Proceedings of the 10th International Conference on

Multi-Material Micro Manufacture

8 — 10 October • San Sebastián, Spain

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Technical Papers

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Session 5 – Novel Material Processing

Time/Date	16:00 – 17:45 hrs / Tuesday, 8 October 2013
Venue	San Sebastián
Chair	**Dr. Luc Federzoni**, *CEA, France*

Precise Micro-Texturing onto DLC Coating via High-Density Oxygen Plasma Etching

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Abstract

A new way to make micro- and nano-patterning was developed by using a high density oxygen plasma etching with masking technology. This approach became a non-thermal process in a dry chemical etching by optimum selection of DC bias. The un-masked regions were selectively removed by using the controlled oxygen plasma state or a mixture of activated oxygen atoms with ionized oxygen atoms through the quantitative plasma diagnosis. The reactive ion etching behavior was described together with a measurement of etching rate. Both two dimensional line- and grid-masking patterns were prepared to investigate the geometric accuracy imprinted onto DLC coating films toward a direct fabrication of micro-forming dies.

Keywords: Surface Engineering, Micro forming, DLC coating, Plasma etching, Masking, Tool and Dies

1. Introduction

Diamond like carbon (DLC) coating has been widely utilized as a protective coating of tools and dies [1, 2]. In particular, its application to stamping die as a protective coating became a standard approach to be free from adhesive wearing and to prolong the die life time [3, 4]. Hence, a lot of research and development has been performed to improve its wear toughness, its stability at elevated temperature and its engineering durability. In particular, DLC coating was indispensable to reduce the wearing of dies for mold-stamping of the oxide-glass optical elements. Among the various coating materials, DLC coating had the most endurable life time in practical operation [5]. In addition, a micro-pattern or micro-texture was often imprinted onto these mold-dies to control the optical functions; high geometric qualification in this micro-pattern on the mold-die also became an important issue [6-8]. In the present paper, this plasma etching behaviour is quantitatively described with consideration on the optimum plasma conditions. First, details in experimental procedure and set-up are explained on our developing etching system. A plasma etching with metallic masking is applied to make a micro-patterning onto DLC coated silicon substrates. The etching rates as well as geometric accuracy in micro-patterning, are discussed together with the optimum design of plasma state for a micro-patterning.

2. Experimental Procedure

2.1. High-density plasma etching system.

Our developing high density plasma etching system was shown in Fig. 1. This system was composed of three sections: a vacuum chamber, a plasma generator and a control unit. The main chamber, which was neutral in electricity, included RF dipole electrodes, a DC-biased plate and a carrier gas supply. Hence, ionized species and activated radicals were attracted to this DC biased plate with kinetic energy. Either RF-plasma or DC-plasma or both, were ignited by switching on either or both on the control panel. Being different from the conventional plasma processing, both RF- and DC-plasmas were generated and controlled in relatively wide range of oxygen partial pressure.

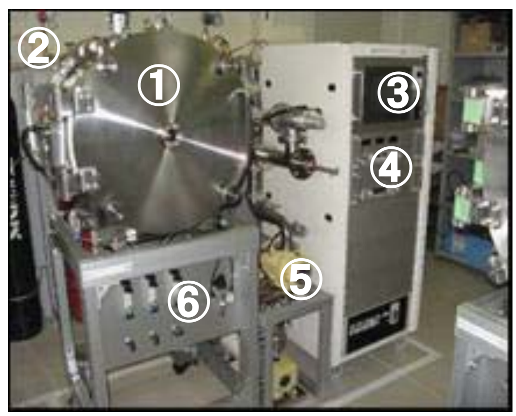

Fig. 1. High-density RF-DC plasma etching system.
① Vacuum chamber, ② RF-generator, ③ Control-panel, ④ RF- and DC-power generator,
⑤ Evacuation units, ⑥ Carrier gas supply.

In the above, there was no mechanical matching box in this system. In the conventional plasma generating systems, the operating frequency was limited to be 13. 56 MHz by regulation; electric

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matching between input and output powers must be mechanically adjusted. Then, these traditional processes required for longer duration of matching in the order of seconds or 10 seconds. In the present system, this matching process was executed by a frequency control around 2 MHz; the measured noise level was less than that from PC computers. Furthermore, the matching response to the change of plasma state became less than 1 ms. This prompt response is significantly favoured by the plasma etching behaviour. In the following experiments, oxygen and argon gases with a purity of 99. 99 % were used as a carrier gas. Both flow rates automatically were controlled to keep the pressure. The chamber was evacuated down to 0.1 Pa before introduction of carrier gases.

2.2. Measurement

A spectroscopic analysis by Hamamatsu-Photonics (C8808-01) was made for in-situ plasma diagnosis with a resolution of 1 nm in wave-length. NIST data-base was also utilized to identify the measured peaks by activated species. A laser-microscope and profilometer were also utilized to measure the surface profile and to determine the etching rate. SEM (scanning electron microscope) was also used for observation and measurement.

2.3. Specimens

Two masking patterns were formed by a photo-lithography onto DLC coated silicon substrates: micro-line and micro-grid patterns. The thickness of DLC coating was constant of 5 μm.

3. Experimental Results and Discussion

3.1. Oxygen plasma state for etching

Emission light spectra from oxygen plasmas were shown in Fig. 2. Strong intensities found at the range of 700-950 nm were mostly related to the transitions of atomic oxygen. On the other hand, some molecular transition was detected from weak radiation intensities in the range of 350-700 nm.

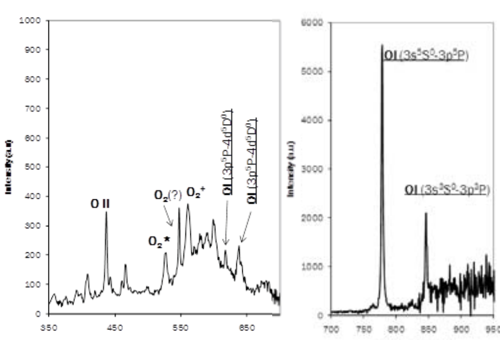

Fig. 2. A typical emission light spectrum of oxygen plasmas for etching in the shorter wave length (in left) and in the longer wave length (in right).

The short wave-length spectrum in Fig. 2 reveals that two types of activated oxygen atoms should be detected together with molecular species in this high density plasma state: singly ionized oxygen (OII) at 435 nm and neutral oxygen (OI) at 615 nm and 635 nm, respectively. Two states of molecular species are identified by O_2* at 524 nm and O_2^+ at 558 nm, respectively. Between two lines, a distinct slim line was observed at 547 nm, which cannot be identified in the reference data. It might be corresponding to the meta-stable transitions of oxygen molecules according [9]. A bump of signals observed from 550 to 650 nm is attributed to instrumental baseline amplification of weak signals; this accommodates the thermal motion vibration of emitted species. Two strong lines at the longer wave-length in a Fig. 2 are assigned to two neutral atomic transitions: 3s5S0 - 3p5P transition at 788 nm and 3s3S0 – 3p3P transition around 845 nm. As stated in the above, oxygen plasma consists of many species: {O_2^+; O, O*; O^+, O^{2+},…}. The oxygen atoms in the plasma are formed primarily by two competing processes: i.e. electron impact dissociation and dissociative attachment. The oxygen molecules collide with electron and create ions. Some of these oxygen ions are further attached by other electrons. The following four possible reactions are thought to occur in different conditions of plasma etching processes:

$$O_2 + e \rightarrow O^- + O,$$
$$O_2 + e \rightarrow 2O + e,$$
$$O_2 + e \rightarrow O^+ + O + 2e, \qquad (1)$$
$$O_2 + e \rightarrow O^* + O + e.$$

In the above, both positive and negative ions or O^+ and O^- are generated by this dissociation. Furthermore, neutral atom (O) and activated radical (O*) are both generated by series of reactions. The above reactions are sustained by a rich presence of neutral atoms. In fact, strong transition lines for OI are detected at 788 and 845 nm in Fig. 2, respectively. This measurement proves that neutral oxygen atoms should be responsible for reactions (1) in the plasma state. The latter peak looks broad; this might be because this line is a multiplet around 844.8 nm related to the 3S0 – 3P transitions [10].

The chemical process during etching the DLC films is mainly driven by reactions between the neutral oxygen atoms (OI) with oxygen radicals and the carbon atoms in DLC. Functional groups or species are produced by the above reactions and desorbed from the surface of films [11]. In case of a plasma etching for DLC films, oxygen atoms are easy to react with carbon atoms and to form oxygen-carbon bonding on the surface of DLC films. In fact, two reaction processes are thought to drive the etching behavior by formation single molecules of CO:

$$O + C \rightarrow \text{C-O binding}, \qquad (2)$$
$$O^* + C \rightarrow CO.$$

3.2. Micro-groove patterning

Two dimensional line-patterns were imprinted onto the surface of DLC coating as a masking pattern for various line widths from 100 μm down to 5 μm. The oxygen plasma processing parameters were fixed as follows: RF-voltage was 250 V, DC-bias, -600 V, plasma pressure, 40 Pa and the processing time, 2000s. Figure 3 a) depicts the top view of etched specimen by laser microscope. Corresponding to the original line patterns, micro-grooves are successfully etched into DLC-coating.

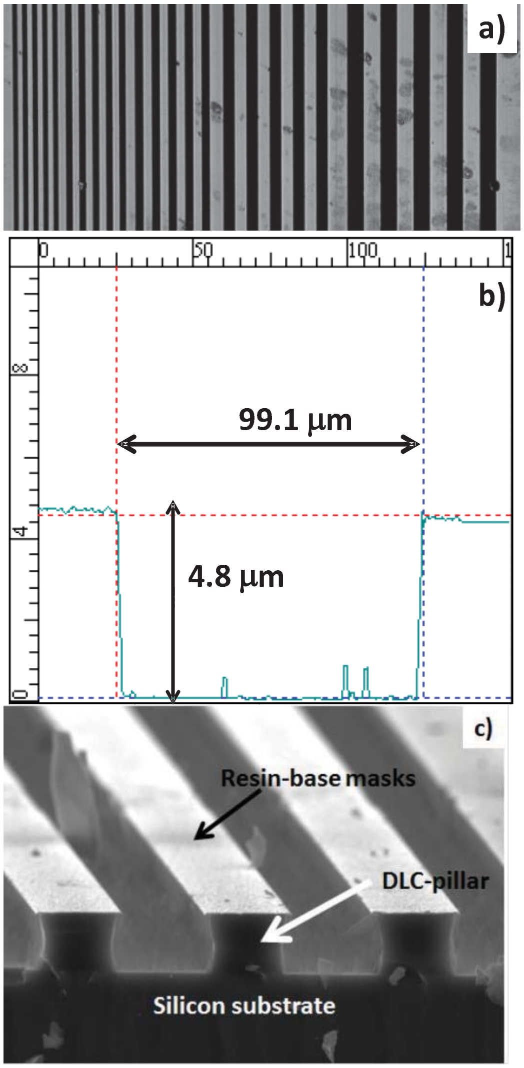

Fig. 3. Observation and measurement of micro-groove patterns imprinted onto the DLC coating via the oxygen plasma etching. a) Top view, b) Depth profile, and, c) SEM perspective view.

Figure 3 b) showed the depth profile of a single micro-groove with the width (W_G) of 100 μm. The measured micro-groove width was 99.1 μm and its depth, 4.8 μm, respectively. Both were in fairy good agreement with the initial line width of 100 μm and the DLC film thickness of 5 μm. It was noticed that the depth profile of this micro-groove should be shaped in stepwise to have steep side walls. Figure 3 c) depicted the SEM micrograph on the cross-sectional view of narrow micro-grooves with the skew angle of 30 degrees. Although slightly over-etched regions were seen on the side walls, narrow micro-grooving patterns were etched in stepwise to have the same line-width and line-pitch as the original masks without deterioration of resin-base masks. This proves that the present resin-base masking technique should be suitable to oxygen plasma etching with sufficient accuracy even to micro-patterning in the order of μm range. The over-etching behavior seen on the side walls could be suppressed by controlling the plasma processing parameters.

3.3. Micro-lattice patterning

Two dimensional square dot masking pattern was also formed on the DLC-coated silicon substrate to imprint the micro-lattice patterns onto the DLC coating in the similar way. As shown in Fig, 4, original two dimensional grid mask-patterns were changed to a micro-lattice pattern, where square pillars stood on the substrate. This homogeneous etching might be preferable to large-area micro-texturing onto the DLC-coated molds and dies as a mother tool.

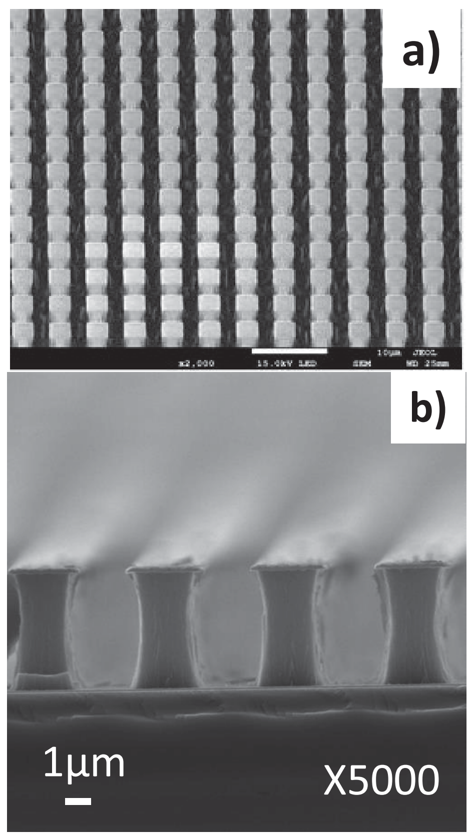

Fig. 4: Micro-lattice formation of DLC micro-pillars via the oxygen plasma etching. a) Perspective SEM image in low magnification, and, b) Perspective SEM image in high magnification.

3.4. Reactive ion etching behavior

Both micro-grooving and micro-lattice patterning are driven by the reactive ion etching, where the un-masked DLC films were selectively removed in the depth direction, homogeneously on the surface. This anisotropic etching behavior is thought to be strongly dependent on the plasma processing parameters and patterning geometry. In fact, the over-etching was enhanced with increasing the DC bias; optimization in processing made us free from over-etching. Figure 5 depicted the effect of line width in the original masking pattern on this reactive ion etching by using the laser profilometer. In each micro-groove where W_G = 10, 20, 50 and 70 μm, the measured depth profile at the designated processing time was superposed in a Fig. 5. The etching front in each micro-grooving advances with time in nearly the same etching rate. This time evolution of depth profiles in micro-grooving proves that micro-etching process should be insensitive to the line width; that is, homogeneous etching takes place irrespective of any original masking patterns.

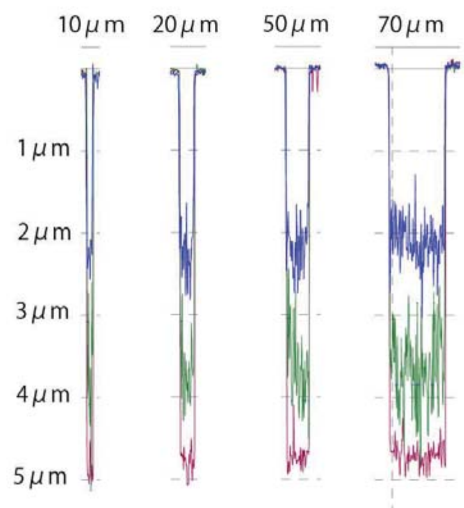

Fig. 5: Time evolution of depth profile in each micro-grooving during the present etching process by measurement of laser profilometer.

4. Discussion

The total etching rate by oxygen plasma processing is compared with the reference data. According [12] DLC coating was also removed with the etching rate of 0.5 μm/H by hollow cathode discharging (HCD) oxygen plasma processing. In the present method, the DLC-layer with the thickness of 5 μm, was etched away by 3520 s; the average etching rate was estimated to be 5 μm/H. The present processing enables us to make the etching rate ten times faster. This higher etching rate must be preferable to industrial applications in addition to the homogeneous etching behaviour mentioned above.

5. Conclusions

High density plasma etching system has been developed for efficient micro-patterning onto diamond like carbon coating on the die substrate with aide of metallic masking technique. Fine two-dimensional patterns of metallic mask are imprinted onto the DLC coating with sufficient accuracy. This geometric accuracy is controlled by physical and chemical processes in a plasma etching. Plasma processing parameters must be controlled to drive chemical etching for efficient removal of carbons from DLC films together with ion bombardment for directional etching. In future studies, these two processes have to be optimized for accurate and fast-rate etching by quantitative diagnosis of plasmas including spectroscopic analysis. Furthermore, dry micro-stamping is to be executed to utilize this patterned DLC die for fabrication of optical polymer and oxide glass elements in practice.

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