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The growth of organosilicon film using a hexamethyldisilazane/oxygen atmospheric pressure plasma jet

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ABSTRACT

An atmospheric pressure plasma jet, using a hexamethyldisilazane and oxygen mixture, was used to deposit an organosilicon thin film on polycarbonate (PC) substrates. The atmospheric pressure plasma jet deposited homogeneous thin films without unfavorable contamination from the plasma source. The surface properties of the organosilicon thin films were studied as a function of oxygen gas flow rate. The atmospheric pressure plasma deposited organosilicon thin films were analyzed using Fourier transform infrared spectroscopy, X-ray photoelectron spectroscopy, UV–vis spectrometry and atomic forced microscopy. Surface analysis showed that atmospheric pressure plasma deposited films are more inorganic as the oxygen flow rate increases. The UV–vis spectra, detected in the range 300–800 nm, demonstrated improved transparency in the visible region and increased absorption in UV region of the spectrum. The improved hardness of the atmospheric pressure plasma deposited PC substrates was measured using a pencil hardness testing method and this was related to the chemical composition of the plasma deposited organosilicon thin films. The plasma jet allowed deposition of the coating without a chamber.

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1. Introduction

In recent years, polycarbonate substrates have been progressively replacing glass substrates, because of their lighter weight, low cost and light transmission characteristics similar to glass. Many commercial products, such as optical lenses, digital electronic panels and automotive headlamp lenses, use plastic substrates. However, the components of plastic substrates are intrinsically soft, so the use of polycarbonate (PC) is limited to light applications.

To address the inherent restrictions of PC substrates, a variety of fabrication methods involving protective coatings have been proposed during the last decade [1–3]. For most of the protective coatings used for modern technologies, organosilicon (SiOx) films are required to be ultra-thin, uniform, adhesive and scratch-resistant. The atmospheric plasma chemical vapor deposition process seems to be an ideal technique for the application of protective coatings [4–8]. It overcomes many of the inherent problems to provide an ultra-thin, extremely hard, crack-resistant coating using a simple process. In addition, atmospheric pressure plasma deposition coating onto PC substrates allows the modification of the PC substrate surface, without altering the substrate's bulk properties.

The atmospheric pressure plasma process is particularly attractive for thin film deposition, because the process is not limited by the size of the reactor chamber [5,6]. However, residual deposition of the electrodes inside the atmospheric pressure plasma source causes an undesirable degradation in the performance of the atmospheric pressure plasma source. To address the unfavorable deposition of electrodes, a new atmospheric pressure plasma source is proposed. Measurement of the temperature of atmospheric pressure plasma indicates that the gas phase temperature is very close to room temperature. The use of a pure organosilica precursor in atmospheric pressure plasma deposition could produce polymer-like coatings, in which hydrocarbons in the form of methylene and methyl groups remain in the SiOx films. By adding oxygen to the plasma deposition process, the hydrocarbon content is etched away by oxygen plasma species and consequently forms hard SiOx films.

The removal of the methyl groups and the subsequent altering of the electrical properties such as the k-value are referred to as plasma-damage. Hence, it is critical to heal plasma-damaged SiOx films and restore their intrinsic structural and electrical properties. In recent years a few studies have tried to minimize plasma-damage on thin films. Processing with a hexamethyldisilazane (HMDSN) precursor is one way to heal the damaged films [9,10]. In this paper, SiOx films are produced using low temperature atmospheric pressure plasma chemical vapor deposition and surface characteristics are examined using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), UV–vis spectrometry and Atomic forced microscopy (AFM) analysis.

2. Experimental details

2.1. Atmospheric pressure plasma deposition system

SiOx films were deposited in an atmospheric pressure plasma system, as shown in Fig. 1. This system contained a plasma jet and a movable

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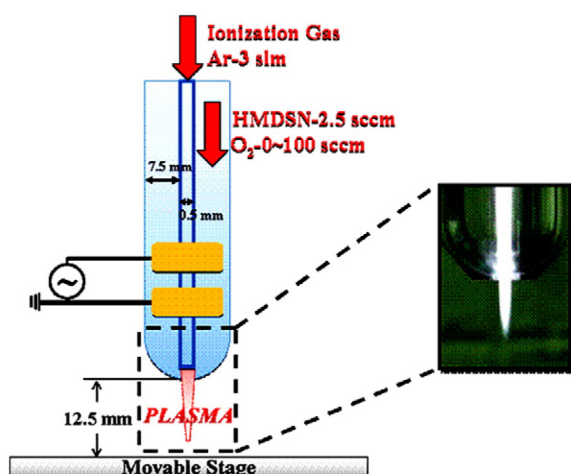

Fig. 1. Schematic diagram of the atmospheric-pressure plasma system.

table. In most atmospheric pressure plasma setups, the residential plasma polymers are always deposited in a plasma jet. To address this problem, a double-pipe type quartz tube was used as the plasma jet system, through which various gases flowed at controllable rates of flow [5]. A quartz capillary (0.5 mm diameter) was inserted into a quartz tube with a larger inner diameter (15.5 mm diameter), to form double-pipe quartz tube. In this design, the precursor and the carrier gas do not interfere with plasma deposition, since the quartz capillary acts as a barrier. High-speed Argon gas (3000 sccm) flows from the top of the plasma system and passes through the quartz capillary as the ionization gas.

The precursor and oxygen (0–100 sccm) are guided into the plasma system through the annular space between the quartz tube and the capillary and serve as a monomer. The precursor flow rate is maintained by the carrier gas (argon) at 100 sccm, using a mass flow controller. Two copper annular electrodes are placed face to face inside the quartz tube. An electrical field is applied to the two electrodes, using a 13.56 MHz RF power supply, in order to ignite the plasma glow discharge. A capacitive coupled RF plasma source power is in continuous mode.

The HMDSN precursor was introduced into the mixing system (evaporator) and the temperature was maintained at 150 °C. The HMDSN precursor gas flow rate was maintained at 2.5 sccm, using a mass flow controller. Fig. 1 also shows the luminous gas phase of this atmospheric pressure plasma jet. The stable and characteristic plume-shaped atmospheric pressure plasma glow is clearly seen in the dark space. The gas phase temperature of the atmospheric pressure plasma jet, maintained by a 100 W electrical power supply, was measured using a thermocouple thermometer. The thermocouple was placed on the tip of the characteristic plume-shaped atmospheric pressure plasma glow, to measure the gas phase temperature. When the flow rate of the Argon increases from 3000 to 10,000 sccm, the gas temperature of the atmospheric pressure plasma jet is reduced from 78 °C to 40 °C, which clearly shows the low-temperature nature of this atmospheric plasma source. An increase in the gas flow rate causes a further decrease in the temperature of the atmospheric pressure plasma to almost room temperature.

2.2. Film characterization and analysis

The thickness of the atmospheric-pressure plasma deposited SiOx film was measured using an optical thin-film thickness detector at a wavelength of 632.8 nm. The chemical structure of the atmospheric pressure plasma deposited SiOx films was characterized using an FTIR spectrometer (Perkin-Elmer LX 20000 G). Each spectrum represents an average of 32 scans in the range 400–4000 cm^{-1} at a resolution of 4 cm^{-1}. The chemical composition of the atmospheric pressure plasma deposited SiOx films was examined using an XPS. XPS measurements were performed on a VG Scientific Microlab 310F system, using a monochromatic Al Kα X-ray source. Sputter depth profiling was performed using a beam of Ar ions with an acceleration voltage and spot size of 1 kV and 400 μm. Spectra were acquired with the angle between the direction of the emitted photoelectrons and the surface equal to the take-off analysis angle of 60°. UV–VIS transmission detection was performed using a GBC Cintra 202 UV spectrophotometer, in order to determine the transmittance of the atmospheric pressure plasma deposited SiOx films. The surface morphology and roughness of the atmospheric pressure plasma deposited SiOx films were examined by AFM, using a Veeco Dimension 5000 Scanning Probe Microscope. In each case, an area of $10 \times 10\ \mu m^2$ was scanned, using the tapping mode. The hardness of the atmospheric pressure plasma deposited SiOx film was determined by a pencil test (loading 500 g), according to ASTM D3363-05. Scratch samples were examined with an optical microscope [11]. The pencil hardness of the atmospheric pressure plasma deposited SiOx films ranged from 9H to 6B (hard to soft). This method involves placing a flat pencil head against the substrates at a 45° angle and pushing it forward to make a scratch on the substrate. Pencils with hardness levels from hard to soft were used, until a pencil was found that could not make a scratch on the substrate. The hardness of the final test pencil defined the hardness of the atmospheric pressure plasma deposited SiOx films.

3. Results and discussion

3.1. Deposition characteristics of the atmospheric plasma chemical vapor deposition process

Fig. 2 shows the dependence of the average thickness of atmospheric pressure plasma deposited SiOx films on oxygen gas flow rate. The atmospheric pressure plasma deposited SiOx films were characterized as hard and transparent film on PC substrates. An increase in the oxygen concentration of the HMDSN/O_2 mixture used for atmospheric pressure plasma chemical vapor deposition produced an initial increase in the deposition rate onto the PC substrates, which then reached a maximum. The deposition rate is increased when the oxygen concentration is increased, however an excessive amount of oxygen dilutes the concentration of the HMDSN precursor and so reduces the deposition rate for the atmospheric pressure plasma chemical vapor deposition process. In addition, the hardness of the atmospheric pressure plasma SiOx films deposited on the PC substrate improves to greater than HB, measured using the pencil hardness method, as shown in Fig. 2.

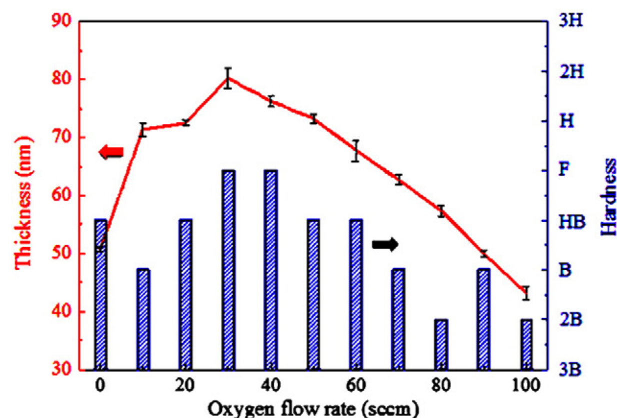

Fig. 2. The average thickness and hardness of atmospheric pressure plasma deposited SiOx films with oxygen gas flow rate inputs. Plasma conditions: RF plasma power 100 W, HMDSN 2.5 sccm, Ar 3000 sccm, O_2 0–100 sccm, and 12.5 mm distance of nozzle to substrate. The statistical error bars are determined from 5 measurements of 10 films deposited with the same conditions.

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