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High-rate deposition and mechanical properties of SiO_x film at low temperature by plasma enhanced chemical vapor deposition with the dual frequencies ultra high frequency and high frequency

Su B. Jin *, Joon S. Lee, Yoon S. Choi, In S. Choi, Jeon G. Han

Center for Advanced Plasma Surface Technology, Sungkyunkwan University, 300 ChunChun-dong, Jangan-gu, Suwon 440-746, South Korea

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ABSTRACT

A high efficiency, high-rate deposition process was developed for silicon oxide films using plasma enhanced chemical vapor deposition (PECVD) with an additional ultra high frequency (UHF) power with high frequency (HF) bias. The effect of the UHF input power with HF bias on the anti-scratch properties of the silicon oxide films was examined. The hybrid plasma process was also examined by advanced plasma source. Dissociation of the octamethylcyclodisiloxane (OMCTS) precursor was controlled by the plasma processing parameters. SiO_x films were deposited on polycarbonate substrates by PECVD using OMCTS and oxygen carrier gas. The rate of SiO_x film deposition increased with increasing input energy. The plasma was analyzed by optical emission spectroscopy. The deposition rate was characterized using an alpha-step. The mechanical properties of the coatings were examined using a nano-indenter and pencil hardness measurements. The chemical properties of the coatings were examined by Fourier transform infrared spectroscopy. The deposition rate of the SiO_x films was controlled by the dissociation of OMCTS using the appropriate intensity of excited neutrals, ionized atoms and input UHF input power with HF bias at room temperature.

1. Introduction

Over the last few decades, plasma enhanced chemical vapor deposition (PECVD) using organo-silicon reactants has been developed as a low temperature deposition process for producing silicon oxide films [1–3]. A range of functional coatings on polymers have been studied extensively for applications to flexible electronic devices. The prime functional films for such applications are barrier films with high wear resistance, optical transparency and anti-finger print properties [4–6]. SiO_x films are candidates for those requirements. On the other hand, further improvements in the film properties will require process development, particularly for low temperature synthesis on temperature sensitive polymers including polycarbonate (PC) substrates. The improvement in the density and electronic bonding of a film is a key factor that is controlled by the plasma density, radical species and kinetic energy of particles. This study examined the formation of hybrid functional SiO_x films deposited at a high deposition rate with high optical transparency and high wear resistance on a range of substrates by PECVD. The plasma density and radical species were modulated by controlling the high frequency (HF) input power density on the capacitive-coupled dual electrodes at different power frequencies up to ultra high frequency (UHF). The kinetic energy of the particles was also controlled by the HF bias on the substrate electrode. The process plasma during PECVD was analyzed to determine the ion current density on the substrate, film temperature and radicals for process design to modulate the film properties including the film density, electronic binding energy and stoichiometry.

This paper reports the relationship between the plasma parameters and film properties in terms of the process parameters by PECVD with different plasma power densities and frequencies. The design and synthesis of various functional hybrid film systems for SiO_x film coatings with good mechanical properties at high deposition rates are reported. The formation mechanism and effects of the hybrid plasma CVD system on the deposition rate, chemical composition, film hardness and optical emission spectroscopy of the plasma are also discussed.

2. Experimental procedure

Fig. 1 shows a schematic diagram of the plasma configuration used for deposition. Two circular electrodes (ø = 200 mm) covered with a ceramic plate were placed within a cylindrical enclosure containing both electrodes. Two line UHF electrodes (ø = 10 mm and length = 25 mm) covered with a ceramic textile tube were placed in the chamber. Table 1 lists the coating parameters. During the experiment, the base pressure was approximately 3×10^{-2} Pa. Prior to plasma polymerization, a polycarbonate (PC) and Si wafer (100) substrate was placed on the bottom electrode. During the plasma process, a gas comprised of OMCTS and oxygen gas was allowed to flow to the top electrode (shower head).

* Corresponding author. Tel.: +82 31 299 6646; fax: +82 31 290 5669.
E-mail address: jinsubong@skku.edu (S.B. Jin).

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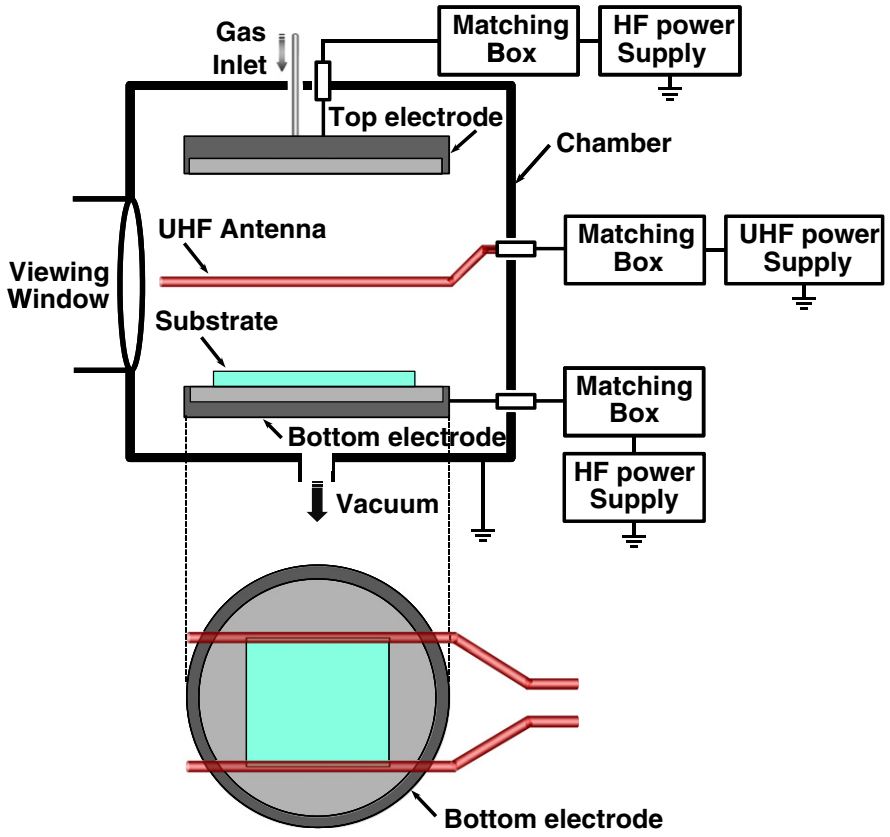

Fig. 1. Schematic diagram of the PECVD with the dual frequencies UHF and HF apparatus used to deposit the SiO_x film.

Octamethylycyclodisiloxane (OMCTS) precursor has one cyclic Si–O skeleton, and little organic matter and many Si–O bonds compared to different precursors (TEOS and HMDSO). The deposition rate was assumed to be improved by reducing wasteful photodissociation of the organic material and the film properties improved by reducing the organic material and OH impurities. The SiO_x films were deposited as two types. In the first type, the top electrode was connected to a 13.56 MHz HF power source at 120 W, whereas the bottom electrode was connected to the ground with a UHF power source (320 MHz). In the second type, the top and bottom electrode was connected to a 13.56 MHz HF power source and a 13.56 MHz HF power source with a UHF power source (320 MHz), respectively. The SiO_x films coatings were deposited on unheated PC and Si wafer (100) substrates at room temperature. In all experiments, the SiO_x film thickness was 1 μm.

The plasma chamber was equipped with a single fiber optic probe to detect the excited species generated in the plasma on the PC substrate. The plasma was characterized using an Acton Spectrapro 500i (Action Research) optical emission spectrometer with a resolution of 0.1 nm operating in the 250–850 nm region. Acquisition of the output spectra after the spectrometer was performed using an Acton PIXIS 400 CCD camera with the sensor cooled to −21 °C during operation.

Table 1
Deposition parameters.

Parameter	Condition
Base pressure	$<3\times10^{-2}$ Pa
Deposition pressure	1.7×10^{-1}–2.8×10^{-1} Pa
Top electrode (HF, 13.56 MHz)	120 W
UHF power (320 MHz)	0, 80 150 220 W
Bottom electrode (HF, 13.56 MHz)	0, 70, 90, 120 W
Film thickness	1 μm
Temperature	Room temperature
Substrates	PC and Si wafer (100)

Attenuated total reflection Fourier transform infrared absorption (ATR FT-IR) microscopy provided spatially resolved information on the qualitative chemical binding composition over the foot print area. The spectra were obtained at a spectral resolution of 0.4 cm^{-1} between 4000 and 600 cm^{-1} using an ATR germanium crystal. The number of scans was 64.

The hardness was measured using a MTS Systems Nano-Indenter XP continuous stiffness measurement technique. Using this technique, the indent provided the hardness as a continuous function of the displacement of the indenter into the samples. The surface approach velocity was 5 m/s. The experiments were terminated at a depth of approximately 400 nm. The films were 1 μm or greater in thickness to minimize the substrate effects. The substrate had minimal impact on the mechanical properties at penetration depths of <10% of the film thickness [7,8]. Using the standard protocol, the hardness was measured at 10% of the film thickness and the modulus was taken at 100 nm.

The surface hardness of the SiO_x film on the PC substrate was measured using a pencil hardness test according to the standard ASTM D3363 method. Pencils with a hardness ranging from B to 9H were used to scratch the surfaces of the flexible PC substrates at an angle of 45° [9,10]. No scratch was recorded on the surfaces of the flexible PC substrates.

3. Results and discussion

The SiO_x film deposition rate on the PC substrates coated for 10 min was determined. The rate of SiO_x film deposition increased with increasing UHF power to the top electrode (120 W) at a deposition pressure of 1.7×10^{-1} Pa (Fig. 2 (a)). In addition, the level of dissociation of the OMCTS precursor increased with increasing input energy under the same deposition pressure. In other words, the high input energy (HF power with UHF power) increased the rate of SiO_x film deposition by increasing the deposition pressure. The deposition rate was increased approximately three fold by increasing the deposition pressure from