



# Deposition of silicon oxycarbide thin films from an organosilicon source for polycarbonate glazing

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## ABSTRACT

To enhance the abrasion resistance of polycarbonate used to replace glass, a silicon oxycarbide thin film was deposited at  $< 100$  °C using a slot antenna electron cyclotron resonance plasma enhanced chemical vapor deposition system and an organosilicon source. The thin film deposition rate, which varied as a function of microwave power and whether Ar or O<sub>2</sub> was used to form the plasma, was above 500 nm/min even at 2 Pa, and reached 1 μm/min as the microwave power increased. The transmittance of visible light was over 90% after thin film deposition, indicating performance similar to that of glass. The Taber abrasion test showed that the Δhazes of the thin films were under 5%, which indicates better performance than the siloxane-based wet coating sample (Momentive, AS4700) and the commercial hard plasma coating product LEXAN MR-10. Furthermore, the thin film deposited at 1.7 kW exhibited similar abrasion resistance to that of glass. In addition, adhesion improved significantly when consecutive, minute-long 1.7 kW Ar and O<sub>2</sub> plasma surface treatments were performed before the depositions.

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## 1. Introduction

Interest in polycarbonate as an engineering plastic has risen as researchers have attempted to resolve the disadvantages of weight, difficulty of molding, and fragility encountered with tempered glass. Research on the replacement of glass with polycarbonate has recently been conducted in the mobile phone and automobile industries. Polycarbonate transmits  $> 90\%$  of visible light and has an impact strength  $> 30$  times greater than that of glass. In addition, it is 50% lighter and can be processed inexpensively for use in various applications because flexibility can be added to the product design. However, polycarbonate has lower abrasion, scratch and chemical resistances than glass, and requires a transparent, abrasion-resistant coating [1–3]. In our previous studies, various Si-based thin films (SiN<sub>x</sub>, SiO<sub>x</sub>N<sub>y</sub>, and SiO<sub>x</sub>) were deposited using SiH<sub>4</sub> as the silicon precursor, based on changes in O<sub>2</sub> and N<sub>2</sub> gas flows. The properties of the layers were compared and assessed. However, it was difficult to quickly deposit dense thin films with SiH<sub>4</sub>, and the resulting abrasion resistance was worse than that of existing siloxane-based wet coating [4].

In this study, silicon oxycarbide thin films were deposited using organosilicon instead of SiH<sub>4</sub> as a silicon precursor, and the characteristics of the resulting films were examined as a function of plasma gas selection and microwave power. In addition, the abrasion resistance of the deposited film was compared with those of a siloxane-based wet

coating sample (Momentive, AS4700) and the hard coating product LEXAN MR-10. It is thought that most of the plasma energy is used for dissociation of precursor molecules when silicon oxide or nitride thin films are deposited using SiH<sub>4</sub>, and there is not sufficient energy to make dense Si—O and Si—N networking. However, organosilicon already has C—Si—O bonding, and silicon oxycarbide thin films are deposited by removing H bonding without additional bonding process. In this process, our low process pressure and high ion densities may help to remove the byproducts generated in the reaction and to compact growing film. This contributes significantly to improving abrasion resistance.

## 2. Materials and methods

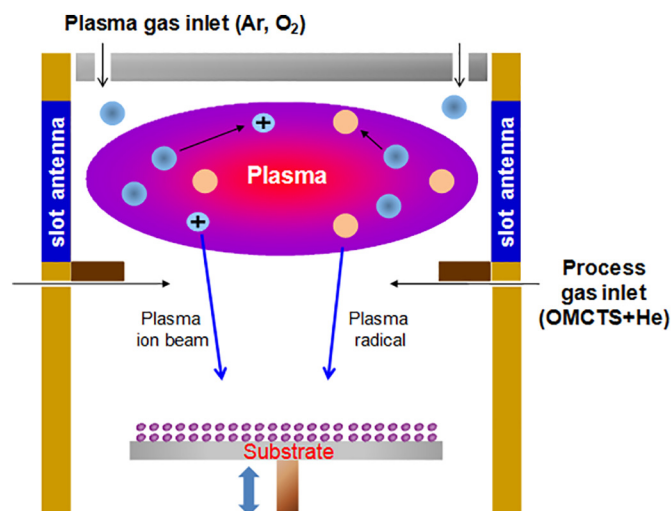
### 2.1. Slot antenna electron cyclotron resonance (SLAN ECR) plasma enhanced chemical vapor deposition (PECVD) system

The SLAN ECR PECVD system uses 2.45 GHz microwave (MW) energy, and has a high ion density of  $10^{10}$ – $10^{11}$  cm<sup>-3</sup>, even at a pressure of 0.2 Pa, which helps fast deposition of high-quality thin films at low temperatures. This contrasts with typical 13.56 MHz capacitive radio frequency plasma sources with ion density of  $10^9$ – $10^{10}$  cm<sup>-3</sup> [5]. Details of the structure and characteristics of the SLAN ECR plasma source have been published previously [6].

Fig. 1 is a schematic diagram of the SLAN ECR PECVD system. The system was composed of a cylindrical plasma source and deposition chamber. The Ar and O<sub>2</sub> gases used in plasma formation were supplied from the plasma source. The octamethylcyclotetrasiloxane (OMCTS)

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**Fig. 1.** Schematic diagram of a SLAN ECR PECVD system with downstream organosilicon/He gas injection and Ar/O<sub>2</sub> plasma gas injection into the slot antenna.

silicon precursor and He carrier gas for thin film deposition were supplied by the deposition chamber. This was done to minimize the effects of particle and byproduct formation on microwave transmission. Particle and byproducts are generated if the precursor is directly inserted to an area in which plasma is generated.

## 2.2. Sample preparation

Organosilicon is a silicon precursor that is frequently used with SiH<sub>4</sub>. It is safer and easier to handle than SiH<sub>4</sub> and the Si—O bonding in its molecular structure facilitates the deposition of silicon oxide-based materials. Widely used organosilicon materials include hexamethyldisiloxane (HMDSO) [7], OMCTS [8], and tetramethylcyclotetrasiloxane (TMCTS) [9]. Their molecular structures and properties are shown in Table 1.

In this experiment, OMCTS was used as a silicon precursor during silicon oxycarbide deposition because it exhibits more C—Si—O bonding than HMDSO and TMCTS, and has exhibited good characteristics in previous studies [11]. OMCTS is a liquid at room temperature and was evaporated using a bubbler system so that it could be supplied to the chamber. Fig. 2 shows a schematic diagram of the bubbler system, which included an organosilicon storage canister, a heater jacket to maintain the temperatures of the canister

and pipeline, and a mass flow controller (MFC) to control the flow of the carrier gas.

The canister temperature was maintained at 105 °C to produce a vapor pressure of 13.3 kPa, and the pipeline was maintained at 120 °C to prevent OMCTS condensation. The OMCTS flow rate was approximately 40 sccm. Nonreactive, high-purity (>99.99%) He was used as a carrier gas. In addition, high-purity (>99.99%) O<sub>2</sub> or Ar was supplied directly to the chamber for plasma generation. The p-type (100) c-Si wafer and Lexan ULG 1003 polycarbonate sheet (100 mm × 100 mm × 3 mm) that were used as substrates were cleaned before deposition. The c-Si wafer was cleaned using a standard RCA process [12], and the polycarbonate sheet was dipped in isopropyl alcohol for 10 min and rinsed with de-ionized water. The surface of polycarbonate sheet was pretreated before thin film deposition with consecutive Ar and O<sub>2</sub> plasmas for 1 min each to improve adhesion between the substrate and the thin film. Immediately after the surface treatment, a silicon oxycarbide film was deposited for a period of 5 min. The substrate temperature was determined by using a temperature label tape which was attached to the front-side of the substrate (THERMO LABEL-8E, NiGK Corporation). The substrate was maintained at room temperature (RT) before processing and heated to 80 ± 5 °C by plasma after processing. The detailed deposition conditions are listed in Table 2 and the characteristics of the thin film were examined at microwave power levels of 1.2, 1.7, and 2.0 kW, and with Ar and O<sub>2</sub> as plasma gases.

## 2.3. Measurement techniques

The thickness and transmittance of the thin film were measured via spectroscopic ellipsometry (M2000D, Woollam) with a wavelength range of 193–1000 nm (incident angle: 75°, five-point mapping) and UV–Vis spectroscopy (Carry 300, Agilent) with a wavelength range of 400–4000 nm, respectively. Hardness was measured using a nano-indenter (Nanoinder-XP, MTS) with a Berkovich tip at loads ranging from 0 to 50 mN (load resolution: 50 nN, displacement resolution: <0.01 nm, five point mapping). The bonding configurations of the film components were measured via Fourier transform infrared spectroscopy using transmission mode (FTIR, IFS66V/S & HYPERION 3000, Bruker) with a wavenumber range of 500–4000 nm (optical resolution: 0.085/cm, time resolved spectroscopy: <5 ns). The film composition was measured using X-ray photoelectron spectroscopy with monochromatic Al K $\alpha$  (ESCALAB 250, Thermo VG Scientific) after sputtering the surface with Ar ions to a depth of 10 nm to remove surface impurities. The density of the thin film was measured using high resolution X-ray

**Table 1**  
Properties of HMDSO, OMCTS and TMCTS [10].

HMDSO	OMCTS	TMCTS					
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\   \quad   \\ \text{H}_3\text{C}-\text{Si}-\text{O}-\text{Si}-\text{CH}_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$			Precursor	Molecular weight	Vapor pressure	Boiling point	Melting point
HMDSO	162.38	6650 Pa at 30 °C	99–100 °C	−67 °C			
OMCTS	296.62	133 Pa at 23 °C	175–176 °C	17.4 °C			
TMCTS	240.51	133 Pa at 30 °C	134–135 °C	−69 °C			

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