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SiO_2 Photo-CVD Using Reactive Oxygen by Double Light Excitation

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SiO_2 films having good electronic properties have been prepared at low temperatures from R.T. to 280°C by photo-CVD using double irradiation of D_2 and Xe lamps. Refractive indices of the deposited films increase with substrate temperature and by light irradiation. Fixed oxide charge is reduced considerably by adding Xe lamp irradiation and/or increasing substrate temperature. Interface state of Si MOS diode is also reduced by depositing the SiO_2 in O_2 excess atmosphere and annealing at 280°C. The minimum oxide charge density and interface state density are 5×10^{10} cm^{-2} in the film of thickness about 2000Å and 1.4×10^{11} $cm^{-2}eV^{-1}$ near mid gap, respectively.

§1. Introduction

In recent years, much attention has been paid to photo-CVD for preparing various kinds of thin films. Because the photo-CVD has some advantages such as low-temperature process, little bombardment by energetic particle and selectivity of deposition area. Many works have been done for preparing various materials such as Si,[1,2] a-Si,[3] SiO_2,[4-6] Si_3N_4[7] and refractory metal,[8] however many of them are using H_g sensitization or excimer lasers, which are not so adequate method because of toxicity, incorporation of H_g and high cost. Recently a-Si and SiO_2 films have been prepared without these Hg and lasers by using Si_2H_6 source[9] or getting UV emission from glow discharge inside reaction chamber.[10] We have also tried to prepare SiO_2 thin films by the photo-CVD using deuterium(D_2) lamp[11] which radiates much VUV light near 160 nm. These photo-CVD films can be grown at very low temperature, however their electronic properties such as oxide charge density and interface state density of Si MOS diode are not satisfactory. In this work, we have tried to improve the film quality by photo-CVD using double UV light irradiation of D_2 and Xe lamps.

§2 Excitation of Oxygen by the Double Excitation

Oxygen has large absorption in wavelength region between 140 and 170 nm(maximum absorption coefficient: about 400 cm^{-1}) as shown in Fig. 1.[12] Oxygen molecule is dissociated by VUV irradiation of D_2 lamp, and the excited states of oxygen atom, $O(^1S)$, $O(^1D)$ and $O(^3P)$ are produced,[13]

$$O_2 \xrightarrow{h\nu} O(^3P) + O(^1S), \quad h\nu<133.2\text{nm},$$

$$O_2 \xrightarrow{h\nu} O(^3P) + O(^1D), \quad h\nu<175.0\text{nm},$$

$$O_2 \xrightarrow{h\nu} O(^3P) + O(^3P), \quad h\nu<242.4\text{nm}.$$

Ozone is also produced finally by their reaction with O_2. Ozone well absorbs UV light between 200 and 300 nm which is radiated much by Xe lamp, and is again changed to $O(^1D)$,

$$O_3 \xrightarrow{h\nu} O_2(^1\Delta) + O(^1D), \quad h\nu<310\text{nm}.$$

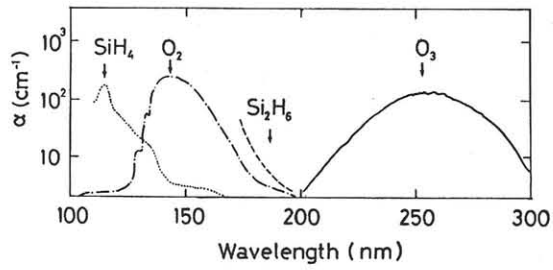

Fig. 1 Absorption coefficient spectra of SiH_4, Si_2H_6, O_2 and O_3 gases.

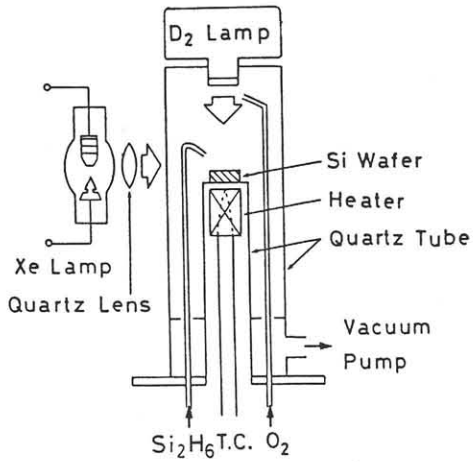

Fig. 2 Schematic illustration of apparatus for the photo-CVD of SiO_2 films.

Chemical reactivity of $O(^1D)$ is one to five orders of magnitude larger than that of the other excited states. For example, rate constants of chemical reaction of $O(^1D)$, $O(^1S)$ and $O(^3P)$ with CH_4 are 1.5×10^{-10}, 2.7×10^{-14} and 1.7×10^{-17} $cm^3 molecules^{-1} s^{-1}$, respectively. Therefore it is considered that the double excitation of both the D_2 and Xe lamps accelerates production of active oxygen($O(^1D)$) which reacts easily with various kinds of active species of silicon hydrides produced from Si_2H_6 by VUV light absorption.

§3. Deposition of SiO_2

The reaction chamber consisted of two quartz tubes of diameters 3 and 6cm arranged vertically, as shown in Fig. 2. The space between them was evacuated before and during the deposition. The D_2 lamp of input power 150W having MgF_2 window (Hamamatsu Photonics L1835) was set on the upper part of the outer tube and another MgF_2 window was installed underneath the D_2 lamp to isolate the lamp from the deposition atmosphere. The distance between the MgF_2 window and the substrate was about 7 cm. The Xe lamp of input power 500W(Ushio UXL 500D) was set beside the chamber. The substrate was n-type (100)Si wafer of 0.75-1.4 Ωcm and was put on the top of the inner tube which was heated up by a resistive heater set inside the inner tube.

UV and VUV light emitted from the D_2 lamp irradiated the Si substrate vertically and UV light from the Xe lamp was directed horizontally just over the substrate not to heat up the substrate. As intensity of UV light radiated from the D_2 lamp is some mW at most, its substrate temperature rises little by the irradiation. However, when the Xe lamp was used at 150°C, its temperature rise measured by a thermocouple inside the heater was about several degrees centigrade. Si_2H_6 source gas was supplied by blowing the Si wafer directly, and oxygen gas blowed against the MgF_2 window to prevent contamination of the window. The SiO_2 thin films were grown on the Si wafers at 0.2 Torr and mainly at flow rate ratio of Si_2H_6/O_2 of 0.11 under the irradiation of the D_2 lamp or under the irradiation of both the lamps. Depth of the oxygen for optical density = 1 is about 10 cm at 0.2 Torr and around 140nm, and so more than a half of the VUV light approaches the substrate surface.

Prepared films are flat and show no blur induced by intense gaseous reaction. Thicknesses and refractive indices of the deposited films were measured by an ellipsometer(Mizojiri DVA-36V). The thicknesses are about 2000Å for electrical measurement. Figure 3 shows substrate temperature dependence of growth rate of the SiO_2 films. The growth phenomena are considered to be very different by the irradiation of UV light. The growth rate of the photo-CVD films(open and closed circles) has the maximum of about 90 Å/min at R.T. and decreases with increase of the substrate temperature, however changes little by adding the Xe lamp irradiation. From this dependence, adsorption of reactive species on the substrate

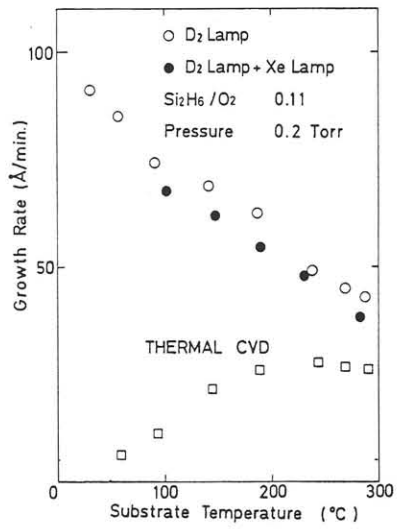

Fig. 3 Growth rate vs. substrate temperature for the films made by (□) the thermal CVD and the photo-CVD using (o) D_2 lamp and (●) D_2 and Xe lamps.

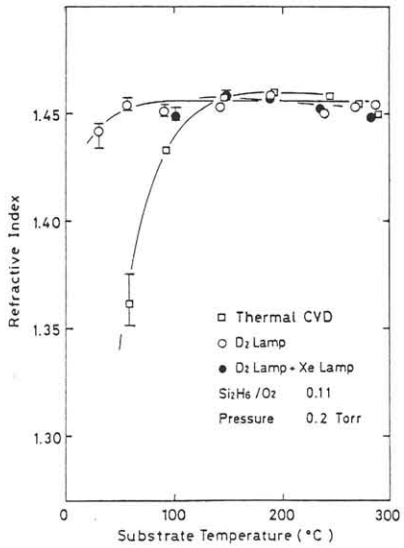

Fig. 4 Refractive indices vs. substrate temperature for the films made by (□) the thermal CVD and the photo-CVD using (o) D_2 lamp and (●) D_2 & Xe lamps.

might play an important role to the growth. The temperature dependence can be also explained by the fact that the desorption of some molecules and atoms are affected by the temperature but not by photon-associated phenomena in this light intensity region.[14] On the other hand, the SiO_2 film of the thermal CVD didn't grow below about 60°C, and the growth rate(squares) increases with the temperature as the growth is attributed to thermal reaction on the surface.

Figure 4 shows refractive indices of the SiO_2 films vs. the substrate temperature. The refractive indices increase with the substrate temperature, and saturate above about 60°C for the photo-CVD films and above about 140°C for the thermal CVD films. The refractive indices of the photo-CVD films are larger than those of the thermal CVD films below about 140°C. The saturated refractive indices are about 1.454 for the photo-CVD films and about 1.459 for the thermal CVD. It is difficult to decide which film is better from this result, as both high density and Si-Si bonding increase the refractive index, however the obtained values are close to the value of thermally-oxydized SiO_2, 1.457.

§4. Optical and Electrical Properties

Infrared transmission spectra were measured for the SiO_2 films of thickness about 5000Å on semi-insulating Si by fourier transform infrared

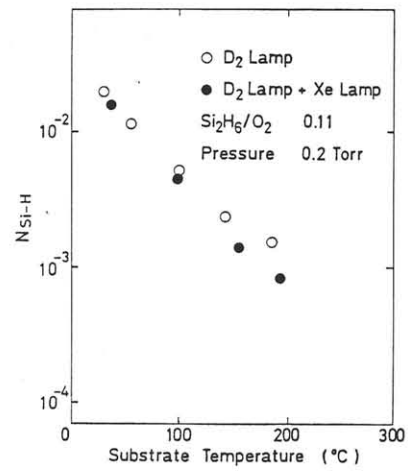

Fig. 5 Substrate temperature dependence of integrated absorption coefficient of the SiH normalized by that of the SiO for the photo-CVD films made by using (o) D_2 lamp and (●) D_2 & Xe lamps.

spectrometer(Japan Spectroscopic FT/IR-3). There are several lines corresponding to SiO(1060-1070, 800cm^{-1}), SiOH(3600cm^{-1}), SiH(2260cm^{-1}) and Si_2O_3 (880cm^{-1}) bondings in the spectra of the thermal and photo-CVD films. These lines corresponding to the SiH, SiOH and Si_2O_3 bondings decrease a little by the Xe lamp irradiation. In order to obtain contents of the SiH, SiOH and Si_2O_3, the absorption coefficient spectra divided by photon frequency were integrated over the photon frequency. Figure 5 shows the substrate temperature dependence of the integrals of the Si-H normalized by that of the SiO, N_{Si-H}. This decreases with the substrate temperature and those of the SiOH and

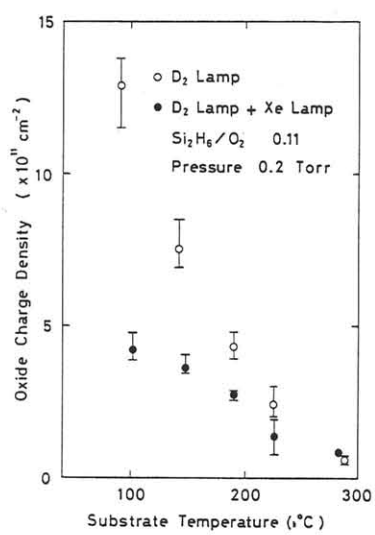

Fig. 6 Oxide charge densities of the films of thickness about 2000A made by the photo-CVD using (o) D_2 lamp and (●) D_2 & Xe lamps.

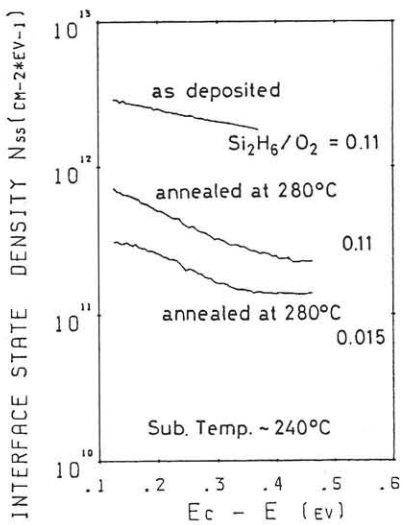

Fig. 7 Interface state density of Si MOS diodes made at 240°C by the photo-CVD using D_2 and Xe lamps annealed at 280°C. The ratios of the flow rate of Si_2H_6/O_2 are 0.11 and 0.015.

Si_2O_3 have the similar dependence, as high substrate temperature increases chemical reaction on the surface such as scavenging of hydrogen and oxidation of adsorbed species of silicon hydrides. However the additive Xe-lamp irradiation is not so effective to reduce their contents.

C-V characteristics were measured at 1MHz on MOS diodes whose thicknesses of the SiO_2 were about 2000Å and electrode was evaporated Al dot. Figure 6 shows substrate temperature dependence of fixed oxide charge obtained from flat band voltage shifts of the C-V curves of the diodes. The charge decreases abruptly with the substrate temperature, and the double excitation is effective to reduce the charge, especially in low temperature range. This might be attributed to formation of strong atomic-bonding induced by adding the Xe lamp irradiation, as the contents of the SiH, SiOH and Si_2O_3 are not so changed. The minimum oxide charge density was $5\times10^{10}cm^{-2}$ in the SiO_2 film of thickness 2000Å.

Figure 7 shows interface state density of the Si MOS diode, N_{ss} obtained by DLTS measurement. The top curve shows N_{ss} of the film deposited at 240°C, and decreased after annealing at 280°C(middle). MOS diode of the film deposited at 240°C in the flow ratio of 0.015 shows the least N_{ss} after the annealing (bottom) and the minimum value is $1.4\times10^{11}/cm^2eV$ near the mid gap. Therefore enough active oxygen atmosphere is effective to reduce the interface state density.

§5. Conclusion

The influence to the film quality by the double light excitation of the D_2 and Xe lamps in the photo-CVD has been investigated. The double excitation gave little change in the growth rate, the refractive indices and inclusion of SiH, SiOH and Si_2O_3 in comparison with that of the photo-CVD using only the D_2 lamp, however reduced the oxide charge density and interface state density remarkably.

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