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Fabrication of Diamond-Like Carbon Emitter Patterns by Room-Temperature Curing Nanoimprint Lithography with PDMS Molds Using Polysiloxane

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ABSTRACT

We investigated the fabrication of diamond-like carbon (DLC) emitter patterns by room-temperature curing nanoimprint lithography (RTC-NIL) with polydimethylsiloxane (PDMS) molds using polysiloxane, as an application to the emitter for the next generation flat panel display.

The DLC which has excellent properties similar to diamond properties was used as a pattern material. A PDMS was used as a mold material and fabricated by the following optimum conditions of the first curing time at RT for 36 h and the second curing time at the temperature of 150 ℃ for 15 mins. The polysiloxane is in the state of sticky liquid at RT and stable in air. Therefore, the polysiloxane was used the electron beam (EB) resist and oxide mask material in EB lithography, and also used as RT-imprint material.

First, we fabricated the PDMS mold with pit array. Each dot is 5 μm-diameter and 400 nm-depth. We carried out the RTC-NIL process with PDMS molds using polysiloxane under the following optimum imprint conditions of 0.5 MPa-imprinting pressure, 1.5 min-the time between spin-coat and imprint, and 5 min-imprinting time. Next, the residual layer of imprinted polysiloxane pattern was 450 nm and then was removed with electron cyclotron resonance (ECR) trifluoromethane (CHF_3) ion shower under the conditions of 300 eV-ion energy and 3 min-etching time. Then, we processed the imprinted polysiloxane patterns on the DLC film with an ECR oxygen (O_2) ion shower under the conditions of 400 eV-ion energy and 12 min-etching time. As a result, we succeeded in fabricating convex DLC emitter patterns with high accuracy which has 5 μm-diameter and 500 nm-height.

INTRODUCTION

The diamond-like carbon (DLC) film exhibits unique properties such as wear resistance, chemical stability, biocompatibility, gas barrier, low coefficient of friction and negative electron affinity [1,2], and so it is expected to have various applications. For example, it can be used emitter for the next generation flat panel display (FPD), microgear for medical micro electro mechanical systems (MEMS) as electrical and mechanical applications respectively. Therefore, the nanopatterning technique for DLC films is essential to the fabrication of functional DLC based micro and nano devices.

The room-temperature curing nanoimprint lithography (RTC-NIL) using polysiloxane that we developed, which has certain advantages, including short process, high throughput and low cost, and keeping molds from thermal expansion and contraction, compared with conventional thermal-cycle NIL [3] and traditional electron beam (EB) lithography. We have already investigated the micropatterning of DLC films by RTC-NIL using glass-like carbon (GLC) molds, which have been fabricated with electron cyclotron resonance (ECR) oxygen (O_2) ion shower etching using polysiloxane in the EB lithography technology that we developed [4]. However, we found that convex DLC emitter patterns cannot be fabricated by this process because of the use of GLC mold with convex patterns. To overcome this problem, we proposed the use of polydimethylsiloxane (PDMS) molds which have reverse patterns of GLC molds.

Here we report the fabrication of PDMS mold with pit array. Moreover, we demonstrate the fabrication of DLC emitter patterns by RTC-NIL with PDMS molds using polysiloxane.

EXPERIMENTAL PROCEDURE AND APPARATUS

Fabrication process of PDMS mold for RTC-NIL

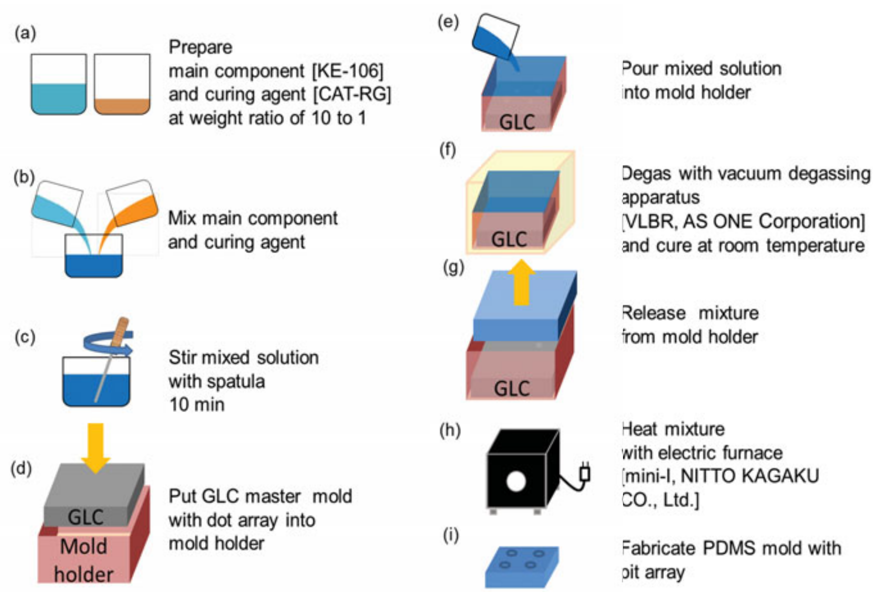

Figure 1. Fabrication process of the PDMS mold with pit array for RTC-NIL.

Figure 1 shows the fabrication process of the PDMS mold with pit array for RTC-NIL. First, the PDMS consist of main component [KE-106, Shin-Etsu Chemical Co., Ltd., Japan] and curing agent [CAT-RG, Shin-Etsu Chemical Co., Ltd., Japan] (a). The main component and curing agent were mixing at weight ratio of 10 to 1 respectively (b). The mixed solution was stirred with spatula for 10 min (c). Next, we fabricated the GLC master mold with dot array which has 500 nm-diameter and 700 nm-height put into mold holder (d). In addition, the mixed solution poured into mold holder (e) and then degassed with vacuum degassing apparatus [VLBR, AS ONE Corporation, Japan] and cured at room temperature for 36 h (f). The mixture released from mold holder (g), and heated with electric furnace [mini-I, NITTO KAGAKU CO., Ltd., Japan] at the temperature of 150 ℃ for 15 min (h). Finally, we fabricated the PDMS mold with pit array (i).

Fabrication process of DLC emitter patterns by RTC-NIL with PDMS molds using polysiloxane

Figure 2 shows the fabrication process of DLC emitter patterns by RTC-NIL with PDMS molds using polysiloxane. The DLC film (ta-C: tetrahedral amorphous carbon, 500 nm-thickness, 2 nm-arithmetic average roughness R_a) was synthesized by T-shaped filtered arc deposition method [5] on Si substrate (10 mm-square, 0.5 mm-thickness) and was used as pattern material.

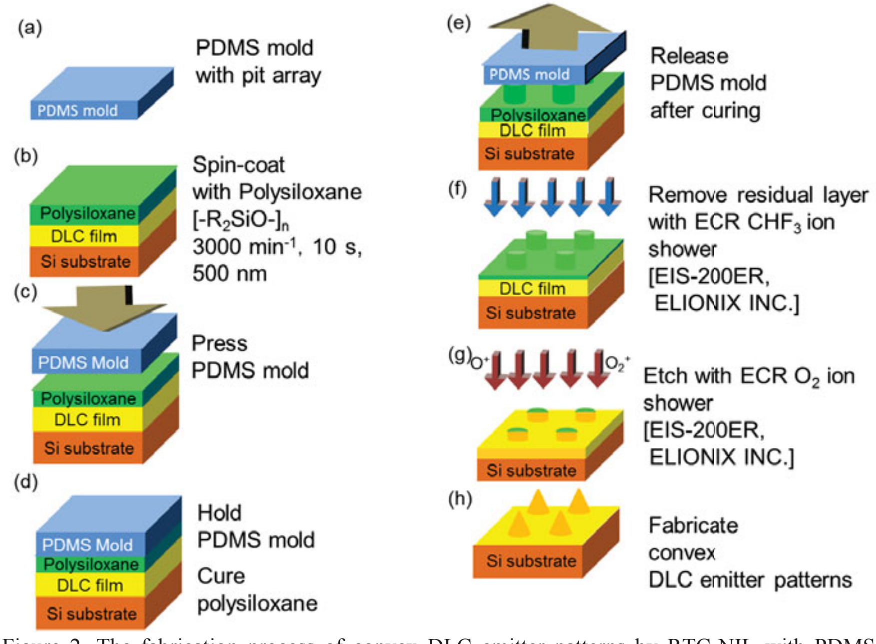

Figure 2. The fabrication process of convex DLC emitter patterns by RTC-NIL with PDMS molds using polysiloxane.

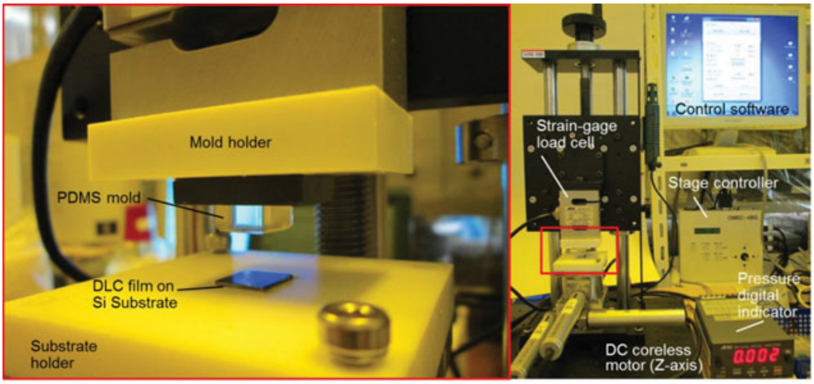

Figure 3. The appearance of desktop imprinting system driven by a DC coreless motor.

First, the DLC film deposited on Si substrate was spin-coated with polysiloxane (HSG-R7-13, Hitachi Chemical CO., LTD., Japan) at 3000 min^{-1} for 10 s (b). The PDMS mold and a 500 nm-thickness polysiloxane coted substrate without curing were pressed and holded under the optimum imprinting conditions of the time between spin-coat and imprint, the imprinting time and the imprinting pressure (c), (d). Next, PDMS molds was released after curing (e).

We carried out RTC-NIL using the desktop imprinting system driven by a DC coreless motor (SOM-B13E, SIGMA KOKI CO., LTD., Japan) that we developed, as shown in figure 3. The imprinting apparatus is 300 mm-length, 300 mm-width and 470 mm-height and has 30 mm × 50 mm-mold holder and 60 mm × 60 mm-imprint stage. The imprinting pressure measurements up to 0.8 MPa and its indication were performed with the aid of a strain-gage load cell (LC1205-K020, A & D Co., Ltd., Japan) and a pressure digital indicator (AD-4531A, A & D Co., Ltd., Japan) respectively. In order to obtain imprinted patterns with high accuracy, this imprinting system using the driving power of a DC coreless motor is capable of constant pressure control by sending pressure values of digital indicator to a personal computer [6].

The samples were removed residual layer with an electron cyclotron resonance (ECR) trifluoromethane (CHF_3) ion shower (f) and etched with an ECR oxygen (O_2) ion shower under etching conditions of high etching selectivity (g). Finally, we observed the DLC emitter patterns using a three-dimensional scanning electron microscope (3D-SEM) with four secondary electron detectors (ERA-8900FE, ELIONIX INC., Japan) (h) [7].

Optimum conditions for RTC-NIL

In order to obtain the optimum conditions for RTC-NIL with PDMS molds using polysiloxane, the time between spin-coat and imprint: t_1, the imprinting time: t_2, the imprinting pressure: P were investigated. First, the DLC film on the Si substrate was spin-coated with polysiloxane at 3000 min^{-1} for 10 s. The PDMS mold and a 500 nm-thickness polysiloxane coated DLC film without curing were pressed under the following conditions: t_1 ranges from 1 to 2 min, t_2 ranges from 3 to 7 min and P ranges from 0.3 to 0.7 MPa. Next, the PDMS mold was released after curing. Consequently, the imprinted polysiloxane patterns were observed with a 3D-SEM.

EXPERIMENTAL RESULT AND DISCUSSION

Optimum imprinting conditions for RTC-NIL

We investigated the optimum imprinting conditions for RTC-NIL with PDMS molds using polysiloxane. As a result, we found that the time from spin-coat to imprint: t_1 and the imprinting time: t_2 were 1.5 min and 5 min respectively. Figure 4 shows the SEM images and its cross-sectional profiles of the imprinted polysiloxane patterns. As shown in figure 4 (b), the imprinted polysiloxane patterns under 0.5 MPa-imprinting pressure: *P* were fabricated with high accuracy. However, as shown in figure 4 (a) and (c), the imprinted polysiloxane patterns under 0.3 MPa-*P* were lacking and dirty, and that under 0.7 MPa-*P* were missing because the PDMS mold was clashed flat. Thus we found that the optimum imprinting pressure was 0.5 MPa.

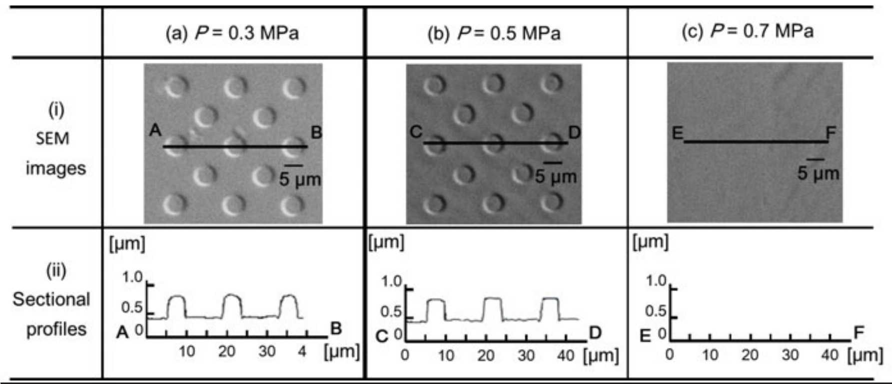

Figure 4. The SEM images and its cross-sectional profiles of imprinted polysiloxane patterns.

Fabrication of DLC emitter patterns by RTC-NIL

Figure 5 shows the SEM images and its cross-sectional profiles of DLC emitter patterns fabricated by RTC-NIL with PDMS molds using polysiloxane. As shown in figure 5 (a), we fabricated the PDMS mold with pit array for RTC-NIL which have 5 μm-diameter and 400 nm-depth. We carried out RTC-NIL with PDMS molds using polysiloxane, and found that residual layer of imprinted polysiloxane pattern was 450 nm, as shown in figure 5 (b). We removed residual layer in ECR CHF_3 ion shower etching under conditions of 300-ion energy and 3 min-etching time and then etched DLC film in ECR O_2 ion shower etching under conditions of 400-ion energy and 12 min-etching time [6]. The resulting convex DLC emitter patterns which have 5 μm-diameter and 500 nm-height with an aspect ratio of 0.1 were fabricated with high accuracy, as shown in figure 5 (c).

The DLC emitter patterns were sharpened with increase of etching time because the etching rate of ion incident angle of slant face is faster than that of ion incident angle of plane. Here, an incident angle is defined as the angle between the surface normal and the incident ions [8].

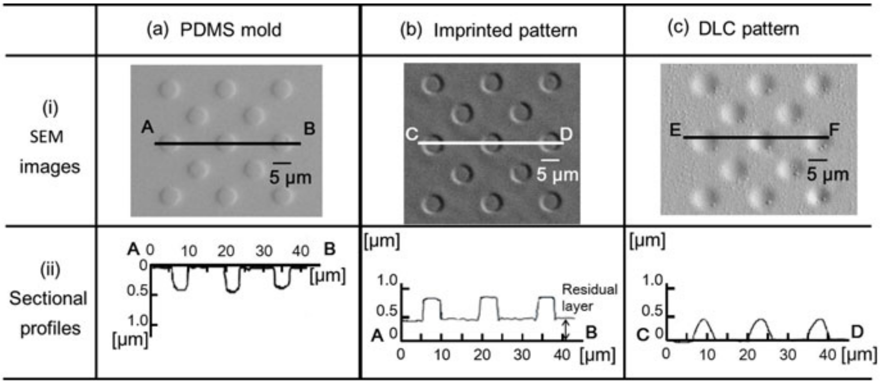

Figure 5. The SEM images and its cross-sectional profiles of DLC emitter patterns fabricated by RTC-NIL using polysiloxane.

CONCLUSIONS

We investigated the micropatterning of DLC emitter patterns by RTC-NIL with PDMS molds using polysiloxane. As a result, the sharpened DLC emitter patterns which have 5 μm-diameter and 500 nm-height were fabricated with high accuracy. The RTC-NIL technology with PDMS molds using polysiloxane that we developed has been shown to be useful for the nanopatterning of DLC films and is expected to be applied to DLC-based functional micro and nano devices such as an emitter for the next generation FPD.

REFERENCES

1. I. Kleps, A. Angelescu, N. Samfirescu, A. Gil, A. Correia, Solid-State Electron., **45**, 997 (2001).
2. G.A. Cirino, R.D. Mansono, P. Verdonck, R.G. Jasinevicius, L.G. Neto, Surf. Coat. Technol., **204,** 18 (2010).
3. S.Y. Chou, P.R. Krauss, P.J. Renstrom, Appl. Phys. Lett., **67**, 3114 (1995).
4. S. Kiyohara, S. Araki, Y. Kurashima, Y. Taguchi, Y. Sugiyama and Y. Omata, J. Mater. Sci. Mater. Electron., **22**, 183 (2010).
5. M. Kamiya, H. Tanoue, H. Takikawa, M. Taki, Y. Hasegawa, and M. Kumagai, Vucuum, **83**, 510 (2009).
6. S. Kiyohara, T. Ikegaki, C. Ito, I. Ishikawa, H. Tanoue, H. Takikawa, Y. Taguchi, Y. Sugiyama, Y. Omata and Y. Kurashima, edited by J.C. Amault, O.A. Williams, G.M. Swain, M. Nesladek and K.P. Loh, (Mater. Res. Soc. Symp. Proc. **1511**, Boston, MA, 2013) mrsf12-1511-ee05-03.
7. T. Suganuma, J. Electron Microsc., **34**, 328 (1985).
8. S. Kiyohara, C. Ito, I. Ishikawa, H. Takikawa, Y. Taguchi, Y. Sugiyama, Y. Omata and Y. Kurashima, edited by P. Bergonzo, R.B. Jackman, K.P. Loh, G.M. Swain and O.A. Williams, (Mater. Res. Soc. Symp. Proc. **1395**, Boston, MA, 2012) pp.27-32.