate dependence of Si-O absorption coefficient is shown in Fig. 4. Absorption coefficients of films obtained from $\text{SiH}_4(\text{Kr})$ were independent of the oxygen leakage rate, and were about 50% of those of thermal silicon dioxide as shown by open circles in Fig. 4. Therefore, resultant films were composed of SiO_x .

On the other hand, the infra-red absorption spectra of films deposited from $\text{SiH}_4(\text{Xe})$ indicate that Si-O absorption coefficients were smaller than those for $\text{SiH}_4(\text{Kr})$. In addition, absorption coefficients increased with the oxygen leakage rate as shown by solid circles in Fig. 4.

Oxygen leakage rate dependence of the deposition rates are depicted in Fig. 5. When $\text{SiH}_4(\text{Kr})$ was used as a reactant gas, film formation was observed only under intentional oxygen leakage conditions. The deposition rate was proportional to the square root of the oxygen leakage rate. On the other hand, in the case of $\text{SiH}_4(\text{Xe})$, film formation could be seen without intentional oxygen leakage. The deposition rate was also dependent on the oxygen leakage rate, though higher than for $\text{SiH}_4(\text{Kr})$.

4. DISCUSSION

Photo-CVD films deposited from $\text{SiH}_4(\text{Kr})$ were in almost all cases SiO_x , regardless of the oxygen leakage rate. The deposition rate, $R(\text{Kr})_{\text{depo}}$ (nm/min), was proportional to the square root of the oxygen leakage rate, Q_L , that is to the square root of the oxygen partial pressure P_{O_2} (Pa).

$$R(\text{Kr})_{\text{depo}} = A_1 Q_L^{1/2} \quad (\text{nm/min}) \quad (1)$$

On the other hand, in the case of films deposited from $\text{SiH}_4(\text{Xe})$, the deposition rate was higher than that of $\text{SiH}_4(\text{Kr})$. Therefore, the deposition rate, $R(\text{Xe})_{\text{depo}}$, can be expressed as a summation of constant term, R_{Xe} , and oxygen partial pressure dependent term, $A_2 Q_L^{1/2}$. That is,

$$R(\text{Xe})_{\text{depo}} = R_{\text{Xe}} + A_2 Q_L^{1/2} \quad (\text{nm/min}) \quad (2)$$

Comparing Eqs.(1) and (2), following film deposition mechanism can be derived.

- (1) The constant term, R_{Xe} , represents xenon photo-sensitization effect.
- (2) The oxygen partial pressure dependent term, $A_2 Q_L^{1/2}$ represent oxygen photo-excitation effect.

Constants A_1 in Eq.(1) and A_2 in eq.(2) were determined from experimental results shown in Fig. 5 as,

$$A_1 = A_2 = 2.1 \times 10^2 \quad (3)$$

Therefore, the same oxygen photo-excitation mechanism contributes both in the case of film deposition from $\text{SiH}_4(\text{Kr})$ and $\text{SiH}_4(\text{Xe})$. In other words, oxygen molecules are excited by the light to form SiO_x layer.

The constant term, R_{Xe} , was also determined to be

$$R_{\text{Xe}} = 1.4 \quad (\text{nm/min}) \quad (4)$$

Therefore, oxygen-free, mercury-free silicon film deposition is made possible by xenon photo-sensitization, although about one order of magnitude slower than by mercury photo-sensitization. Solid lines in Fig. 5 indicate the oxygen leakage rate dependences of deposition rate calculated from Eqs.(1) and (2).

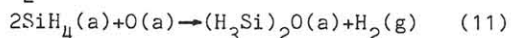
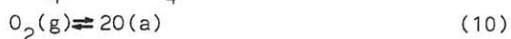
The Si-O absorption coefficient, $\alpha_{\text{Si-O}} (\text{cm}^{-1})$, can also be expressed as follows:

$$\alpha_{\text{Si-O}} = \frac{k A_2 Q_L^{1/2}}{R_{\text{Xe}} + A_2 Q_L^{1/2}} \quad (\text{cm}^{-1}) \quad (8)$$

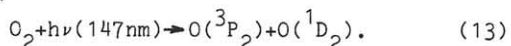
The solid line in Fig. 4 is calculated from

Eq.(8), where $k=2.3 \times 10^4 (\text{cm}^{-1})$, which is almost the same as the absorption coefficient of the film deposited from $\text{SiH}_4(\text{Kr})$. These results also ascertained the above mentioned mechanism.

The film deposition mechanism of the oxygen leakage rate dependent term can be expressed by a similar mechanism with thermal CVD, in which square root dependence was successfully explained as follows⁵⁾. One adsorbed oxygen atom, which is formed by the thermal decomposition of oxygen molecule, reacts with two adsorbed monosilane molecules at the silicon surface, such that



In the present experiment, the oxygen molecule photo-dissociates to oxygen atoms as in place of Eq.(10)⁶⁾,



Therefore, silicon dioxide films were deposited mainly through a reaction between monosilane

molecules and oxygen atoms which were formed by means of photo-dissociation of oxygen molecules.

5.CONCLUSION

In summary, this paper has shown that: (1)photo-dissociated oxygen reacts with monosilane, and SiO_x film is formed, and (2)xenon photo-sensitized deposition of silicon film was observed that could enable oxygen-free, mercury-free silicon film deposition.

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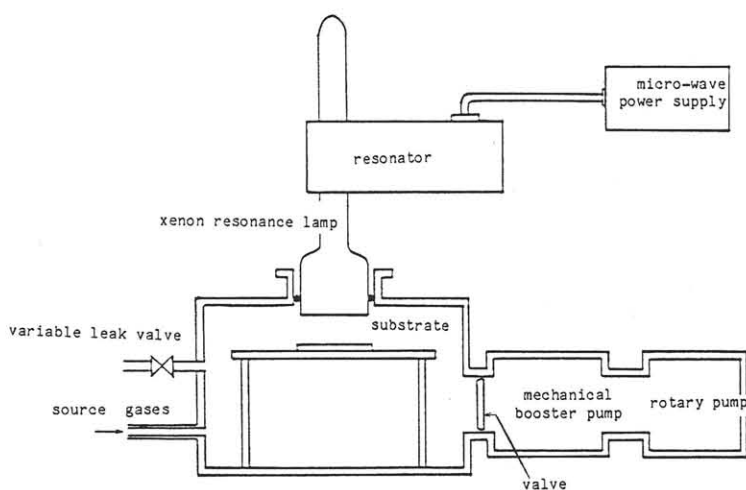


Fig. 1 Experimental Apparatus

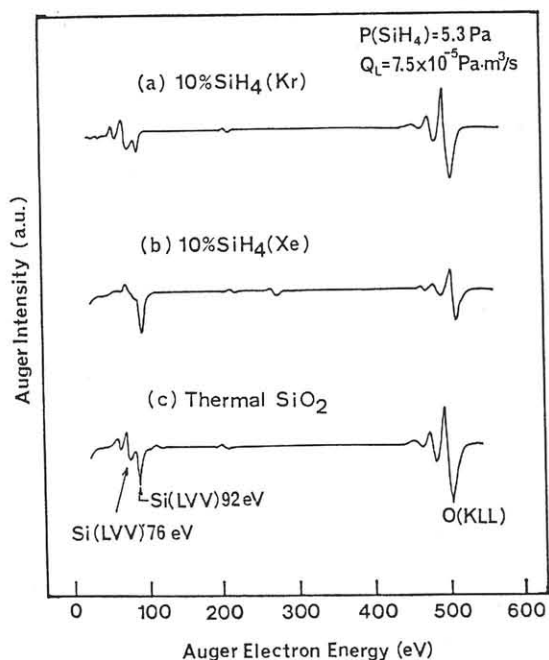


Fig. 2 Auger Electron Spectra of Photo-CVD Films

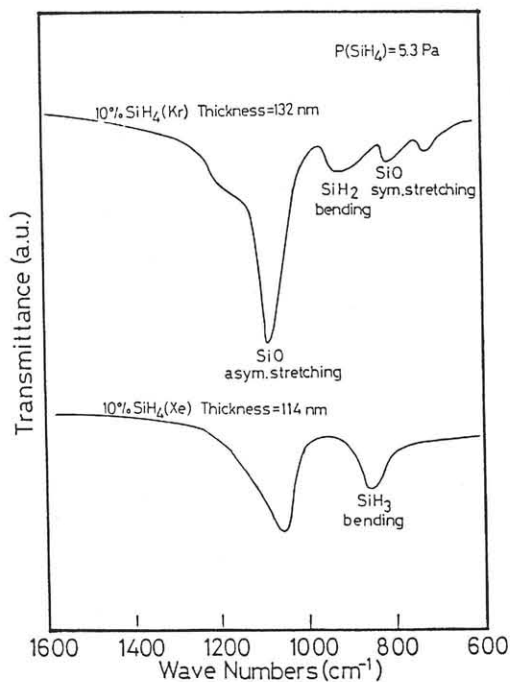


Fig. 3 Infra-red Absorption Spectra of Photo-CVD Films

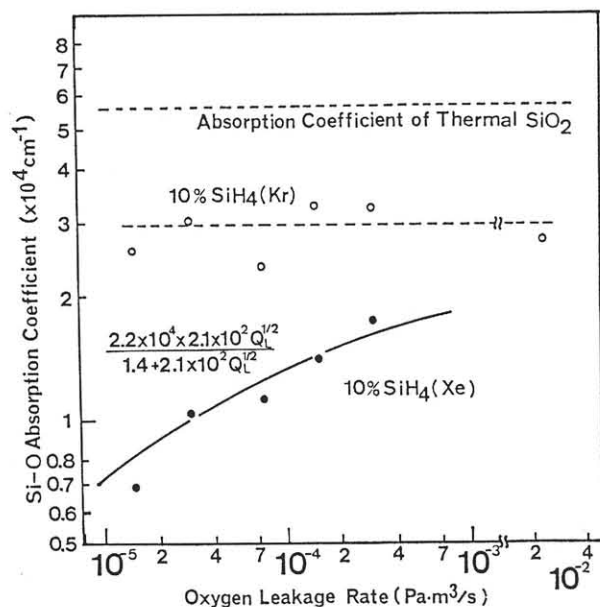


Fig. 4 Si-O Absorption Coefficient Dependence on Oxygen Leakage Rate

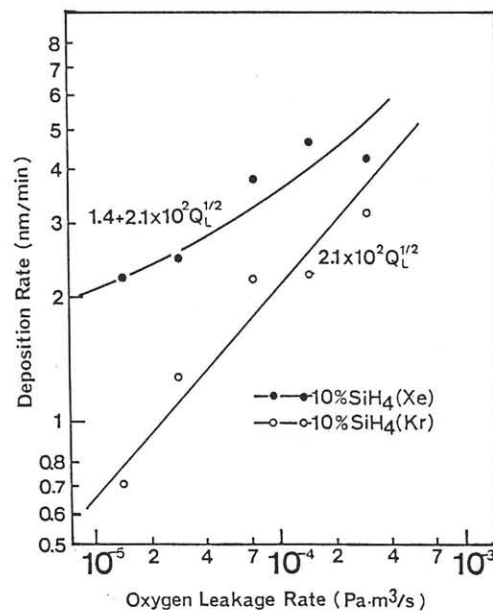


Fig. 5 Deposition Rate Dependence on Oxygen Leakage Rate