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Oxygen plasma etching of diamond-like carbon coated mold-die for micro-texturing

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ABSTRACT

Diamond-like carbon (DLC) coating via PVD/CVD on the SKD11 substrate was employed to make micro-texturing by using high density oxygen plasma etching. Original pattern by metal chromium was first line-drawn on the surface of DLC coating; then, it was subjected to oxygen plasma etching. Even without any hazardous etchants such as CF_4, high etching rate was attained only by using oxygen gas; i.e. 5 μm/H. Plasma diagnosis by spectroscopy proved that this etching process should be controlled by activated oxygen atom flux of {O, O*}. Direct chemical reaction by C (in DLC) + O → CO, or, C (in DLC) + O* → C − O, drove this etching process. Detection of CO peaks in the wave length range from 200 to 300 nm also proved that this oxygen plasma etching should be advanced by chemical reactions. This etching behavior was insensitive to line width (W_G) and pitch width (P_G) for 2 μm<W_G<100 μm and 5 μm<P_G<100 μm. Scanning electron microscope and laser-profilometer were also used to make precise measurement on the etched profiles.

1. Introduction

Carbon-based materials have sufficient high temperature strength in inert atmosphere; they are attractive as a substrate material of mold-die for mold-stamping the oxide glasses into optical elements [1]. In recent, most of optical lens systems have diffractive optical element (DOE) like Fresnel pattern. A new technique is required for glassy carbon substrates or DLC-coated mold-dies to imprint the designed micro-pattern or micro-texture onto them. Carbon nanotube (CNT) film is useful as a transparent electrode to be working instead of ITO; circuit pattern of electrodes must be micro- or nano-patterned onto CNT films [2]. Diamond coating is also effective as a protective coating of tools and dies; its rough surface must be flattened by oxygen plasma ashing to have maximum roughness less than 0.5 μm [3]. The present paper concerns with the development of oxygen plasma etching process to make micro-patterning onto the carbon-based coatings.

In the present paper, a thick DLC (Diamond-Like Carbon) coated substrate is prepared for masking and then oxygen plasma-etching in order to describe the etching behavior of amorphous carbon materials. First, our developing oxygen plasma ashing and etching system [4–6] is introduced with comments on the plasma diagnosis instrument which is equipped to this system. Through comparison of oxygen plasma states, the oxygen atom governing state is selected for effective oxygen plasma etching of DLC coatings. Chromium-masked DLC-coated SKD-11 specimens are used for plasma etching to make deep micro-grooving patterns on them. Homogeneous etching takes place irrespective of the micro-groove widths and pitches. In particular, every micro-groove pattern is successfully etched to have a stepwise depth profile for wide range of micro-groove widths and pitches. This etching process is driven by direct chemical reaction between oxygen atoms in plasmas and carbon atoms in DLC since CO-peaks are detected by spectroscopic diagnosis. Furthermore, in-situ monitoring of plasma state is also effective to describe the etching behavior as time evolution of designated CO-peak in spectra. Termination of oxygen plasma etching is determined by significant reduction of CO-peak; the whole un-masked DLC coating is removed by this etching.

2. Experimental procedure

2.1. High density oxygen plasma etching system

High density RF–DC plasma etching system (OXP-1; YS-Electrics, Co. Ltd.) was developed to investigate the optimum condition for etching of carbon-based materials including DLC coatings, as illustrated in Fig. 1. Different from the conventional DC- or RF-plasma generators, there was no mechanical matching box. In the present system, input and out powers are automatically matched by frequency adjustment around 2 MHz. This difference in power matching reflected on the response time to temporally varying plasma states. The conventional mechanical matching required for long response time in the order of 1 s to 10 s to adjust the RF-power. While, in the present system, it was shortened down to 1 ms; i.e. there was no time delay in power control to drive the etching process. In addition, the vacuum chamber was electrically neutral so that RF-voltage and DC-bias were controlled independently from each other. RF-voltage was controllable up to 250 V, while DC

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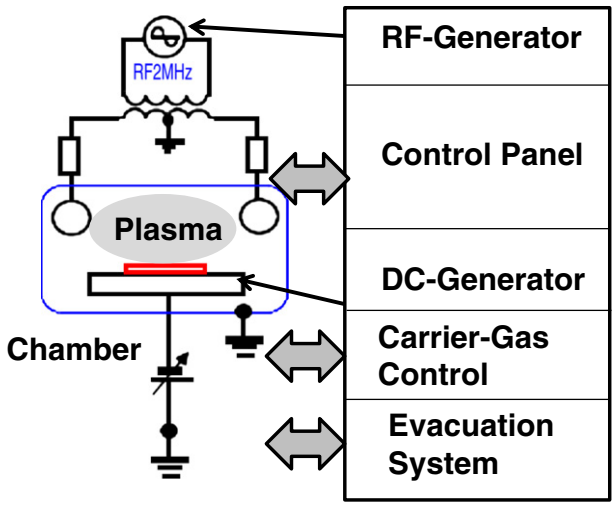

Fig. 1. Schematic view of high density plasma etching system.

Table 1
Capability of spectroscopy for plasma diagnosis instrumentation to developed RF–DC oxygen plasma etching system.

Photo-detector	Image intensifier + BT-CCD linear image sensor	Device cooling temperature	−15 °C
Wavelengths	200 nm to 950 nm	Read-out noise	10 electrons
Wavelengths resolution (FWHM)	<3 nm	Dark current	75 electrons/scan (−15 °C; 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 μm×2.928 mm		

bias, 0 V to −600 V. A dipole electrode was utilized to generate RF-plasma; DC bias was directly applied to the specimens. Heating unit was also located under this DC-biased table.

In the following etching experiments, the specimens were located on the cathode table before evacuation down to the base pressure of 0.1 Pa. Then, a carrier gas was introduced into the chamber to attain the specified pressure. Both oxygen and argon gasses were available in this system besides the nitrogen gas for bent. With the use of magnetic lens, the ignited RF–DC oxygen plasmas were focused onto the surface of specimens during etching. Spectroscopic analyzer was instrumented to a silica window of chamber to make on-line monitoring of plasmas. Carrier gas pressure as well as RF- and DC-voltages, were parametrically controlled to evaluate their effects on the etching rate. After preliminary experiments in [5], RF-voltage, DC bias and pressure were selected to be 250 V, −450 V and 25 to 40 Pa, respectively in the following experiments. Oxygen gas was only used in the present etching process.

2.2. Instrumentation for plasma diagnosis

Activated state of oxygen plasmas was described by using the spectroscopic measurement. Emissive light from plasmas was introduced through the fiber-scope with narrowed aperture and quantitatively evaluated by spectroscopic analyzer (Hamamatsu Photonics, Co. Ltd.). Its capability for spectroscopic measurement was listed in Table 1. All the activated species had their own characteristic peak profiles at the specified wave length. Each peak was identified to be corresponding to species by citing the database [7]. In the case of oxygen plasma state, activated oxygen molecules (O_2^*) and atoms (O^*) coexisted with ionized oxygen molecules and atoms, in general. These population profiles were directly controlled by electron density and temperature distribution in the plasmas, so that plasma diagnosis should be an effective tool to define the plasma state.

In addition, chemical reaction during plasma etching was also in-situ monitored by this system. New peaks corresponding to the reactants often overlapped with the above peaks of activated species in the measured spectra. In the following measurement, rational decomposition algorithm was utilized to separate each characteristic peak from spectra and to identify each decomposed peak by citing analytical results in [7] as well as Refs. [8,9].

2.3. Specimens

Chromium masking technique was employed to draw the initial two-dimensional patterns onto the DLC coating, which was deposited onto SKD-11 substrate by the unbalanced magnetron sputtering. Fig. 2 a) illustrated the present chromium masking method. The masked DLC-coating onto SKD-11 substrate had sandwich-structure of three layers: 1) undercoat of amorphous silicon carbide with the thickness of 10 nm (a-SiC) and chromium layer with the thickness of 100 nm, 2) main-DLC coating with the thickness of 5 μm, and, 3) top-coat of 10 nm a-SiC and chromium mask with the thickness of 100 nm. Various kinds of micro-grooving patterns were printed onto the a-SiC capped DLC coating by chemical etching. Selectively etched lines of chromium looked micro-groove patterns in Fig. 2 b) with the groove width varying from 3 μm to 100 μm. Since the film thickness of DLC coating is 5 μm, this variation in micro-grooving is equivalent to the change of aspect ratio in micro-grooving from 1.67 to 0.05. Apparent etching rate to be measured might be retarded by the residual chromium and a-SiC top-layers.

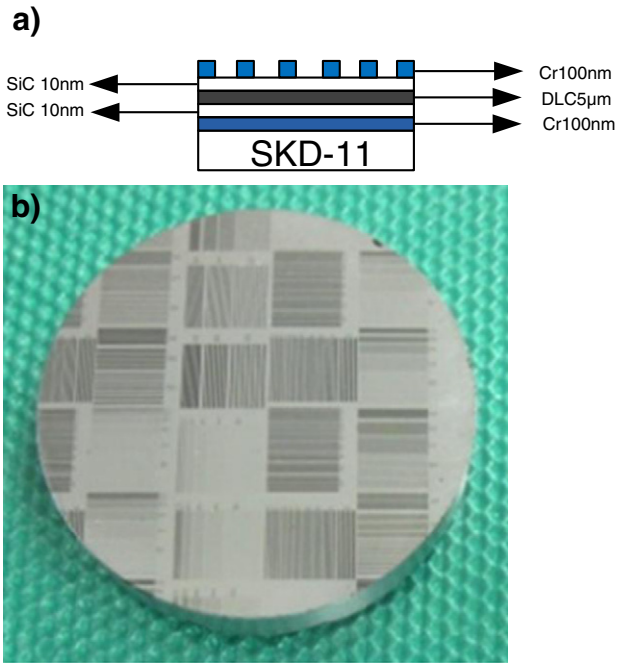

Fig. 2. Chromium masked SKD-11 specimen with variety of micro-groove pattern in the masking. a) Illustration of cross-sectional structure made by metal masking, and, b) optical microscopic image of metal-masked DLC coated SKD-11 specimen.