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EVALUATION OF WATER REPELLENCY FOR SILICON OXIDE FILMS PREPARED BY RF PLASMA-ENTHANCED CVD

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ABSTRACT

Silicom oxide films with good water repellency were prepared by rf plasma-enhanced CVD (rf-PECVD) using four kinds of organosilicon compound, which had different number of methyl(CH_3) groups, and oxygen as gas sources. The differences in the deposition rates, film composition and film properties were studied in detail. Water repellency depended on the number of CH_3 groups in the organosilicon compounds and the partial pressure of oxygen in the plasma. The highest contact angle for water drops, about 95 degrees, was obtained when trimethy lmethoxy silane (TMMOS) was used. The contact angle decreased with the amount of oxygen gas introduced into the plasma. The dissociation of CH_3 groups by adding oxygen was comfirmed by Fourier transform infrared spectroscopy(FTIR) and X-ray photoelectron spectroscopy (XPS). The optical properties were estimated by double-beam spectroscopy and ellipsometry. The transmittance of the glass plate coated by the film prepared with tetramethoxy silane (TMOS) was about 90% and the refractive index of film was 1.44. This value was smaller than the refractive index of a glass plate(soda lime glass, refractive index is 1.515) and this film played a role of anti-refractive coating.

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]. Recently, PECVD using low-temperature plasmas has found inportant applications in the microelectronic, optical, solar cell, mechanical and chemical industries.

The chief advantage of PECVD over the thermal CVD is the ability to prepare films at relatively low substrate temperatures (typically less than 300℃). Instead of requiring thermal energy, the energetic electrons can activate almost any reactions among the gas in plasma. At the same time, the gas and substrates do not reach high temperatures because of non-equilibrium naaature of glow discharge plasma. Another way of stating the temperature advantage is that at reasonable or acceptable temperatures, PECVD often has much higher deposition rate than conventional thermal CVD.

Silicon oxide films are very useful for transparent hard coatings, microelectronic device fabrication, corrosion protection coatings and oxygen-barrier coatings. In previously studies, we studied the preparation of silicon oxide films at low substrate temperatures by inductively couled rf PECVD and microwave PECVD using organosilicon compounds and oxygen as gas sources[3-8]. Recently, water repellency is required in various fields. At present, the most common method is to spread a fluoropolymer of fluoro-alkyl silane(FAS) on a substrate. This method needs the burning process carried out at about 350℃ and can not be applied to low heat resistant substrates like resins. Moreover the films prepared by this techmique have less abrasion resistance and weak adhesion between the films and the substrates, and the materials like FASs are expensive. Therefore, alternative techniques and materials are required at present.

In this study, we have prepared silicon oxide films with good water repellency by rf PECVD using four kinds of organosilicon compounds which have the different number of methyl groups as source materials and studied the film properties. Organosilicon compounds used were tetramethoxysilane(TMOS), methyltrimethoxysilane(MTMOS), dimetyldimethoxysilane(DMDMOS), and trimethymethoxysilane(TMMOS).

This paper reports on the preparation method, the preparation conditions, the composition, the water repellency, the chemical bonding states, and the mechanical and optical properties for silicon oxide films with good water repellency.

EXPERIMENTAL

rf PECVD system

The apparatus for an rf PECVD system was 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 quartz glass cylinder of lenght 1000㎜ and inside diameter 35㎜. Stainless steel holders supported this tube at both ends. The gas pressure was measured with a Pirani gauge.

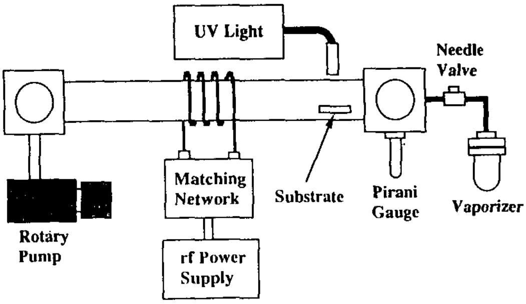

Fig. 1 Schematic diagram of experimental apparatus.

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

Table. 1 Preparation conditions

rf Power(W)	100-300
Total Pressure(Pa)	25
Partial Pressure(Pa)	
O_2 Gas(Pa)	0-25
Reactant Gas(Pa)	0-25
R($R=P_{O_2}/P_{Total} X 100$) (%)	0-80
Deposition Time(min)	15
Substrate Position(㎜) (from the center of plasma)	350

Table. 2 Raw materials used

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

The preparation conditions and raw materials were shown in Tables 1 and 2. An organosilicon compound was contained in a stainless steel vaporizer and was kept at room temperature during deposition. We used the vapor of the compound. Substrates used were poly carbonate(PC), glass and polished Si wafers. They were used after degreasing and located at the positions 350㎜ away from the center of plasma to avoid the direct thermal damage by the plasma especially for the resin substrate. The substrate temperature during deposition was around 100℃ and the typical deposition time was 30 min. The pretreatment by an oxygen plasma was carried out to remove contamination on the substrates and to modify the PC substrate to achieve strong adhesion between the substrate and the deposited film.

Characterization methods of films

The thickness of films was measured with a stylus method. Water repellency was examined by measuring the contact angle. The contact angles for water drops(about 2㎜ f) were measured with a contact-anglemeter (Model : D-013-D2, ERMA Co., Ltd.) by a drop method at 25℃ in air[9]. Water was used as an example of hydrophile material. The contact angles at 5 points were measured and the average value was calculated after eliminating their minimum and maximum values. The contact angle was measured when the constant tine(1 min in this study) passed after dropping of water.

The chemical bonding states of films were investigated by using XPS(Model : ESCA 1000, Shimadzu Co., Ltd.) with MgKα radiation at 10 kV and 30mA and FTIR(Model : FT-IR 5300, Jasco Co., Ltd.).

The hardness of coated substrates was determined by a dynamic ultra-micro hardmess tester(Model : UHT200, Shimadzu Co., Ltd.). Spectroscopic measurements were carried out by using a double-beam spectrometer(Model : UV310PC, Shimadzu Co., Ltd.). The refractive indexes of films were measured by n ellipsometer(Model : SP2300, PLASMOS).

RESULTS AND DISCUSSION

Difference in deposition rates

Preparation conditions such as the kind of organosilicon compounds used and the partial pressure ratio of oxygen to the total gas pressure(R) were changed. The total gas pressure and rf power were kept at 25 Pa and 200W during deposition in this study. The transparent silicon oxide films with good water repellency were prepared under various conditions.

The relationships between the R values and the deposition rates were shown in Fig. 2. As the Rvalue in creased, the deposition rates decreased for every material. This was due to the decrease in partial pressure of the reactant gas and the enhancement of ablation of carbon in the deposited films. The deposition rates increased in the order TMOS,

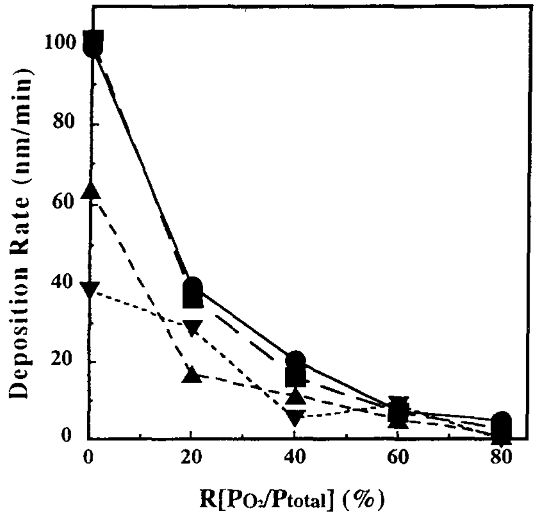

Fig. 2 Relationships between the R values and the deposition rates for silicon oxide film preparation; ● : TMMOS, ■ : DMDMOS, ▲ : MTMOS, ▼ : TMOS and rf power=200W.

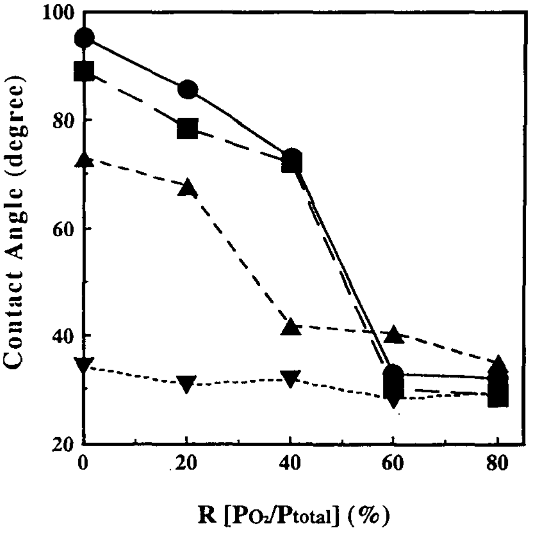

Fig. 3 Relationships between the R values and the contact angles for water drops;
● : TMMOS, ■ : DMDMOS, ▲ : MTMOS, ▼ : TMOS and rf power=200W.

MTMOS, DMDMOS, TMMOS and the maximum deposition rate was about 90 nm/min when TMMOS was used at R=0.

Inoue and Takai explained the formation mechanism of silicon oxide films using organosilicon compounds and oxygen by optical emission spectroscopy(OES) and XPS in the rf PECVDD[10]. They explained that oxygen was not necessary to disociate O-C bonds in the methoxy(-OCH_3) groups but was necessary for Si-C bonds between Si and CH_3 groups[10]. Therefore, O-C bonds were dissociated and Si-C bpmds were still remain at R =0. The deposition rates increased with number of Si-C bonds in appearance, however, the concentration of carbon in the films increased with number of CH_3 groups at R=0.

Water repellency of groups obtained silicon oxide films

Figure 3 shows the relationships between the R vakyes abd tge cibtact abgkes fir water drops. The contact angle for the film prepared with TMMOS at R=0 was about 95 degrees and that for the film prepared with TMOS was about 35 degrees. This angle for TMOS was almost the same value as the contact angle for a glass substrate(27 degrees). Water repellency of films was improved with the number of CH_3 groups in the organosilicon compounds and decreased with the R value. Generally a film which has a contact angle more than 80 degrees repesents high water repellency. Since the contact angle for glass was about 27 degrees, water repellency was improved remarkably by the coating of silicon oxide filims prepared with DMDMOS and TMMOS. Silicone resins have good water repellency because of existence of CH_3 groups inside them[11]. Baba et al. prepared the silicon oxide films with hexamethyldisiloxane(HMDSO) by using audio-frequency(at) and rf discharges[12]. They carried out the

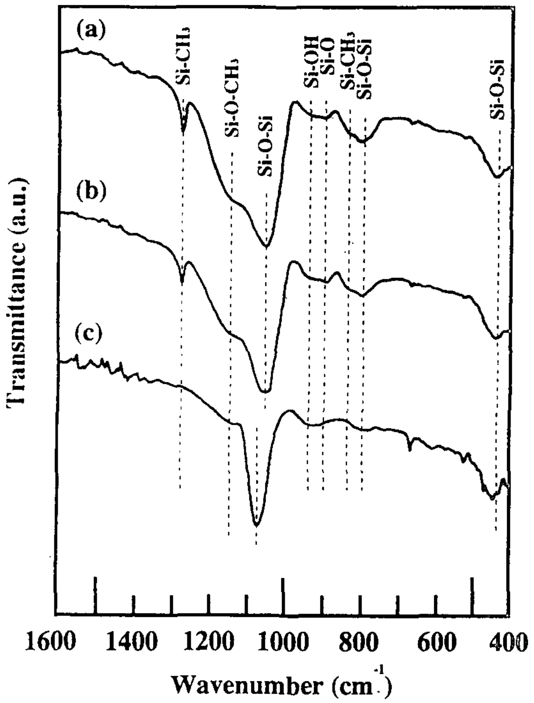

Fig. 4 IR spectra of silicon oxide films prepared with MTMOS; (a) : R=0, (b) : R=40, (c) : R=80 and rf power=200W

deposition in a discharge sustained between two parallel electrodes contained within a glass bell jar. Their results indicated that the contact angles depended on the discharge frequency. The maximum contact angle was about 100 degrees when the af discharge used. The contact angle decreased to about 80 degrees when the rf discharge was used. This was due to the dissociation of CH_3 groups in the organosilicon compounds by plasma. In this study, the substrates were located at the positions between 350mm away from the center of plasma and the dissociation of Si-C bonds was suppressed.

FTIR and XPS measurements were carried out to investigate the changes of chemical bonding states in films which were used in the contact angle measurements.

Figure 4 shows the IR spectra of the silicon oxide films prepared with and TMMOS. The IR spectra of the prepared films were slightly varied according to the organosilicon compounds used and the R value. Three major peaks around 1070-1080, 800 and 450 cm^{-1} are observed and due to the absorption by Si-O-Si bonding[13]. The peak around 1070-1080cm^{-1} corresponds to Si-O-Si asymmetric ssstret-ching vibration, that at 800cm^{-1} does to Si-O-Si bending vibration, and that at 450cm^{-1} does to Si-O-Si rocking vibration. The peak at 955cm^{-1} due to the Si-OH bonding and the peaks at 870 and 1270cm^{-1} due to the absorption by Si-CH_3 bonding were observed in the spectra. The contents of carbon in the films prepared with MTMOS, DMDMOS and TMMOS were larger than the content in the film prepared with TMOS. This well corresponds to the contact angle measurment shown in Fig. 3. The Si-O-CH_3 absorption band was not detected. Almost-OCH_3 groups

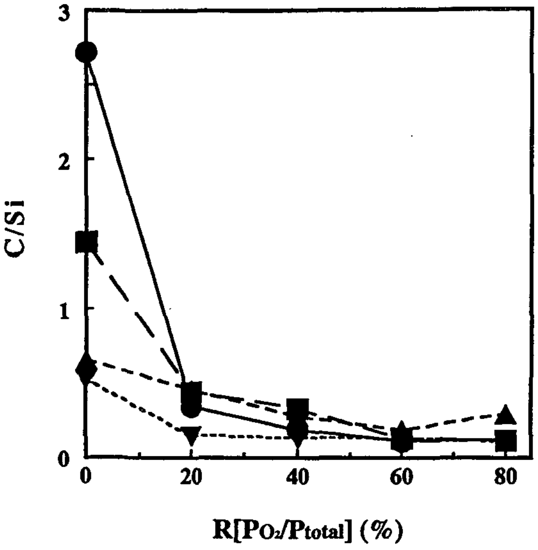

Fig. 5 Relationships between the R values and the C/Si ratio at the surface analyzed by XPS; ● : TMMOS, ■ : DMDMOS, ▲ : MTMOS, ▼ : TMOS and rf power=200W.

in the organosilicon compounds, therefore, dissociate without the existence of the oxidizer, Contrary the CH_3 groups directly combined with Si atoms remain in the deposited films. The intensity of absorption bands of Si-CH_3 bonds gradusliy decreased with the R value in the spectr(b), (c) and (d). Dissociation of Si-CH_3 bonding needs oxygen and the contact angles also decreased with the R vallue as shown in Fig. 3. From these results, the Si-CH_3 bonds were necessary to improve the water repellency. DMDMOS and TMMOS were, therefore, suitable reactants to prepare the silicon oxide films with good water repellency.

Figure 5 shows the relationships between the R values and the C/Si rations at the surface composition analyzed by XPS. The films prepared with TMOS contained very small amount of carbon impurities even if the R value changed from 0 to 80%. The C/Si ratios of the films deposited without oxygen correspond to the number of CH_3 groups in the organosilicon compounds. It was clear that the Si-CH_3 bonds were not dissociated in the plasma without oxygen. The carbon impurities decreased when the R value increased except for TMOS. This result also well corresponds to the contact angle measurement shown in Fig. 3.

Difference in film properties

The dynamic ultra-microhardness of the prepared films increased with the R value and decreased with the number of CH_3 groups in the organosilicon compounds. The hardness of films prepared with TMOS is about 691 at R=80. This value is comparable for a glass substrate.

The optical transmission spectra were obtained for glass substrates coated under various conditions. The solid line in Fig. 6 shows the optical transmission spectra of a glass substrate with the silicon oxide film prepared with TMOS(R=0, rf power=200W). The spectrum of the uncoated glass subsstrate was indicated by the dotted line. The thickness of film was about 0.24㎜. Air was adopted as a reference. Compared the solid line, the transmittance of the coated substrate increased to about 91%. The refractive index of this film was 1.44. Since, the film with lower refractive index is coated on the substrate(soda-lime glass, refractive index=1.515), the reflection decreases and the transmittance increases[14]. Therefore, this film plays a role of anti-reflective coating.

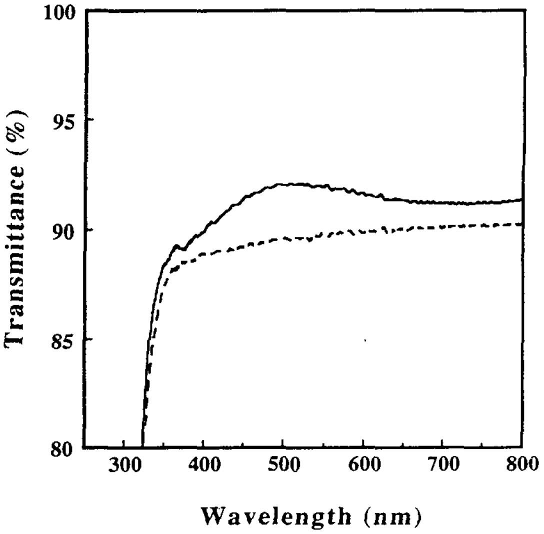

Fig. 6 Optical transmission spectra of glass substrate with and without the silicon oxide film prepared with TMOS; R=0, rf power=200W, real line : coated glass and dot line : uncoated glass.

CONCLUSION

Silicon oxide films with high water repellency were prepared by rf PECVD using four kinds of organosilicon compound which had different numbers of methyl groups and oxygen as source gases. The highest contact angle for water drops was about 95 degrees when TMMOS was used. The lowest one was about 35 degrees when TMOS used. Water repellency depended on the number of CH_3 groups in the organosilicon compounds and was degrat-ed by adding oxygen into the plasma. This was due to the dissociation of CH_3 groups from Si and was comfirmed by FTIR and XPS.

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