PLASMA OXIDATION PRINTING ONTO THE DLC AND CERAMIC COATINGS FOR FABRICATION OF MICRO-STAMPING DIES

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ABSTRACT

The miniature punch and core die for micro-texturing as well as micro-stamping processes must have not only complex, fine micro- and nano-textures but also sufficient engineering endurance. Furthermore, its micro-pattern itself must be uniform and fine for its duplication onto the metallic and plastic sheets in larger area. In addition, the surface of punch and die had to be coated to have sufficient wear-, erosion- and corrosion resistance even in dry stamping conditions. In the present paper, the coating material was directly employed as a punch and die substrate for dry stamping process. Through the plasma oxidation printing, micro- and nano-textures were formed into this coating substrate. This plasma printing consisted of three steps; i.e. (1) drawing the micro-pattern onto the coating by using the ink-jet printing, (2) forming the pillar by selectively etching away the unprinted area through chemical reaction with plasma species, and, (3) stripping the un-etched ink from the substrate. Besides for DLC coating, both TiN and TiCN coated SKD11 also were prepared in order to describe the etching behavior of ceramic coating through plasma oxidation printing.

1. INTRODUCTION

Miniaturization in products has become a trend not only in the electronics, but also in the communication devices, the medical parts, the micro-electromechanical systems (MEMS), and the micro system technology (MST). Under these trends, both the metallic and polymeric micro-parts have been utilized more in practical application. Micro-sheet forming process is a promising approach to fabricate those micro-parts due to its high productivity, low production cost, low energy consumption, good mechanical properties and stable dimensional accuracy (Wang, et al., 2014). However, this micro-sheet forming process encounters the difficulties where complex and fine micro- and nano-textures are duplicated. To overcome them, micro-stamping requires for punch and core with the sufficient engineering endurance even in dry condition. Diamond-like carbon (DLC) was chosen as a substrate to prolong its lifetime and to reduce the production cost (Aizawa, 2013-1, 2). However, its thickness is limited to several micro-meters at most since it is designed and used for protective coating of tools (Aizawa, 2014).

In the present paper, a thick DLC coatings are prepared for micro-punch and die substrate itself. First, the micro-patterns are ink-jet printed or maskless drawn onto this DLC film. Through the plasma oxidation printing, these two dimensional patterns are transformed into three dimensional micro-textures into DLC coating. High dimensional accuracy is attained by this micro-texturing together with wide variety of micro-textured geometry. Besides DLC films, the ceramic coatings, which have been used for protection of cutting and medical tools (Serro et al., 2009), are also employed to make micro-texturing. Different from the previous approach by (Woo et al., 2009) where CF_4/Ar, CHF_3/Ar, CF_4/O_2 are utilized for dry etching, or, by (Walker & Tarn, 1991) where HF, HNO3, and peroxide are used for etching, pure oxygen gas is only utilized in the present etching processes for micro-texturing into TiN and TiCN coatings.

2. EXPERIMENT

The present micro-texturing process consists of three steps as shown in Fig. 1. In the first step, the initial micro-patterns are drawn onto the coated film on the metallic substrate by using the inkjet printing or the maskless patterning. In second, the unmasked surface area of film is selectively removed by plasma oxidation. Finally, the un-etched ink or the residual metallic masks are stripped from the coating to form the DLC or the TiN/TiCN pillars on the metallic substrate.

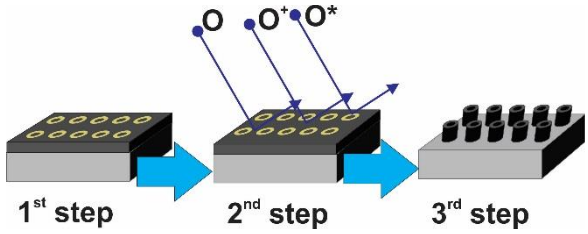

Fig. 1 Plasma Oxidation Printing Principal

The SUJ-2 substrate with the size of 12 x 12 x 5 mm^3 was DLC-coated to have the thickness of 12 μm. Both the ink-jet printing and the maskless patterning by lithography were employed to draw the initial micro-patterns onto the DLC and the ceramic coatings. In particular, pure platinum was used as the ink to draw various patterns in four areas with detail information in Table 1. and the micrograph of pattern in Fig. 2.

Table 1 Four patterned area and details

Area	Detail information
I	- Circular ring patterns with the size from 30 μm to 3 μm - 85 μm in pitch
II	- Net-work pattern with the line-width of 1 μm - 10 μm in pitch
III	- Rectangular patterns with the edge length of 2 μm - 6 μm in pitch
IV	- Rectangular patterns with the edge length of 2 μm - 4 μm in pitch

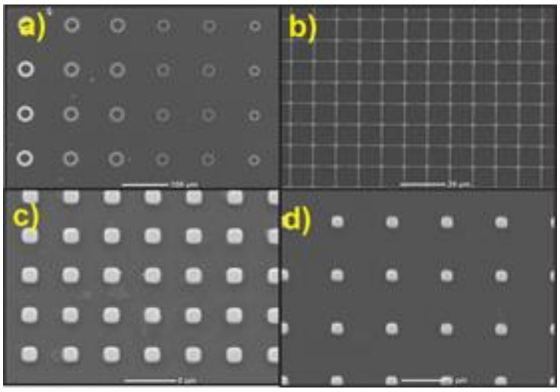

Fig. 2 SEM images of the initial micro-patterns drawn onto DLC coating: a) Area I, b) Area II, c) Area III, and d) Area IV.

In the plasma oxidation process, both DLC and TiN/TiCN films are etched away by the chemical reaction between the coating constituents and plasma species, e.g. in DLC coating case, C (in DLC) + O (in plasma) → CO.

The present plasma oxidation system consists of the vacuum chamber, the power supply for generation of plasmas, the control unit, the carrier gas supply, and the measurement instruments. In this system, the RF plasma is attracted to DC biased cathode. The input-output power matching is automatically tuned by frequency adjustment around 2 MHz. As illustrated in Fig. 3, due to its electrical neutrality of the vacuum chamber, both RF-voltage and DC-bias voltage are controlled independently from each other to generate RF and DC plasmas respectively. The RF-voltage was controllable up to 250 V while the DC-bias voltage was controllable from 0 V to -600V. All the parameter set up for processing such gas pressure, RF-voltage, DC- voltage, process duration, and gas flow rate was controlled from the control panel.

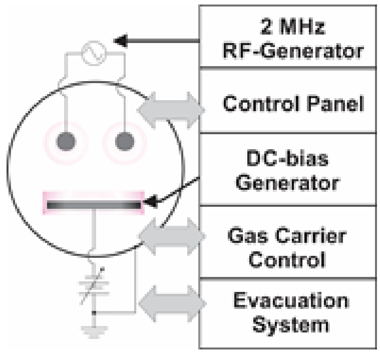

Fig. 3 Schematic view of plasma oxidation system.

In the following experiments, the sample was placed in the middle of the cathode table before evacuation of the chamber down to the base pressure less than 0.5 Pa. Then, the pure oxygen was introduced into the chamber with the constant flow rate during the plasma oxidation. The pressure, RF voltage, DC bias, and duration time were varied to search for the suitable etching process parameters from 30-70 Pa, 150-250 V, -200 V to -450 V, and 1800 to 3600 s respectively. Both the optical microscope and SEM (JEOL 6000) were utilized to observe and measure the specimen before and after plasma oxidation processing.

In case of plasma printing into TiN and TiCN coatings, TiN- and TiCN-coated SKD 11 specimen with the size of 25 x 25 x 3 mm^3. In experiments, half of TiN and TiCN film surfaces is masked by the polyimide tape only to make etching of another halves. After preliminary experiments, this specimen was subjected to plasma oxidation at following parameters; e.g., the RF-voltage was 250 V, the DC-bias, -450V, the pressure, 30 Pa, and the duration time, 3.6 ks. In particular, the plasma state during etching is measured by using the emissive light spectroscopy (Hamamatsu photonics, Ltd) to describe the plasma oxidation process of TiN and TiCN films.

3. RESULTS AND DISCUSSION

3.1 Micro-Textured DLC Films

The micro-patterned DLC films as shown in Fig. 2 were subjected to plasma oxidation process for 1800 s.

Among four micro-patterns, both the Area-III and Area-IV were selected to be micro-textured. In case of Area-III with the rectangular micro-patterns in Fig. 2 (c), the rectangular DLC-pillars stand on the substrate with the pitch of 6 μm and the top surface size of 2 x 2 μm^2 in Fig. 4 a). To be notices, the DLC residuals were left even after oxygen etching for 1.8 ks. This might be because of inhomogeneous oxygen flux distribution. In fact, DLC-residuals are present together with damage to DLC-pillars at the same time. Figure 4 b) shows the DLC-pillar alignment with the size of 2 x 2 μm^2 and the pitch of 4 μm when starting from the Area-IV. Little residuals or damages are seen in Fig. 4 b); this implies that optimization of plasma oxidation printing conditions should provide the three micro-textures.

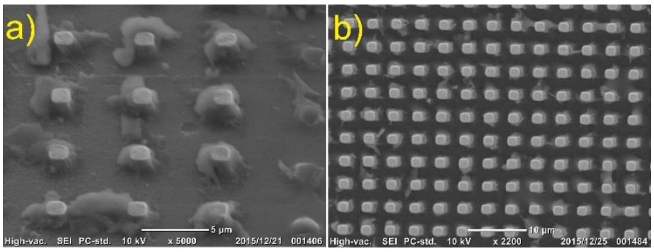

Fig. 4 SEM image on the plasma-oxidation printed DLC films. a) Area III printed with the pressure of 60 Pa and the RF-voltage of 250 V, and, b) Area IV printed with the pressure of 70 Pa and the RF-voltage of 150 V.

3.2 Plasma Oxidation Printing of DLC Films

The plasma oxidation printing is possibly driven by several chemical routes in case of the DLC coating after (Aizawa & Fukuda, 2013); e.g., $C + O_2^* \rightarrow CO_2$, $C + O_2^+ + e \rightarrow CO_2$, or $C + O^* \rightarrow CO$ for the activated oxygen molecules of O_2^*, the ionized oxygen molecules of O_2^+, and, the activated atoms of O^*. Through the quantitative plasma diagnosis on the chemical reactions during the present plasma oxidation printing, the activated atomic species is responsible for efficient etching of DLC films. For example, higher pressure and lower RF-voltage drive the damage-less plasma oxidation printing.

3.3 Plasma Oxidation Etching Behavior of Ceramic Coating

Both the dry- and wet-etching methods were applied to make micro-texturing of ceramic coatings; however, no processing routes were reported. In the following, the plasma oxidation printing behavior of ceramic coating is investigated by using the emissive light optical spectroscopy (EOS). The original EOS of activated species in the same plasma state as used in plasma oxidation printing is characterized by two strong intensities located at the longer wave-length range. These two peaks located at 776.34 nm and 843.778 nm in EOS represent the transition states of atomic oxygen after the previous work (Yunata, 2015). The oxygen flux to be utilized in the plasma oxidation printing is mainly driven by two processes; i.e. electron dissociation reaction ($O^* \rightarrow O^+ + e$) and electron attachment reaction (O). At the presence of TiN and TiCN films, both two constituents are resolved by activated oxygen atom flux bombardment; e.g., in case of TiN, TiN is resolved to Ti and N atoms.

EOS measurement was employed to describe this reaction during the plasma oxidation printing onto the TiN coated SKD11 substrate under the conditions with the pressure pf 30 Pa, the RF voltage, 250V, and DC-bias voltage, -450 V, and the duration time, 3600 s. Figure 5 a) compares the measured spectra with and without TiN films. New peaks other than oxygen related species are detected in this spectrum.

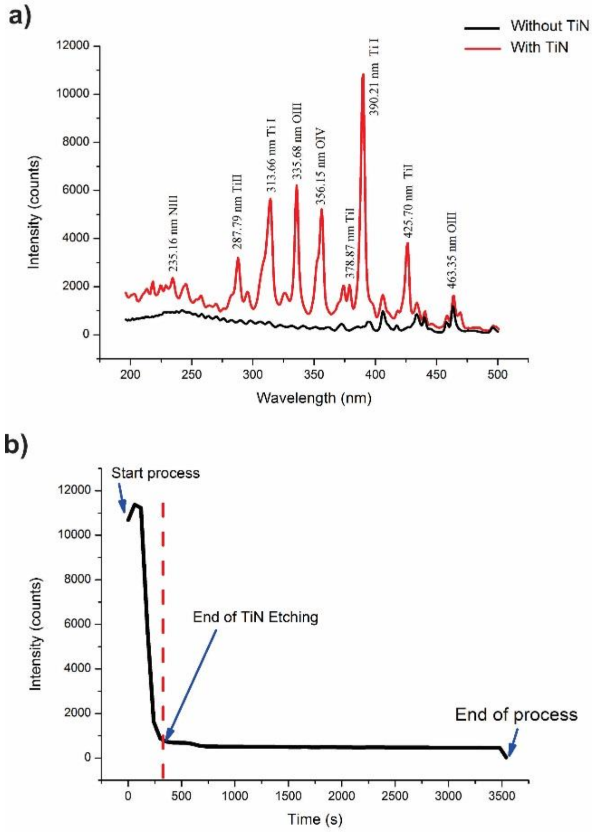

Fig. 5 Emissive light optical spectroscopy. a) A typical analyzed spectrum during TiN plasma etching, b) temporal variation of Ti*-intensity (detected at 390 nm).

After literatures (Ricard, 1985; Neuhäuser, 1999) and with comparison to NIST atomic spectra database (Kramida, 2015), the peaks located at the wave length of 313 nm, 378 nm, 390 nm, and 425 nm are identified as an activated titanium atom of Ti* (or Ti (I)); a peak located at the wave length of 287 nm, as an ionized atom of Ti^+ (or Ti (II)). On the other hand, activated nitrogen species are detected in the shorter wave length range. This drastic change of spectra in Fig. 5 a) proves that the un-masked TiN surface on the substrate should be selectively removed by a series of chemical reaction with oxygen atom flux bombardment. Among peaks for Ti*, the peak located at the wave length of 390 nm is chosen as an indicator to describe the actual etching behavior of TiN. Figure 5 b) depicts the temporal variation of Ti* intensity. The actual etching process itself works effectively only for 300 s. In corresponding to EOS spectra, only area at boundary between masked and un-masked TiN/TiCN coated SKD11 surface was selectively removed during plasma oxidation as shown in Fig. 6.

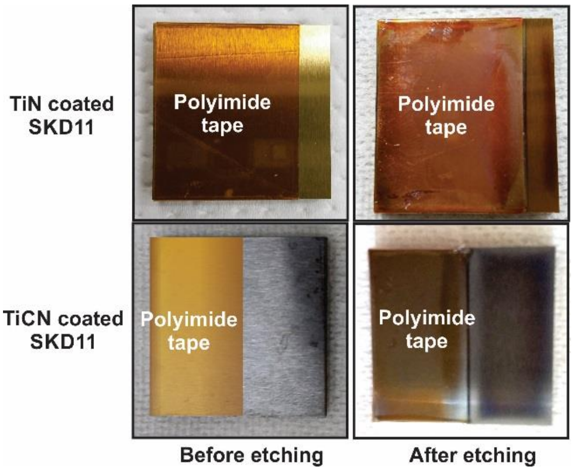

Fig. 6 Comparison of TiN/TiCN coated SKD11 before and after plasma oxidation

4. CONCLUSION

Two dimensional micro-patterns drawn on the DLC coating is transformed into three dimensional micro-textured by the present plasma oxidation printing. This process is directly utilized to fabricate the micro-textured punch and die for micro-stamping. Its homogeneous micro-texturing with less damage to DLC films is preferable to high qualification of punches and dies. The ceramic coating such as TiN and TiCN is also efficiently plasma-printed to have fine micro-textures relatively in short duration. High controllability of oxygen species as well as high densification of oxygen plasma in O_2/Ar system provides to improve the spatial resolution of micro-textures.

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