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EFFECTS OF SUBSTRATE TEMPERATURE ON PROPERTIES OF FLUORINE CONTAINED SILICON OXIDE FILMS PREPARED BY MICROWAVE PLASMA-ENHANCED CVD

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ABSTRACT

Silicon oxide films with high hardness and water repellency were prepared by microwave plasma-enhanced CVD using four kind of organosilicon compound-fluoro-alkyl silane mixtures as source gases. An argon gas was used as a carrier gas for fluoro-alkyl silane. The substrate temperatures during deposition were controlled by resistant heating at a constant value between 50 and 300℃. The hardness of the films increased, but the deposition rate and the contact angle for a water drop decreased with increasing substrate temperature. The number of methoxy groups also affected the water repellency and hardness. The deposited films became more inorganic with increasing substrate temperature because of the thermal dissociation of reactants.

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 plasma has found important applications in the microelectronic, optics, solar cell, mechanical industries and plastic ones.

The chief advantage of PECVD over 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 bulk of the plasma and substrates do not reach high temperatures because of the non-equilibrium nature of the glow discharge plasmas. Another way of stating the temperature advantage is that at reasonable or acceptable temperatures, PECVD often has much higher deposition rates than conventional thermal CVD. Especilly, microwave plasma-enhanced CVD (MW PECVD) has several possible advantages over dc and rf induced plasmas : high electron temperature, high ion and radical densities, long life-time of radicals, low contamination and ease of operation etc. Silicon oxide films are very useful for transparent hard coatings, microelectronics-device fabrication, corrosion-protection coatings and oxygen-barrier coatings.

We have stdied the preparation of silicon oxide films at low substrate temperatures by PECVD using organosilicon compounds and oxygen as gas sources[3-8].

Recently water repellency is required in various fields. Tsuchiya et al. reported the silicon oxide films with high water repellency deposited onto glass plates by sol-gel method[9]. This method needs a curing process carried out at about 350℃ and can not be applied to the low heat-resistant substrates like resins. Many studies concerning the low temperature deposition of silicon oxide films by PECVD have been reported, but there are very few trials to add the water repellency on the silicon oxide films by PECVD.

In previous studies we reported on the preparation of silicon oxide films with high water repellency at low substrate temperatures by MW PECVD using mixtures of organosilicon compounds and FAS-17 with Ar as source gases.

In this study we investigate the effect of the substrate temperature during deposition on water repellency and hardness of the deposited films.

EXPERIMENTAL

Preparation of silicon oxide films with water repellency

The apparatus for a MW PECVD system is shown in Fig. 1. The preparation conditions are summarized in Table 1. This reactor was evacuated below 1 Pa by a rotary pump and then the vapors of reactants were fed above the substrate. Organosilicon compounds used were trimethylmethoxysilane(TMMOS), dimethyldimethoxysilane(DMDMOS), methyltrixmethoxysilane(MTMOS) and tetramethoxysilane(TMOS), Fluoro-alkyl silane (FAS-17; (heptadecafluoro-1,1,2,2, tetrahydro-decyl)-1-trimethoxysilane, $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)$ was also used. The properties of these compounds are shown in Table 2.

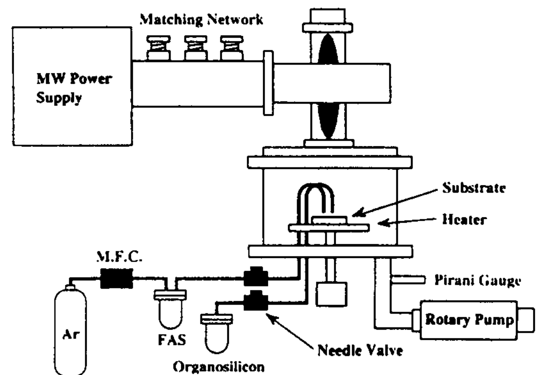

Fig. 1 Schematic diagram of experimental apparatus.

Table 1 N. Suginoto et al.

Total Pressure(Pa)	50
Partial Pressure of FAS-17/Ar(Pa)	25
Partial Pressure of Organosilicon Compound(Pa)	25
MW Power(W)	300
Substrate Temperature(℃)	R.T.~300
Substrate Position(mm) (form the center of plasma)	100
Substate[Si(100) size(mm×mm)	25×25
Deposition Time(min)	15

Table 2 N. Sugimoto et al.

Materials	Chemical Formula	B.P.(℃/Pa)	M.W
FAS-17	$CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$	85-87/133	568.1
TMMOS	$(CH_3)_3Si(OCH_3)$	57-58/ 1.0×10^5	104.2
DMDMOS	$(CH_3)_2Si(OCH_3)_2$	82-83/ 1.0×10^5	120.2
MTMOS	$CH_3Si(OCH_3)_3$	102-103/ 1.0×10^5	136.2
TMOS	$Si(OCH_3)_4$	121-122/ 1.0×10^5	152.2

Ar was used as a carrier gas for FAS-17 because because FAS-17 had high boiling temperature(85-87℃/133Pa). Ar flow rate was controlled with a mass flow controller at 20 sccm and Ar was bubbled in the FAS-17 vaporizer kept at 70℃. The gas tubing was also heated at 70℃ to prevent the vapor condensation. The gas pressure was measured with a Pirani gauge. The total pressure was fixed at 50 Pa.

A 2.45 GHz generator was used to induce a plasma with a cavity around the reactor. A 2.45 GHz microwave generated with a magnetron propagated to the discharge region through rectangular waveguides and a cavity. Substrates used were polished Si wafers which were used fter degreasing. The substrate temperature was measured by a chromel-alumel thermocouple and controlled at a constant value between at 60 and 300℃ using a heating unit. Microwave power was fixed at 300W. The pre-treatment by an oxygen plasma was carried out to remove contaminants on the substrate and to get the strong adhesion between the substrate and the deposited film. The film thicken was measured with a profilometer(Model:SV-600, Mitsutoyo Co., Ltd.).

Measurement of contact angles

Waer repellency was examined by measuring the contact angles. The contact angles for water drops(about 1.8㎜ diameter)were measured with an automatic contact-anglemeter (Model:CA-X 150, Kyowa Surface Science Co., Ltd.) by a drop method at 25℃ in the air. Contact angles at 10 points on a film picked up at random were measured and the average value was calculated after eliminating their minimum and maximum values.

Measurement of micro hardness

Micro hardness of the deposited films ws measured with a dynamic ultra micro hardness tester(Model : DUH-200, Shimadzu Co., Ltd.). A trigonal pyramidal diamond indenter was used at the load of 0.5gf. We indicate the total depth hardness corresponding to the sum of elastic and plastic deformation in this study.

Analyses of chemical bonding states

The changes in chemical bonding states of the deposited films with increasing substrate temperature were investigated with both Fourier-transform infrared spectroscopy(FTIR, Model:FT-IR-5300, JEOL Co., Ltd.) and X-ray photoelectron spectroscopy(XPS, Model : ESCA 1000, Shimadzu Co., Ltd.) with Mg Kα radiation at 10 kV and 30mA. XPS depth profiles of the films were obtained with Ar ion sputtering(8.0 kV, 30 mA).

RESULTD AND DISCUSSION

Deposition rate

The deposition rate depends on the preparation conditions such as the kind of orgnosilicon compounds and the substrate temperature.

Figure 2 shows the relationships between the substrate temperatures and the deposition rates of the films prepared with FAS-17/Ar and organosilicon compounds. The deposition rate decreases with increasing substrate temperature by every organosilicon compound.

The organosilicon compound which has more methyl(CH_3) gro-ups (that is, less methoxy (OCH_3)groups) gaves higher deposition rate at every substrate temperature. The maxi-

mum deposition rate is about 130nm/min when the film is prepared by FAS-17/Ar and TMMOS plasma at room temperature. Other rates are below 100nm/min. It is well known that perfluorocarbon is one of the useful plasma etching gases for silicon. Therefore, it is expected that perflu-orocarbon produced by the decomposition of FAS-17 acts as an inhibitor of plasma polymerization of a silicon compound.

Water repellency of the eposited films

Figure 3 shows the relationships between the substrate temperatures and the contact angles for water drops. The contact angles slightl decrease with increasing substrate temperature. The maximum contact angle is about 109℃ for the film prepared with FAS-17/Ar and TMMOS at room temperature. This value is comparable to the contact angle for polytetrafluoroethylene(PTFE, 108℃). The contact angles depend on the substrate temperature because of decreasing in C and F concentration due to pyrolysis of Si-C, O-C and C-C bonds in the deposited films.

The contact angles for the films prepared with FAS-17/Ar and TMMOS are above 100° at every substrate temperature. The contact angles depend on the number of $-OCH_3$ groups in the reactants. Because oxygen from the organosilicon compounds dissociates C-F bonds in the deposited films[10]. CH_3 is the hydrophobic group. Hence the more CH_3 groups the organosilicon molecule contains, the higher the contact angle becomes. Generally a film which has a contact angle more than 80° repressents high water repellency. The water repellency is improved enough by this method.

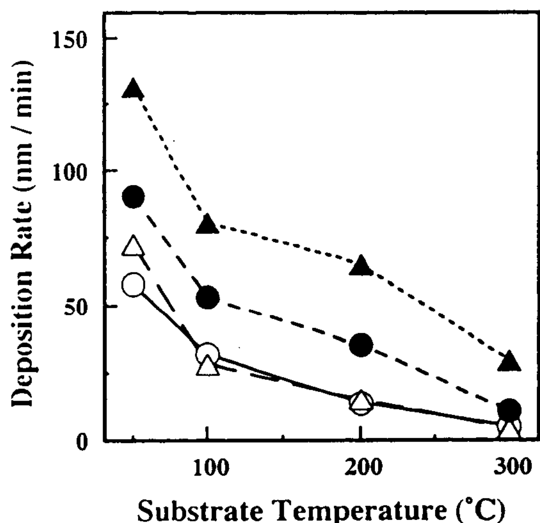

Fig. 2 Relationships between the substrate temperatures and the deposition rates ;
○:TMOS, △:MTMOS, ●:DMDMOS and ▲:TMMOS

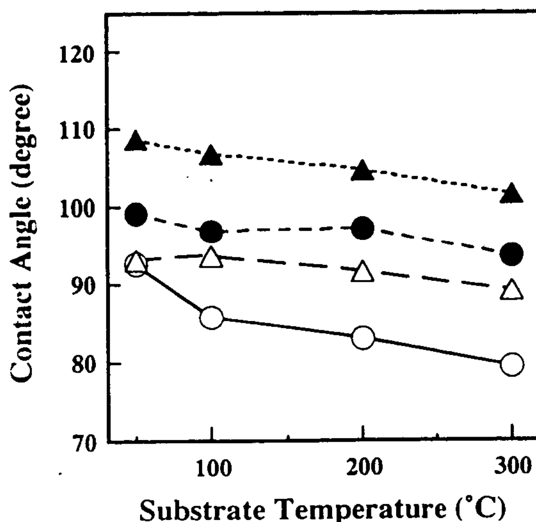

Fig. 3 Relationships between the substrate temperatures and the hardness;
○:TMOS, △:MTMOS, ●:DMDMOS and ▲:TMMOS.

Mechanical properties

Figure 4 shows the relationships between the substrate temperatures and the dynamic ultra micro hardness. Hardness of the deposited films increases with substrate temperature. The maximum hardness is about 900 for the films prepared with TMOS and FAS-17/Ar at 300℃. This value is comparable to glass hardness and is about 4 times larger than the value of the film prepared at room temperature. This tendency shows the promotion of pyrolysis of orgnic components of film, and the enhancement of dehydration and condensation reaction among Si-OH bonds by increasing substrate temperature.

Hardness of the deposited films increases with the numbers of methoxy groups in the organosilicon compounds. Oxygen in the organosilcon compounds plays a role of removing organic components in the deposied films as well as promoting oxidation of the deposited films. In our previous study the higher partial pressure of oxygen gas, the higher hardness of the deposited film was obtained at the high partial pressure of oxygen. Oxygen atoms in the organosilicon compounds work as a kind of oxygen additive gas.

FTIR measurements

Figure 5 shows the IR spectra of the films prepared with FAS-17/Ar and TMMOS as a function of substrate temperature. Three absorption bands due to asymmetric Si-O-Si stretching, Si-O-Si deformation and Si-O-Si rocking vibration are detected around 1075, 800 and 450cm^{-1}[11]. Bands due to C-F stretching vibration of the $-CF_2-$or CF_3-CF_2-groups are detected around 1250 and 1210cm^{-1}[11]. These bands indicate the formation of the fluorine-contained silicon oxide thin films.

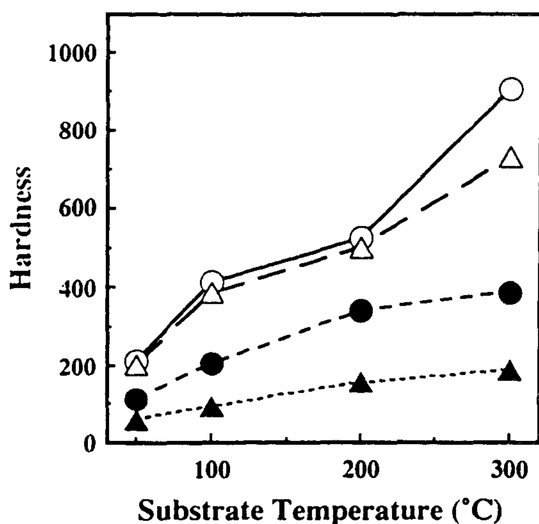

Fig. 4 Relationships between the substrate temperatures and the hardness;
○:TMOS, △:MTMOS, ●:DMDMOS and ▲:TMMOS.

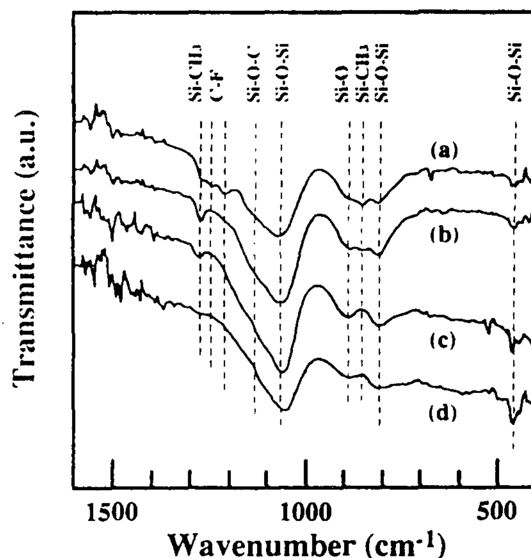

Fig. 5 IR spectra of the deposited films prepared with FAS-17/Ar and TMMOS; MW power =300W and total pressure=50Pa.

The bands due to C-F vibration becomeunclear with increasing substrate tempera-ture. The bands due to symmetric Si-CH_3 deformation vibration in the Si-CH_3 groups and due to Si-C rocking vibration are also detected around 1270cm^{-1} and 850cm^{-1}[11]. These bands also weaken with increasing substrate temperature. The bonding energies of Si-C(75.9kcal/mol), O-C(81.1kcal/mol) and C-C(96.0kcal/mol) are lower than those of C-F(129kcal/mol) and Si-O(126.7kcal/mol)[12]. Therefore, the decrease in C and F concentrations with increasing substrate temperature is explained by the dissoiation of Si-C, O-C and C-C bonds by increasing substrate temperature.

XPS measurements

Figures 6(a) and (b) show the depth profiles of the elemental concentrations in the films prepared with FAS-17/Ar and DMDMOS. For the film prepared at room temperature, the C concentration is about 45at% and F concentration is about 14at%. Since O is a little in the TMMOS molecules, the concentration of O is quite small. At 300 ℃(Fig.6 (b)), the concentrations of C and F decrease and O concentration increases. This result is due to promotion of pyrolysis of Si-C, O-C and C-C bonds, dehydration and condensation reaction among Si-OH bonds.

From these figures, it is found that the four elements are dispersed almost uniformly in the inner regions. In the study by Hozumi et al. 사hat prepared the silicon oxide films contained FAS-17 on PC substrates by dip coating[13], the fluorine was condensed at the surface and dilutes in the inner regions. The fluorine at the surface will decrease during long-period use due to abrasion or to decomposition of C-F bonds by ultra-violet rays. The homogeneous film prepared by this process, however, is expected to have, long lifetime in practical usage.

Figures 7(a) and (b) show the depth profiles of the elemental concentrations in the films prepared with TMMOS and FAS-17/Ar, and TMOS and FAS-17/Ar at room temperature. Compared two figures, we find that the C and F concentrations decrease and

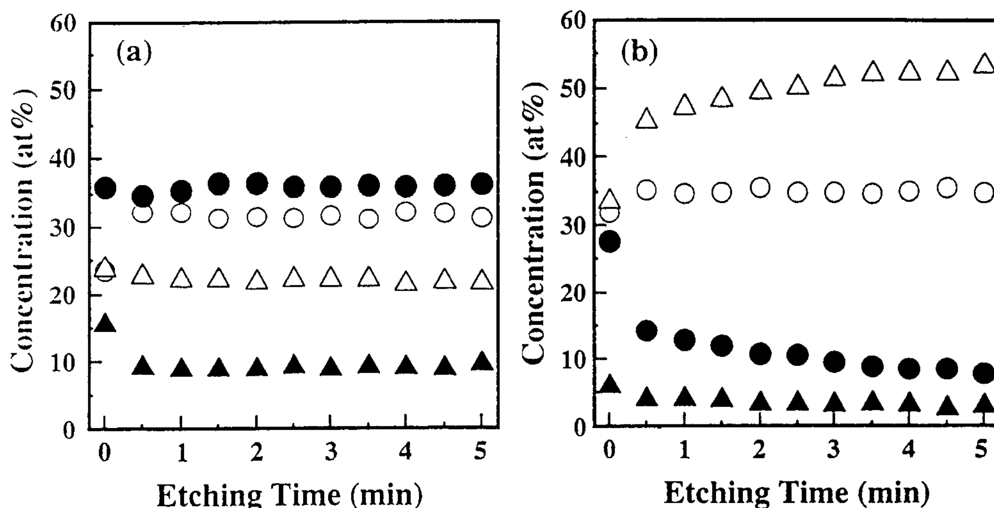

Fig. 6 Depth profiles of the element concentrations in the deposited films prepared with FAS-17/Ar and DMDMos; (a) T_s=R.T., (b) Ts=300℃, ○:Si, △:O, ●:C and ▲:F.

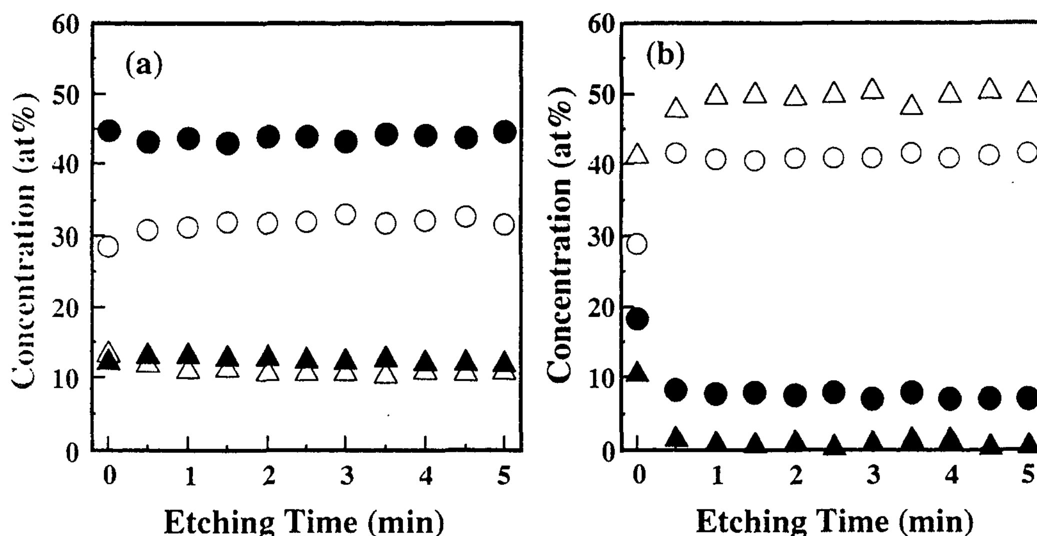

Fig. 7 Depth profiles of the element concentrations in the deposited films at room temperature; (a) prepared with TMMOS, (b) prepared with TMOS, ○ : Si, △ : O, ● : C and ▲ : F.

O increases with increasing numbers of methoxy groups in the organosilicon compounds. From these results, it is evident that methoxy groups plays a role of removing organic components of the deposited films.

CONCLUSIONS

We studied the effect of substrate temperature on film properties of silicon oxide films contained fluorine. We obtained the following conclusions:

1) The deposition rate and the contact angle of the deposited films decreased with increasing substrate temperature, but the hardness of the films increased.

2) The deposition rate and the contact angle decreased with increasing the numbers of the methoxy groups, but the hardness increased.

3) The pyrolysis of Si-C, O-C and C-C bonds, and the dehydration and condensation reactions among Si-OH bonds were promoted with increasing substrate temperature.

4) Oxygen in the organosilicon compounds played a role of not only promotion the dehydration and concentration reaction but removement of the organic components in the deposited films.

5) By this technique we can prepare the homogeneous films in depth which are very useful for long lifetime of water repellency.

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