PLASMA POLYMERIZATION OF ORGANOSILICON COMPOUNDS BY THE SELF-BIAS METHOD

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Organosilicon compounds were deposited in an RF cathode coupled plasma using Tetramethoxy silane. The films were deposited on silicon and glass substrates in negative self-bias voltages over the range of -80V to -580V. The deposited films were highly crosslinked and optically highly transparent between optical wavelengths from 420 nm to 1000 nm when oxygen was infused with the monomer.

1. Introduction

Plasma deposited silicon oxide films have been used for protective hard coating and optically transparent film for plastics and optical windows.[1] We have reported an RF plasma self-bias reactor system for deposition of silicon oxide films using an organosilicon compound as a Vinyltrimethoxy silane monomer. In the previous paper[2], we have reported self-bias method gives much higher deposition rate other than anode-coupled plasma reactor.

In this paper we present the results of deposited films under various plasma conditions as a function of negative self-bias voltage using Tetramethoxy silane (TMOS). We discuss the film characteristics and investigate the growth mechanism of the films in the self-bias cathode coupled plasma.

2. Experimental

The plasma polymerization equipment used in the present experiment is the PD-10S manufactured by SAMCO International, Kyoto Japan. Figure 1 shows a schematic of its reactor which has been modified into a cathode coupled plasma reactor. The experimental procedure involved pumping the reactor evacuate to a pressure below 5×10^{-5} torr using a mechanical rotary pump and oil diffusion pump, after which TMOS monomer was introduced with reactor pressure regulated by a fine needle valve. RF power between 10 - 150 watts was then applied for the deposition times of 5 - 15 minutes, and films were deposited on the silicon or cover glass substrate.

Figure 1. An RF Self-bias Plasma Reactor

3. Results and Discussion

Deposition Rate and Density

The level of self-bias voltage (V_b) is directly related to such factors as applied power, reactor pressure, distance between electrodes, and the ratio upper and lower electrode areas. As we shown in Fig. 2, self-bias is proportional to applied voltage, and is affected by reactor pressure.

Figure 3 shows the relationship between self-bias voltage, deposition rate, and film density. This data indicates clearly that as

Figure 2. Dependence of Self-Bias Potential on RF Power

Vb grows, the deposition rate increases at both levels of reactor pressure until eventually leveling off. We observe surface temperature of the substrate electrode by thermo-tape during polymerization, it was noticed that there was an increase in temperature proportional to time and self-bias Voltage.

Wood et al [3] examined the relationship between substrate temperature and deposition rate during the deposition of amorphous carbon film, and concluded that the deposition rate was faster at low temperatures than at high substrate temperatures because at low substrate temperatures the adsorption of fragments increases and the sputtering effects are reduced.

In the case of polymerization of TMOS it also shows that an increase of Vb causes a increase of substrate temperature. As the result, the deposition rate seems to be increased by the above factors. It is also suggest that films deposited under high Vb show highly crosslinking due to increased ion bombardment.

Composition of Films

Figure 4 shows the result of EDS spectrum of a typical film. This equipment is configured for boron (B) and is not able to qualify hydrogen, but C, O and Si were detected from the film.

Figure 5 shows the infrared spectrum of each films. Each reversion is assigned as follows:

Figure 3. Deposition Rate and Film Density at Different Self-Bias Potential

— ○ : 0.15 torr , — ● : 0.3 torr

Figure 4. EDS Spectrum of the Deposited Films

2950,2850cm ⁻¹ (C-H)	2230cm ⁻¹ (Si-H)
1460cm ⁻¹ (-CH ₂ or -OCH ₃)	1270cm ⁻¹ (SiCH ₃ , Si(CH ₃) ₂)
1195cm ⁻¹ (Si-O-CH ₃)	1100-1000cm ⁻¹ (Si-O-Si)
885cm ⁻¹ (Si-C)	805cm ⁻¹ (Si-O-Si)
440cm ⁻¹ (Si-O-Si)	

Films obtained in low V_b are polymers that leave intact part of the source monomer composition. Since the adsorption peak shows bonding between silicon, hydrogen and carbon atoms, it is suggested that Si-C, O-C, and C-H rebonded after initial disassociation.

On the other hand, absorption peak of films obtained at high V_b is almost all absorption peaks based on Si-O-Si(1032,805,440cm⁻¹), and some absorption peak of Si-C(885cm⁻¹) and -OH(around 3600cm⁻¹) are observed. From this results it can be seen that the film configuration shows highly crosslinked Si-O-Si crosslinked bonding, but it suggested that the films are not completely oxidized as a silicon dioxide.

Wettability of Films

Figure 6 shows the wettability of films deposited at different V_b levels were measured contact angle after deposition (Thickness: about 1 μm). Wettability of the surface is variable and dependent on V_b. We observed the higher V_b is, the more hydrophilic surfaces. This results suggested influenced by the amounts of hydrophobic functional groups (methyl radical etc.) and

Figure 5. IR Spectra of the Films Deposited at Different Self-Bias Potential
a: Si(OCH₃)₄, b: -80V c: -580V

Figure 6. Self-Bias Voltage and Wettability

corresponds with the result of infrared absorption spectrum.

Reaction in Plasma and Ion Sheath

It is known that different film structure are produced by reactions in bulk plasma and reactions in the ion sheath. This is because the substrate electrode is negatively charged and is affected by the bombardment of positive ion impacts. In order to further examine this, we examine moved the position of substrate and compared the reaction in the plasma.

Figure 7 shows a comparison of the deposition rate. As the substrate is moved further away from the cathode, the deposition rate and films hardness are decrease. The boundary was the area dividing the plasma and the ion sheath.

Regarding the reaction mechanism of plasma polymerization, whether the polymerization activated species are ions or neutral radicals depends on reactor structure. Our experimental data shows clearly that the influence of ion impact on deposition rate, hardness and film density.

Figure 8 shows infrared absorption spectrum of films grown in the sheath and the bulk plasma.

Films grown in bulk plasma show absorption of $-\text{CH}_3(2950\text{cm}^{-1})$, $-\text{CH}(2847\text{cm}^{-1})$, $\text{SiH}(2235\text{cm}^{-1})$, $-\text{SiCH}_3$, $-\text{Si}(\text{CH}_3)_3(1268\text{cm}^{-1})$, $-\text{SiC}(885\text{cm}^{-1})$ etc., which is similar to the films obtaining at low V_b . Therefore, reaction mechanism in the

Figure 7. Deposition Rate and the Different Substrates Position

Figure 8. IR Spectra of the Deposited Films in a Sheath (a) and Bulk Plasma (b)

ion sheath is assumed to be formed activated species by ion bombardment and simultaneously form crosslinking structures by dissociate molecular chains due to the polymerization process.

Effect of Addition of Oxygen with the Monomer

The higher Vb condition, the resulting high hardness films. But at the same time the coloring of the film itself also becomes low transparency. To improve the low transparency of the films we examined the effect of adding oxygen. Figure 9 shows transmission of the spectrum for visible and near infrared.

When oxygen is added, transparency much improves visibly and allows for the growth of transparent films. Especially, the transparency of wavelengths below 570nm was greatly improved.

The composition of the films was shown in figure 10, we obtained at Vb; -380V, O₂; 200ml/min shows infrared absorption spectrum a patterns similar to that of amorphous silicon dioxide. On the other hand, when films(b) obtained at Vb;-110V, O₂;200ml/min show clearly absorption based on -OH(3350, 929cm⁻¹).

If one of the possibility is that even when the ratio of monomer to oxygen is the same the difference of Vb (ion impact) influences film composition, it could be thought that ion impact affects and disassociation of dimer or polymer in the SiO₂ formation process, and that

Figure 9. VIS/Near IR Spectra of the Deposited Films from TMOS and TMOS with O₂
a: monomer only, b: monomer/O₂ gas

Figure 10. IR Spectra of the Deposited Films with Oxygen and TMOS
a: -380V, O₂ 200ml/min ;
b: -110V, 200ml/min

the reaction must be greatly contributed to by ion bombardment.

Table 1 shows film density and knoop hardness obtained when oxygen is added. Adding oxygen increases film density to near the level of silicon dioxide. This is consistent with the results of infrared absorption spectrum as described above. Adding oxygen is also effective in improving knoop hardness, since with only monomer the hardness was 618 kg/mm² and when 100 ml/min of oxygen was added the hardness was 668 kg/mm² respectively.

Table 1. Film Density and Hardness of the Films with TMOS

O ₂ flow rate (ml/ min)	density (g/cm ³)	knoop hardness (kg/mm ²)
0	2.1	618
20	2.2	-
50	2.2	-
100	2.3	668
200	2.3	-

4. Conclusion

Organosilicon compounds were deposited in a cathode coupled parallel plate electrode configured reactor using Tetramethoxy silane (TMOS) source materials. Under low self-bias conditions the resulting films displayed Si-C, O-C, and C-H bonding. In high self-bias potential ranges the films were almost Si-O-Si silicon oxides. The addition of O₂ during film deposition resulted in the improvement of film hardness and optical transparency. The increase in optical transparency was especially noteworthy for wavelengths below 590 nm.

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