PLASMA DIAGNOSIS IN ETCHING AND ASHING OF DIAMOND CARBON COATING

by Nereus Redationo

PLASMA DIAGNOSIS IN ETCHING AND ASHING OF DIAMOND CARBON COATING

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ABSTRACT

Diamond-like carbon (DLC) coating has been widely used as an efficient and reliable protective coating. To recycle the mold-die substrates, the used DLC coating must be perfectly removed before re-coating without damage to substrates and residuals. The RF-DC high dense plasma etching or ashing process is utilized to describe the plasma-etching behavior by using the spectroscopic analysis. First, RF- and DC-voltages together with pressure are varied in this oxygen plasma etching to search for an optimum condition; DC-bias is -450 V, RF voltage is 250 V and oxygen gas pressure 40 Pa. Oxygen plasma spectrum is analyzed to define the pure oxygen plasma. It is composed of oxygen atoms, activated oxygen atoms, and molecules. In-situ plasma monitoring is also used to measure CO peak in the range 200-300 nm. Detection of CO peak proves that carbon in DLC coating is reacted with oxygen flux; i.e. C (in DLC) + O → CO. Variation of CO peaks correspond to etching behavior.

1. INTRODUCTION

Diamond-like carbon (DLC) is a meta-stable form of carbon. It has preferable mechanical properties for protective coating; low friction coefficient and high hardness (Marciano, 2009). This DLC coating is widely used not only for protective coating but also for mold-die substrate in micro-patterning (Matilainen, 2010).RF-DC high dense plasma etching or ashing were developed as a common tool to make micro patterning on the DLC-coated molds and dies.

In general, the etching process is defined by removal of coatings on the selected areas (Ricci, 2005). Oxygen gas is used to generate plasma. Treatment of different materials with oxygen plasma has become a technique widely used on experimental and industrial scale. In recent years, oxygen plasma generated with RF discharge has been found to be very effective for plasma etching, surface activation, cleaning, and oxidation of different materials (Cvelbar, 2008). Controlling and understanding etching process by plasma diagnosis are needed. Optical emission spectroscopy is a method for plasma diagnosis. Optical Emission spectroscopy is a non-invasive probe to investigate the activated state of atoms, ions and molecules in the plasmas. It provides the information about excited state of atoms, radicals, molecules or ions. From the measured spectrum, various physical parameters are estimated with aid of simulation; e.g. the species density, the electron-atom and ion-atom collision effect, and the energy distribution of species (Villpando, 2010).

In this present study, plasma diagnosis is used to describe pure oxygen plasma and also chemical reaction in plasma etching. In-situ plasma measurement is done to control plasma etching. Through indentifying and analyzing CO peaks, time variation of reactivity during plasma etching is monitored on time.

2. EXPERIMENT

2.1 High Dense Plasma Etching System

Main cylindrical chamber was made of stainless steel with the diameter of 480 mm and the length of 580 mm, as shown in Fig. 1. This chamber was connected to the vacuum system through a leak valve. The system was pumped with two-stage; oil rotary pump with a pumping speed of 1000 L/min and ultimate pressure of 4.0 x 10^{-2} Pa. This chamber was connected to RF generator. Instead of the conventional mechanical matching, input-output matching was automatically performed in the frequency range around 2 MHz. The chamber was cooled by water cooling system and forced air.

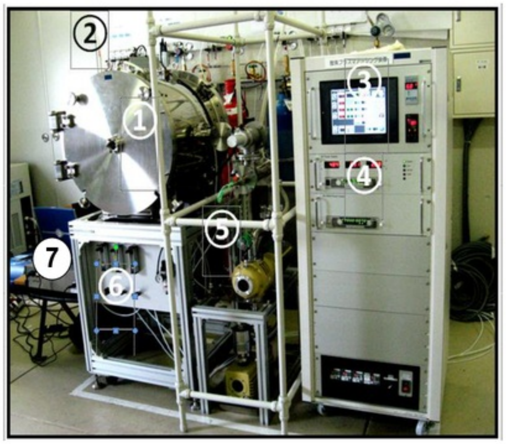
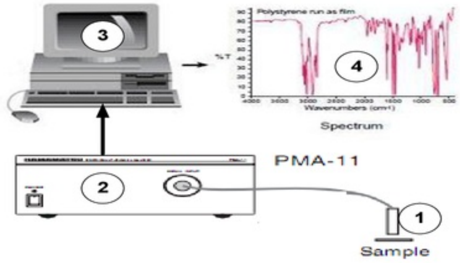


Figure 1. High dense plasma etching system. 1: Chamber, 2: RF-plasma generator, 3: Control-panel, 4: Electric sources, 5: Evacuation system, 6: Gas supply, 7: Plasma Diagnosis (PMA-11)

2.2 Plasma Diagnosis System

The parameters of plasma in the chamber were measured with optical fiber detector. The spectrum was measured by an optical emission spectroscopy (OES) PMA-11 (Hamamatsu Photonica, Ltd.). Observation was done through a quartz window mounted on the top of the chamber perpendicularly to the sample. The spectra detected by optical detector transfer to the computer. Those data were analyzed by using OES software. Typical experimental set-up and specification of (OES) PMA-11 (Hamamatsu Photonica, Ltd.) are depicted in Fig. 2.



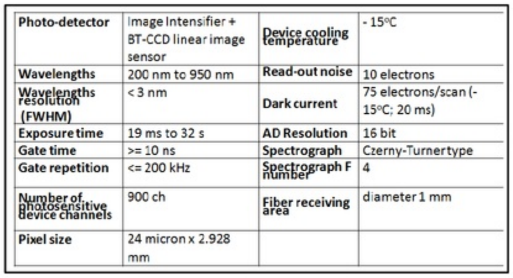


Photo-detector	Image Intensifier + BT-CCD linear image sensor	**Device cooling temperature**	- 15ºC
Wavelengths	200 nm to 950 nm	**Read-out noise**	10 electrons
Wavelengths resolution (FWHM)	< 3 nm	**Dark current**	75 electrons/scan (-15ºC; 20 ms)
Exposure time	19 ms to 32 s	**AD Resolution**	16 bit
Gate time	>= 10 ns	**Spectrograph**	Czerny-Turner type
Gate repetition	<= 200 kHz	**Spectrograph F number**	4
Number of photosensitive device channels	900 ch	**Fiber receiving area**	diameter 1 mm
Pixel size	24 micron x 2.928 mm		

Figure 2. 1: Chamber, 2: OES PMA-11 Hamamatsu, 3: Computer and software, 4: Spectrum Display

3. EXPERIMENTAL RESULTS

3.1 Plasma Diagnosis of Oxygen Plasmas

The emission spectra were measured and analyzed when plasma oxygen was generated at the pressure 40 Pa and by RF, 250 V and DC-bias, -450 V. Figure 3 represents the pure oxygen plasma spectra in two different state. In Fig.3. (A), activated oxygen molecules such O_2* and O_2^+ prevails the whole spectrum; little oxygen activated atoms and ions are detected in this plasma diagnosis. Both oxygen atoms and activated atoms have much more intensities than molecules in Fig. 3. (B). This difference of activated species in the oxygen plasmas reflects on the plasma etching behavior.

In normal plasma-state control, the activated oxygen molecules and molecule ions coexist with activated oxygen atoms. In fact, most of detected peaks from 120 to 376 nm correspond to the atomic oxygen transition. The molecular oxygen in the Schumann-Runge system ($B^3\Sigma_u^- - X^3\Sigma_j^-$), is detected at 374 nm and 437 nm as well; they have much lower intensity. The ionized oxygen molecules in positive system ($b^4\Sigma_g^- - a^4\Pi_u$), are also observed at 555 nm and 774 nm, as summarized in Table 1. This implies that oxygen molecules are gradually activated to atomic species and ions in the normally controlled plasma-state.

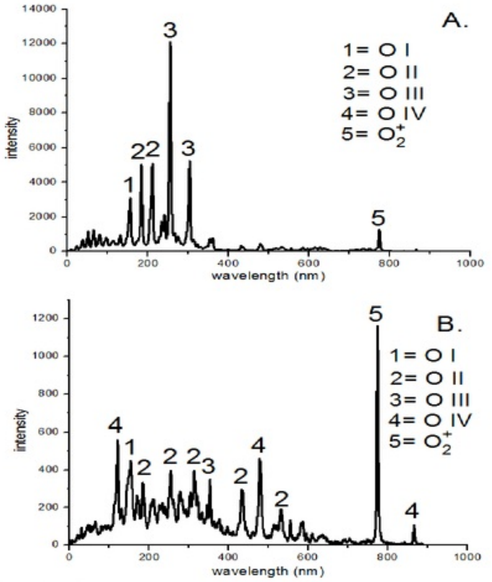


Fig. 3. Emission spectra of oxygen plasma in the wave-length range of 0 - 900 nm. In (A), the activated oxygen molecules is prevailing the plasma state, while main activated oxygen atoms are governing the plasma state in (B).

Table.1 Emission bands monitored for oxygen atomic, oxygen molecule, and ionized oxygen molecule during oxygen plasma activation.

Atomic Oxygen	Molecule Oxygen	Ionized Molecule Oxygen
155 nm (O VII)	374 nm (O_2)	555 nm (O_2^+)
183 nm (O II)	437 nm (O_2)	774 nm (O_2^+))
210 nm (O II)		
234 nm (O II)		
240 nm (O III)		
255 nm (O III)		
303 nm (O III)		

3.2 Effect of Process Parameters on Plasma-State

RF-voltage, DC bias, and oxygen pressure are main parameters affecting on the plasma etching behavior. RF-voltage and pressure during the process give the different effect on the oxygen plasma. Fig.4 explains the variation of plasma parameters on the measured spectrum. The dash line explains that the spectrum using low RF-voltage, DC bias and pressure. The dot line is the spectrum using low RF, but high DC bias and pressure. From both spectrums the etching rate isn't so good. The solid line is the combination in matching plasma parameters and have high etching rate.

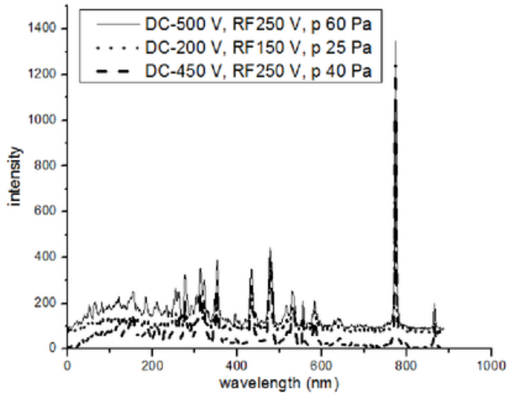


Fig.4. Effect of RF-voltage, DC-bias, and pressure on the oxygen plasma.

3.3 Chemical Reaction in Etching

Plasma diagnosis was also performed to investigate the chemical reaction between oxygen and carbon in DLC coating during plasma etching. Figure 5 depicts the measured spectrum when using RF 250, DC -450 V, and pressure 40 Pa.

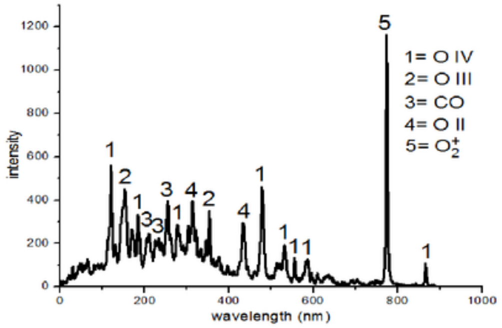


Fig.5. Measured spectrum during plasma etching. New peaks were identified to be corresponding to CO.

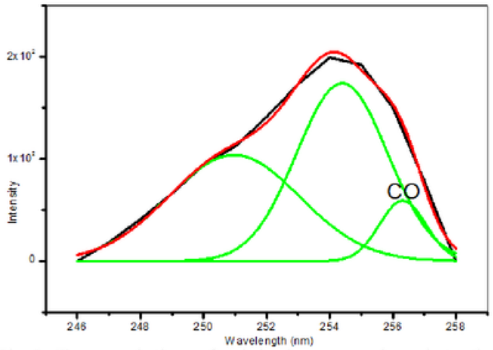


Fig.6. Deconvolution of original measured peak to three profiles: oxygen atoms and CO.

Figure 6 explains the deconvolution process from the original measured peak to three profiles in the range 248 nm- 258 nm. The fourth positive system of CO ($A^1\prod$ - $X^1\sum$) appears and is indentified at 256.31 nm. In the similar data acquisition as done in the above, other two characteristic CO-peaks at the wave length of 210.72 nm and 240.76 nm were detected besides above peak qt 256.31 nm.

DISCUSSION

In general, movement of electrons and ions are enhanced by increasing DC-bias; this is a typical ion/electro bombardment effect on the etching process. As shown in Fig. 4, RF-voltage has a direct effect on the oxygen plasma spectrum. Peak intensities for oxygen atoms, oxygen molecules, and ionized oxygen molecules increase with this RF-voltage. Intensity of atomic, molecule, and ionized-molecule oxygen depends on the oxygen pressure. Higher RF-voltage and lower pressure is indispensable to generate more oxygen-atom species.

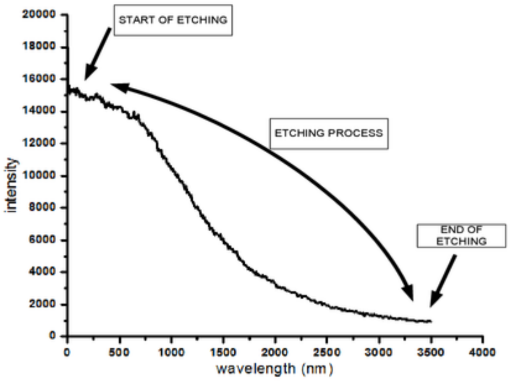


Fig.7. Variation of CO peak intensity by insitu measurement during plasma etching

Variation of CO peak intensity, insitu measured during etching process, was shown in Fig.7. At the beginning, chemical reaction between carbon in DLC and activated oxygen atoms commences to generate CO. This reactant of CO is ejected from the etching front to outlet in gaseous phase, and, is measured in the spectrum. This is a normal etching process where the carbon in DLC coating should be removed. With processing time, the measured CO-peak intensity is gradually reduced as shown in Fig. 7.

Consider that etching process advances in the narrowed micro-grooves in the inside of DLC coating. Oxygen flux comes into this micro-groove while the reactant CO flushes out of this. This turbulent mixing around the inlet of micro-groove drives the reactant CO gas to diffuse in any directions from the substrate surface. This might result in apparent reduction of CO-detection by the sensor, which was placed at the top of chamber. In addition, carbon source also reduces with processing time. In this etching experiment, little or no CO-peak signals were detected at 3450 s. This tells the end of etching.

In-situ measurement of reactants like CO becomes a preferable means to control the plasma etching process without intermission. This suggests that on-line detection of mono-oxides should be effective to consider the possibility of etching in any material systems; e.g. oxygen plasma etching of metallic interlayers like tungsten or chromium.

CONCLUSION

Plasma diagnosis was effective in this experiment and effective to describe the chemical reaction during plasma etching; e.g., the reaction between oxygen and carbon were identified by new peak of CO at 256 nm in spectrum. Plasma diagnosis was also effective to make in-situ monitoring on plasma state during plasma etching and to control the plasma etching process.

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PAGE 1

PAGE 2

PAGE 3

PAGE 4