LOW TEMPERATURE DEPOSITION OF SILICON OXIDE FILMS BY UV-ASSOSTED RF PLASMA-ENHANCED CVD

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ABSTRACT

Silicon oxide films were prepared by using five kinds of organosilicon compound as gas sources without oxygen by rf plasma-enhanced CVD (PECVD). UV light was irradiated on a substrate vertically during deposition to enhance film oxidation and ablation of carbon contamination in a deposited films. Films prepared with UV irradiation contained less carbon than those prepared without UV irradiation. The oxidation of the films was improved by UN irradiation. The effect of UV irradiation was, however, not observed when the films were prepared with tetramethy lsilane (TMS) which contained no oxygen atom. Dissociated oxygen atoms from an organosilicon compound were excited in the plasma with UV irradiation around the substrate surface and affected the enhancement of film oxidation and ablation of carbon in the films.

INTRODUCTION

Plasma-enhanced CVD (PECVD) is a suitable technique for preparing various kinds of films by initiating chemical reactions in a gas with an electric discharge[1,2]. PECVD using low-temperature plasmas has found important applications in the microelectronic, optical, solar cell, mechanical and plastic industries.

Silicon oxide films are very useful for transparent hard coatings, microelectronic device fabrication, corrosion protection coatings and oxygen-barrier coatings. In previous studies we studied the preparation of silicon oxide films at low substrate temperatures by PECVD using organosilicon compounds and oxygen as gas sources[3,8]. The roles of oxygen were to enhance the film oxidation and to ablate carbon in the films. On the other hand, the deposition rates of the films decreased with increasing partial pressure of oxygen.

Recently photo-induced CVD (photo-CVD) has been intensively studied for preparation of silicon dioxide films at relatively low wubstrate temperatures[9-14] UV light has been used to dissociate and activate source gases such as silane (SiH_4), disilane (Si_2H_6), tetraethoxysilane (TEOS, $Si(OC_2H_5)_4$), O_2 and N_2O.

In previous study we reported on the new technique for preparing silicon oxide films by UV-assissted rf PECVD[15]. Carbon contamination in the deposited films decreased remarkably and the oxidation of the films en-

hanced by using this technique in an oxygenless plasma system.

In this study we have prepared silicon oxide films by using five kinds of organosilicon compound by rf PECVD with UV irradiation during film deposition and studied film properties.

EXPERIMENTAL

Preparation of silicon oxide films

The apparatus used is shown in Fig. 1. It was made up of a discharge tube, a vacuum system and a gas supply system. The discharge tube consisted of a high purity quarts glass cylinder of 1000mm length nd an inside diameter of 35mm. Syainless steel holders supported this tube at both ends. Gas pressure was measured with a Pirani gauge.

A 13.56 MHz generator supplied the rf power which was transferred to the reactand gas with an impedance-matching nerwork rerminating in a 5.5 turn inductively coupled coil of copper tubing 6mm in diameter.

Two UV light fiber cables (5mm ϕ, Model: FGB5F1000UVR, Hoya-Schott Co.) were fixed at a position 20mm away from the substrate and irradiated on the substrate
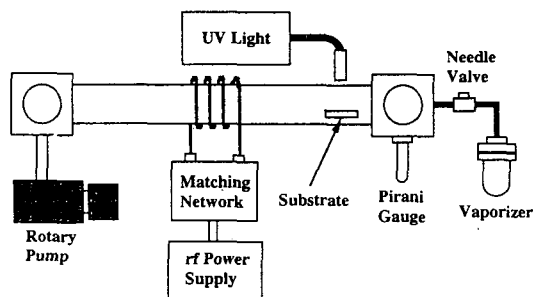
vertcally (we call this vertical UV irradiation). A Hg-Xe lamp (200W, Model : 201HS, Hoya-Schott Co.) was used as an UV light source. This lamp mainly radiated UV light of the wavelength of 313 nm. Around 290 and 305 nm, comparatively strong radiation was also observed. UV intensity at 365 nm per one fiber cable was measure at a position 20mm away from the fiber cable with an irradiance tester(Model : UIT-101, Ushio, Inc.) and was about 292mW/cm² . Other radiation intensity was about 112 mW/cm² at 290 nm, 83mW/cm² at 305 nm and 234mW/cm² at 313 nm.

Usually low-pressure Hg lamp and D_2 lamp are used as UV light sources in photo-CVD[9-14]. The Hg-Xe lamp radiates stronger UV light

Table. 1 Organosilicon compounds used.

Compound	Chemical Formula	Boiling Point(℃)	Molecular Weight
TMS	$(CH_3)4Si$	26-27	88.2
TMMOS	$(CH_3)_3Si(OCH_3)$	57-58	104.2
DMDMOS	$(CH_3)_2Si(OCH_3)_2$	82-83	120.2
MTMOS	$CH_3Si(OCH_3)_3$	102-103	136.2
TMOS	$Si(OCH_3)_4$	121-122	152.2

Table. 2 Preparation conditions.

rf Power(W)	200
Pressure(Pa)	10-25
Substrate Position(mm) (from the center of plasma)	350
UV Fiber Position(mm) (from the surface of substrate)	20(vertical) 3(horizontal)
Substrate Temperature(℃)	< 100
Deposition Time(min)	15

Fig. 1 Schematic diagram of experimental apparatus.

than low pressure Hg lamp and D_2 lamp. There are very few reports about photo-CVD using the Hg-Xe lamp.

Preparation conditions and raw materials used are shown in Tables 1 and 2. Reactants used were five kinds of organosilicon compound, tetramethoxy silane (TMOS, $Si(OCH_3)_4$), methy ltrimethoxy silane (MTMOS, $CH_3Si(OCH_3)_3$), dimety ldimethoxy silane (DMDMOS, $(CH_3)2Si(OCH_3)_2$), trimethy methoxy silane (TMMOS, $(CH_3)_3Si(OCH_3)$) and trimethylsilne (TMS, $Si(CH_3)_4$). These compounds have the different numbers of methyl (CH_3-) groups and methoxy ($-OCH_3$) groups. A reactant contained in a stainless steel vaporizer which was kept at room temperature during deposition. We used its vapor at room temperature. Substrates used were polished Si wafers. After degreasing, they were located at a position 350mm away from the center of plasma. Substrate temperature during deposition was not controlled in this study and measured with a chromel-alumel thermocouple. The highest substrate temperature was about 100℃ during deposition. The rise of substrate temperature by Hg-Xe lamp irradiation was less than 20℃. The deposition time was 15 min. Pretreatment by an oxygen plasma was performed to remove contamination on the substrates and to get strong adhesion between the substrate and the deposited film.

Analyses of chemical bonding states of the deposited films

Chemical bonding states and composition of the deposited films were analyzed with both Fourier transform infrared spectroscopy (FTIR) system (Model : FT/IR -5300, JASCO Co., Ltd.) and X-ray photoelectron spectroscopy (XPS) system (Model : ESCA 1000, Shimadzu Co., Ltd.). Mg K α radiation (8.0 kV, 30 mA) was used as an X-ray source. XPS depth profiles of the films were obtained with Ar ion sputtering(2.0 kV, 30 mA).

RESULTS AND DISCUSSION

Deposition rate

Figure 2 shows the relationships between the pressure and the deposition rate for PECVD using DMDMOS without and with UV irradiation. The deposition rates increase with the pressure in both cases. The deposition rates decrease from 114 to 76 nm/min by UV irradiation at 25 Pa. This deposition rate, 76 nm/min is, however, larger than that obtained in DMDMOS-oxygen plasma system (40 nm/min)[16]. For other organosilicon compounds, the deposition rates decrease between 30 and 40% by UV irradiation.
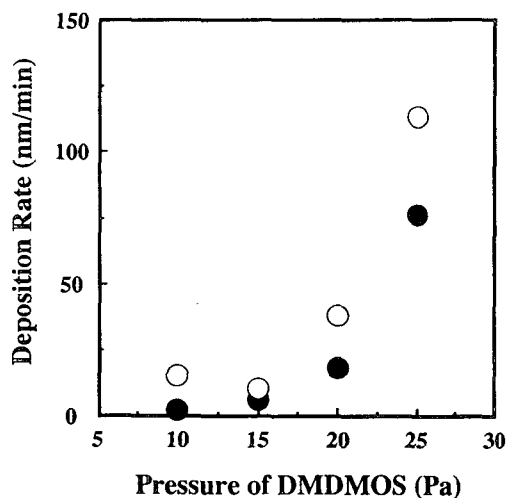

Fig. 2 Relationships between the pressure of DMDMOS and the deposition rate;
  ○ : without UV irradiationand
  ● : with UV irradiation.

FTIR measurements

FTIR measurements were performed to investigate the change in chemical bonding states of films deposited without and with UV irradiation. Films were prepared at 25 Pa.

Figures. 3 and 4 show the IR spectra of the films prepared without and with UV irradiation. In the IR spectra shown in Figs. 3 and 4, three characteristic absorption bands due to the asymmetric Si-O-Si stretching, Si-O-Si deformation and Si-O-Si rocking vibration[17], are observed around 1010-1080, 790-810 and 440-460cm^{-1}

We notice that the peaks around 1270-1280 and 1460-1470cm^{-1} in Fig. 3, due to the symmetric deformation vibration of CH_3 groups directly attached to silicon atoms and the asymmetric deformation vibration of C-H in the -OCH_3 gorups[17], disappear in Fig. 4 except for the spectrum in Fig. 4(a). The intensity of the absorption band around 1190cm^{-1}, due to the rocking vibration of CH_3 in the Si-O-CH_3 groups[17], also decreases. The absorbance ratio of the shoulder around 1100-1110 cm^{-1}, due to the asymmetric Si-O-C stretching vibration, to the asymmetric Si-O-Si sstretching vibration around 1010-1080cm^{-1}, is relatively low. Moreover, the band due to the Si_2O_3[18]or due to nonbridging Si-O interaction[19]around 880cm^{-1} shown in Fig. 3 disappears in Fig. 4. This is connected to a reduction in structural imperfections in SiO_2 networks[20]. The peak due to the asymmetric Si-O -Si stretching vibration shifts to higher frequencies and reaches around 1060-1070cm^{-1} with UV irradiation except for the spectrum in Fig. 4(a). This band appears around 1070 cm^{-1} for fully oxidized silicon[21]. The spectrum of the film prepared with TMS changes
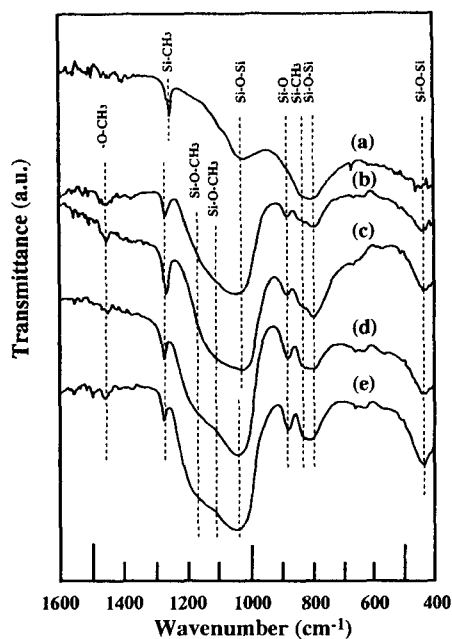

Fig. 3 IR spectra of the films prepared without UV irradiation at 25 Pa; (a) TMS, (b) TMMOS, (c) DMDMOS, (d) MTMOS and (e) TMOS.
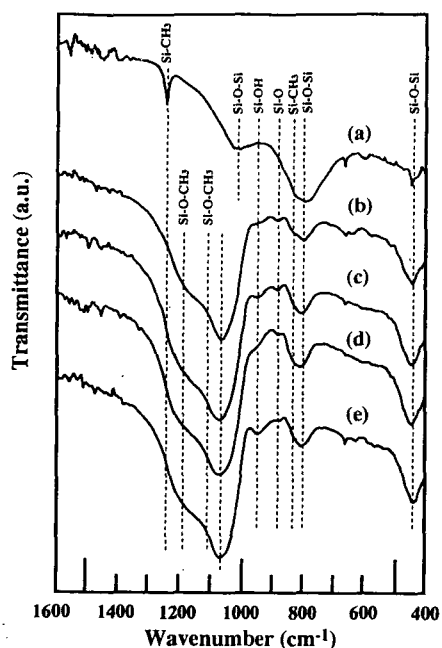

Fig. 4 IR spectra of the films prepared with UV irradiation at 25 Pa; (a) TMS, (b) TMMOS, (c) DMDMOS, (d) MTMOS and (e) TMOS.

scarcely by UV irradiation.

From IR results, film oxidation is enhanced largely and structural imperfections decrease by UV irradiation except for the film prepared with TMS.

XPS measurements

In order to investigate homogeneity in the films deposited onto Si substrates without and with UV irradiation, depth profiles of the concentrations of C, Si and O atoms in the films were measured with XPS.

Figure 5 (a) shows the depth profile of the film prepared with TMOS(pressure : 25 Pa) without UV irradiation. The C concentration at the surface is larger than that in the inner regions because of impurities at the surface. The C concentration is almost constant and about 18.3 at % in the inner regions. The Si and O concentrations are also almost constant and about 31.7 and 50.0 at % in the inner regions. On the other hand, the film prepared with UV irradiation has very small C concentration as shown in Fig. 5 (b). The C concentration decreases from 18.3 to 4.9 at % by UV irradiation. The concentrations of Si and O are about 30 and 56 at %. This result shows that the film oxidation and the ablation of carbon are enhancd by UV irradiation. This result well corresponds to the IR result.

Table 3 shows the composition of the films prepared without and with UV irradiation. For TMMOS, DMDMOS, MTMOS and TMOS, the C concentration decreases remarkably and the concentrations of Si and O change scarcely by UV irradiation. Organ-osilicon compounds which contain oxygen atoms are useful for the enhancement of film oxidation
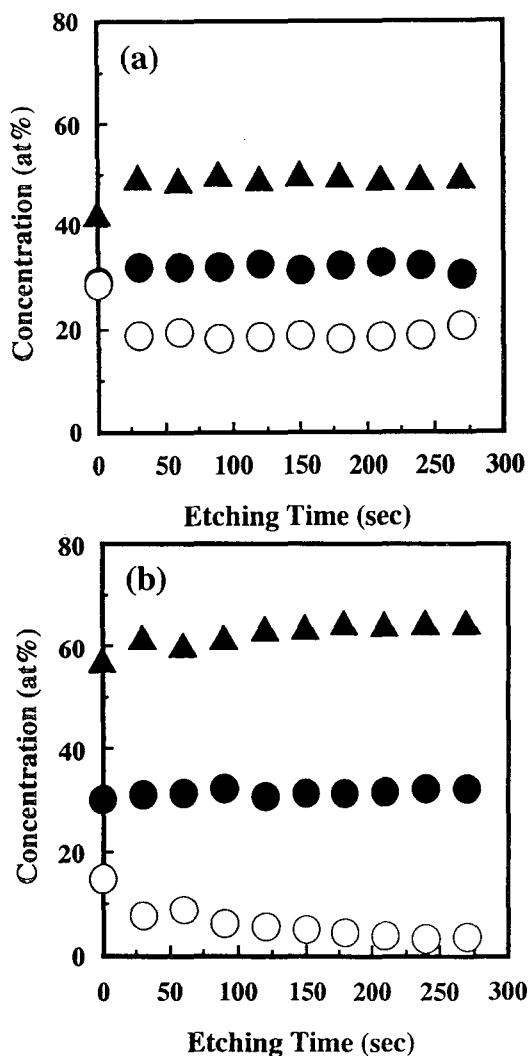

Fig. 5 XPS depth profiles of the films prepared with TMOS at 25Pa; (a) without UV irradiation, (b) with UV irradiation, ● : Si, ▲ : O and ○ : C

Table. 3 Composition of the films prepared without and with UV irradiation (at %)

	Without UV Irradiation			With UV Irradiation		
	Si	O	C	Si	O	C
TMOS	31.7	50.0	18.3	31.9	63.2	4.9
MTMOS	27.7	43.3	29.0	30.7	59.4	9.9
DMDMOS	23.0	26.3	50.7	32.2	50.0	17.8
TMMOS	19.2	21.3	59.5	30.7	46.6	22.7
TMS	18.5	8.3	73.2	18.8	8.7	72.5

and ablation of carbon in the deposited films. The methoxy groups in organosilicon compounds are in portant in UV-assisted rf PECVD.

Here we discuss the effect of UV irradiation on film formation. Film preparation was carried out using UV irradiation without plasma to confirm the effect of UV irradiation on film formation. No film formed using UV irradiation only. The rise of substrate temperature was less than 20°C by UV irradiation . From these results, the reaction was not due to the photolytic and pyrolytic reactions but due to the plasma and photolytic ones. Ozone (O_3) and excited oxygen atom(O) form from O_2 by the irradition of UV light emitted from low-pressure Hg lamp[22]. Hg-Xe lamp used in this study is ineffective for dissociation of O_2, because O_2 can be dissociated by UV irradiation between 133 and 200 nm and O_2 dissociated into the excited oxygen atoms, $O(^1D)$, $O(^1S)$, as well as a ground-state atom, $O(^3P)$[9,23]. This lamp is, however, effective for dissociation of O_3.

In this study the film preparation was performed in an organosilcon plasma system without the mixing of oxygen. However, O is formed from residual O_2 in the reactor and dissociated oxygen atoms from organosilicon compounds by plasma. O_3 is also formed by a three-body reaction among an O atom, an O_2 molecule and third species such as O_2 and N_2 ($O + O_2 + M \rightarrow O_3 + M, M = O_2, N_2$, etc.)[9,23]. O_3 is dissociated by UV irradiation below 310 nm($O_3 \rightarrow O_2$ ($1\triangle$) + $O(^1D)$) and $O(^1D)$ foms[9,23]. In a following dark process, $O(^1D)$ reacts with O_2 and forms excited O_2 molecules or oxygen atoms ($O(^1D) + O_3 \rightarrow O_2$ ($^3\Sigma$ g) + O_2 ($^3\Sigma$u) or $O(^1D) + O_3 \rightarrow 2O(^3P) + O_2$).

O_2 ($^3\Sigma$u) is dissociated into the two oxygen radicals, which react with O_2 and form O_3 again[9,23]. O_3 can be dissociated continuously by Hg-Xe irradiation. For chemical reactivity of three. O radical such as $O(^1S)$, $O(^3P)$ and O (^3D)), $O(^1S)$ is the highest excited radical among them, but, the chemical reactivity of O (^1D) in one to seven orders of magnitude larger than those of $O(^1S)$ and $O(^3P)$[9,24]. Therefore, the formation of $O(^1D)$ is very important in the ablation of carbon and the film oxidation. From FTIR and XPS results, the C concentration in the films prepared with plasma only is large and the film oxidation is insufficient. The means that the amounts of O (^1D) are short in the plasma. In the UV-assisted experiment, UV light emitted from Hg-Xe lamp dissociates O_3 and forms of $O(^1D)$ in the plasma. This $O(^1D)$ reacts with carbon and results in the formation of volatile products such as CO and CO_2[25]. $O(^1D)$ also enhances oxidation of the deposited film. This explanation is confirmed by the fact that the enhancement of film oxidation was not observed for TMS which contained no O atom.

CONCLUSIONS

Silicon oxide films were prepared by rf PECVD with UV irradiation. Carbon contamination in the deposited films remarkably and film oxidation was enhanced largely by UV irradiation in an organosilicon plasma system without the mixing of oxygen. UV irradiation affects the enhancement of dissociation of O_3 and the formation of highly reactive $O(^1D)$. The reason for decrease in the carbon concentration in the deposited films is due to the formation of $O(^1D)$. Oxygen atoms in an

organosilicon compound is used for the formation of O_3 in the plasma and the formed O_3 changes into $O(^1D)$ by UV irradiation. This explanation is good agreement with the results of FTIR and XPS for the films prepared with TMS which contains no O atom. The deposition rate decreased with UV irradiation, but was larger than that obtained in the organosiliconoxygen plasma system. This technique is also able to deposit silicon oxide films at low substrate temperatures below $100\,°C$ and suitable for low heat-resistant materials like resins.

ACKNOWLEDGMENTS

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