Deposition of SiO$_2$ Thin Films by Atmospheric Pressure Glow Plasma on Polycarbonate

Shohei Masuda, Kunihiro Tanaka and Masuhiro Kogoma

Department of Chemistry, Faculty of Science and Technology, Sophia University, Tokyo, Japan
7-1 Kioicho, Chiyoda-ku, Tokyo, Japan

SiO$_2$ films were deposited using both atmospheric glow plasma chemical deposition (APG-CVD) and spin coating as hard coating agents for their abrasion resistance. Tetraethoxyxilane (TEOS) was used as the precursor. We formed films by spin coating on surfaces over APG-CVD as adhesive interlayer, and were able to achieve a hard deposited film without any cracks.

Keywords: SiO$_2$, Plasma CVD, Polycarbonate

1. Introduction
At present the demand of engineering plastic for use in OA devices and precision instruments has been increased. Polycarbonate (PC) is expected as a new material in place of glass, because of lower weight, higher freedom of design and greater safety. Especially at the points of promotion to get better mileage and to limit of scatter fragments, it use as window glass of cars has been anticipated.

However it shows poor abrasion. To solve this problem, we considered applying a thin coating of SiO$_2$ on PC surfaces. But one needs to have a low temperature process, as the glass temperature of PC is low (approximately 130 °C). Therefore, it is necessary to find a method of deposition of SiO$_2$ films at a low temperature.

Atmospheric glow plasma chemical vapor deposition (APG-CVD) is a technology that can work at low temperature without a vacuum chamber and the related pumping system [1]; it has been successfully used for the deposition of SiO$_2$ films uniformly so as to simplify the treatment process and to reduce cost. However, the thermal expansion coefficients of PC and those of the desired SiO$_2$ film differ. Thus, a simple quartz coating on PC will crack under thermal stress. Also in the spin coat method of organosilicon, one does not need heat treatment and one can deposit thin films of SiO$_2$ by hydrolysis. But generally the affinity is not good between PC and SiO$_2$. One can achieve only weak adhesive strength with the deposited film.

In this study, we deposited film by spin coating on surfaces over APG-CVD as adhesive interlayer to achieve surface hardness of glass without any cracks.

2. Experimental
2.1. Materials
In deposition on untreated PC, surfaces are too soft to prevent dents of the surface. In order to attain a certain hardness, we used a hard coating PC (HC-PC) which is a film on PC that can harden its surface. HC-PC film (Tg: 130 °C), 15 mm

Fig. 1. Schematic diagram of the reactor used in this study.

Received April 2, 2008
Accepted May 16, 2008
long × 30 mm wide and 1 mm thick, was provided by Mitsubishi Chemical Co.Ltd. The hard coat layer is compounded from SiO₂ nano particles and polymers having an acryloyl group at side chain, and is cured by UV irradiation.

The HC-PC film was washed with ethanol in an ultra sonic washer prior to the plasma deposition. Tetraethoxysilane (TEOS) was purchased from Wako Co. and was used for plasma deposition and spin coating.

2.2. Plasma deposition

A schematic of the setup is shown in Figure 1. It consisted of a gas introducing system, a discharge part, a pulse-modulated generator (frequency 3 MHz) and a water-cooling system. Helium and oxygen were chosen as the carrier gas and reactive gas; their flows were controlled by mass flow controllers. The flow rate of carrier helium is 20 l/min⁻¹; it contains 0 to 5 cm³ min⁻¹ of mixed oxygen. Liquid TEOS was used as precursor in a reservoir. The reservoir was kept in a temperature-controlled oven at 100 °C to increase the vapor pressure of TEOS. Afterwards, the TEOS vapor flow rate was adjusted to 1.23 cm³ min⁻¹ by bubbling with helium gas. Then the gas with TEOS was introduced into the discharge part to produce plasma. The discharge part was formed by two parallel electrodes. The bottom electrode which is covered by alumina is a copper electrode 6 cm in diameter and the electrode gap is 5.2 mm between the electrodes. To assure deposit uniformity, the upper electrode used a perforated board (0.5 mm φ mulch hollow) to blow the monomer vapor through the upper electrode. The high voltage source (500 W; modulation frequency, 10 kHz; duty ratio, 30%) was connected to the bottom electrode. PC substrate was put on the center of the bottom electrode.

2.3. Spin coating deposition

TEOS was introduced onto the deposited thin film using a micro pipet, then spun with 2000 rpm. A thin liquid layer of the TEOS is formed on the substrate surface by the surface tension of the liquid. The coated film is heat-treated at 60 °C for one day in the atmospheric ambience.

2.4. Characterization

The chemical state of the deposited films was determined by XPS (ESCA-5800ci,ULVAC-Phil Co.Ltd.) and FT-IR(FT-IR-4100,JASCO Co.Ltd.). Thickness was measured by DEKTAK III (SLOAN Co.Ltd.). The surface morphology of the coating PC was characterized using SEM (S-430,HITACHI Ltd.). The surface hardness was measured with a steel wool abrader under 1 kg loading. The extent of abrasion caused by the cycle of the abrasive loading was determined as a relative hardness. Relative hardness is defined as Relative hardness(%) = T_d/T_b × 100, where T_d represents the visible transmittance (wavelength 500 nm) after abrasion test, and T_b is that before abrasion test. Visible transmittance was measured by an UV-spectrophotometer (JASCO, V-650).

3. Results and discussion

3.1. Deposition by APG-CVD

Figure 2 shows the carbon content in the films and the deposition rate when changing the flow rate of oxygen (discharge time 30 min). As the result, the carbon content and the deposition rate were reduced to 4 cm³ min⁻¹ in flowing oxygen. At the same time, in case of increased oxygen flow rate, the carbon content was saturated. TEOS was oxidized and the deposited film was made more precise by adding oxygen, in the condition of oxygen flow 4 cm³ min⁻¹, O/Si=2.02. The deposited film is high purity SiO₂. However, for deposited film close to SiO₂, many cracks were found, caused by large differences of the thermal expansion coefficients between substrate and coated film.

SEM images in Figure 3 show the deposited film without oxygen (a) and at 4 cm³ min⁻¹ of oxygen (b) by APG-CVD. In (a) nothing is cracked; in (b) there are cracked points. This result showed that the crack depends on organic elements in the deposition film. We tried an abrasion test of deposited film surfaces to measure hardness. In Figure 4, the relative hardness is indicated when oxygen flow
Fig. 3. SEM images of the coated HC-PC about 3 μm by APG-CVD (a) O₂ free (b) O₂ 4 cm³ min⁻¹.
rate was changed for about 3 μm deposited film thickness. In case of no oxygen, the film easily shaved and showed low hardness. At 3 cm³ min⁻¹ of oxygen flow rate, hardness is 90.8 % and at 4 cm³ min⁻¹ is 95.7 % in 100 times abrasion test. The more oxygen we added, the more it hardened. The results so far have confirmed that the closer the composition of deposited film becomes to that of SiO₂, the better the film hardened.

At the next stage, we estimated the change of deposited film. Figure 5 shows the relative hardness for several discharge times (oxygen flow rate 4 cm³ min⁻¹). At 3 minutes of discharge time, the relative hardness decreased in 5 times abrasion test. Afterward it increased by 100 times abrasion test. This means that deposited film was shaved and a naked HC-PC sample surface appeared. In abrasion tests of 15 min (thickness 1.68 μm) and 45 min (4.87 μm) in discharge time, results confirmed that the relative hardness will not drop too much. The more time increased, the higher the hardness in these results. But in the discharge time result for more than 3 minutes (film thickness about 300 nm), cracks were confirmed by sight. In the case of discharge time for 45 minutes, high hardness (97.7 %) appeared, but there were cracks in the deposited film. These results show that suitable composition causes relative hardness of deposited films. However, increasing film thickness caused cracks in the film.

3.2. Deposition by spin coating

The spin coat - Sol Gel film with TEOS is known to not crack easily. But it is treated with only spin coat and is difficult to match with polymer. And also the deposited film is easy to peel off. To solve this problem in adhesive interlayer, we deposited the SiO₂ thin film in about 300 nm thickness with APG-CVD. Above it, we deposited by spin coating using TEOS. The network construction in layers will resolve this problem by deposition of a film which is similar to SiO₂ in composition with APG-CVD in adhesive layer. The spin coat method will not affect the substrate much, due to heating. So we are able to expect that this process will totally increase the film thickness in deposited film and reduce the tendency to be cracked.

A SEM image in Figure 6 shows the heated film
on which was deposited APG-CVD to 300 nm and on which TEOS was spin coated. A flat deposition film without cracks is confirmed. We evaluated the surface composition by XPS in spin coat film. Results are as follows: C, 9.58%; O, 60.97%; Si, 29.46%. The thickness is about 1.4 μm. Comparing to APG-CVD, much carbon content is contained in the deposited film; nevertheless we succeeded to make a thin film with no cracks.

Figure 7 shows a comparison of relative film hardness; both APG-CVD and spin coating are shown, along with HC-PC substrate. It is thought that there is an effect in the adhesive interlayer. Also this test with 100 repeated abrasions enabled us to gain a flat film in relative hardness of 94.2%.

When we tried peel tests with scotch tape, it never came off. This result shows good adhesive quality. In Figure 8 we show FTIR-ATR spectra for (a) HC-PC substrate; (b) film deposited by spin coating after APG-CVD treatment; and (c) film deposited by APG-CVD (500W, O₂, flow rate: 4cm² min⁻¹). And as object of comparison, we show the (d) spectrum of pure SiO₂ particles too. In all spectra, sharp peaks like a Si-O-Si stretching vibration appear near 1100 cm⁻¹. We confirmed that the spectra get closer to that of (d) pure SiO₂ in the order of (a), (b), (c). In comparison to this, the spectra show clearly that A peaks (1700 cm⁻¹, COOH stretching bending; 1543 cm⁻¹, C=C stretching

![Graph](image.png)

**Fig. 7.** Relative hardness as a function of number of wear cycles on substrate and spin coated and APG-CVD + spin coated.

![Graph](image.png)

**Fig. 8.** FTIR-ATR spectra of the various films: (a) Hard coating PC substrate, (b) Deposited by spin coating after APG-CVD, (c) Deposited by APG-CVD, (d) SiO₂ powder.

der are soft. This result came from organic compositions. It suggests that APG-CVD film has comparatively pure SiO₂. This is considered the reason why we failed to achieve perfect hardness, like that of glass.

4. Conclusion

We deposited the film with more pure and thin SiO₂ films. Then we could achieve high relative hardness. But such films cracked a lot. In order to resolve this problem, we tried to deposit thin film without cracks of about 300 nm thickness by APG-CVD as adhesive interlayer, and then to spin coat. As a result, we succeeded to make a deposited film of comparatively good hardness without cracks. But it has not been as hard as glass, due to a little organic composition remaining. We have been thinking how we can make purer and harder film by SiO₂ film deposition on spin coated film with APG-CVD.

References