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Nanoimprint glass-like carbon molds fabricated with ECR oxygen ion beams using polysiloxane oxide mask

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Abstract We have investigated the nanofabrication for glass-like carbon molds with electron cyclotron resonance oxygen ion beam etching technologies using polysiloxane $[-R_2SiO-]_n$ as an electron beam mask and a room-temperature imprint resist material. The maximum etching selectivity of polysiloxane film against glass-like carbon was 27, which was obtained with ion energy of 400 eV. It was found that the optimum etching time to fabricate dots of 500 nm in height was 5 min, which was explored according to the computer simulation. The glass-like carbon molds with square pole and cylinder dots were fabricated with 500 nm in width and diameter, respectively. The optimum imprinting pressure and its depth obtained after the press for 5 min were 0.5 MPa and 0.5 μm, respectively. We carried out the room-temperature nanoimprint lithography process using glass-like carbon molds. The resulting width of imprinted polysiloxane patterns was obtained in good agreement with that of the mold.

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1 Introduction

The diamond exhibits unique properties such as high hardness, high thermal conductivity, wide band-gap and chemical stability, and so it is expected to have various applications. For example, it can be used not only for mechanical tools and optical instruments but also for semiconductor devices, electron emission devices, microgears and biosensors [1–3]. Therefore, the nanopatterning technique for a diamond is essential to the fabrication of functional micro/nano devices. We had investigated the nanopatterning for chemical vapor deposited (CVD) diamond films in room-temperature nanoimprint lithography (RT-NIL), using diamond molds [4, 5]. The diamond molds had been fabricated with electron cyclotron resonance (ECR) oxygen ion beam etching using polysiloxane $[-R_2SiO-]_n$ with the electron beam (EB) lithography technology that we developed [4, 5]. The diamond molds have a lifetime approximately 100 times longer than that of silicon dioxide (SiO_2) mold or that of silicon (Si) mold, both using a conventional NIL process. However, the maximum etching selectivity of polysiloxane film against diamond film was as low as 4.7 [5]. Consequently, it was found difficult for the diamond to be applied to micromechanical parts such as gears because only sharpened dots up to a height of 0.5 μm were obtained. To overcome this problem, we have proposed the use of glass-like carbon (GC), as mold materials, which has excellent properties similar to those of the diamond [6], and is inexpensive, i.e., one-fifth of the diamond film (10 × 10 mm square). Compared to the conventional NIL process [7, 8] using PMMA (polymethyl methacrylate) which requires a thermal cycle, the RT-NIL process using polysiloxane has certain advantages, including short steps, high throughput and low cost.

Here we report the nanofabrication for GC molds with EB lithography technology using polysiloxane and the ECR oxygen ion beam etching characteristics for GC. Moreover, we have investigated the optimum conditions for RT-NIL using GC molds that we fabricated.

2 Experimental apparatus and procedure

2.1 The nanopatterning process for a GC

A polished GC (10 × 10 mm square, 3.4 mm thick, surface roughness *Ra*, 1.6 nm) (Hitachi Chemical Co., Ltd., Japan, PXG-35) was used as a mold material. Figure 1 shows the nanopatterning process for a GC to fabricate a GC mold using polysiloxane (Hitachi Chemical Co., Ltd., Japan, HSG-R7-13) oxide mask which is in the state of sticky liquid at room temperature and stable in air. The polysiloxane of mask material in EB lithography was also used as RT-imprint resist material.

The nanofabrication process for a GC mold using polysiloxane was as follows: (1) The GC substrate was first spin-coated with polysiloxane at 3,000 rpm for 10 s. The resulting film thickness of the polysiloxane was 0.5 μm. (2) The polysiloxane exhibited a negative-exposure characteristics and its sensitivity was 5.5×10^{-5} C/cm^2 which is almost the same as that of PMMA. The sensitivity of polysiloxane is in good agreement with that of PMMA [9]. The electron dose of polysiloxane was typically set to be 6.7×10^{-4} C/cm^2. The EB drawing was conducted with an EB lithography system (ELIONIX Co., Japan, ELS-7500). An EB was scanned on polysiloxane films according to patterns entered in the computer. (3) A polysiloxane oxide mask-pattern was developed by removing the unirradiated area where the ratio of MIBK (4-Methl-2-pentanone) to IPA (2-Propanal) is 1 to 2. (4) We have processed the GC with an ECR oxygen ion beam apparatus (ELIONIX Co., Japan, EIS-200ER) under etching conditions with a high

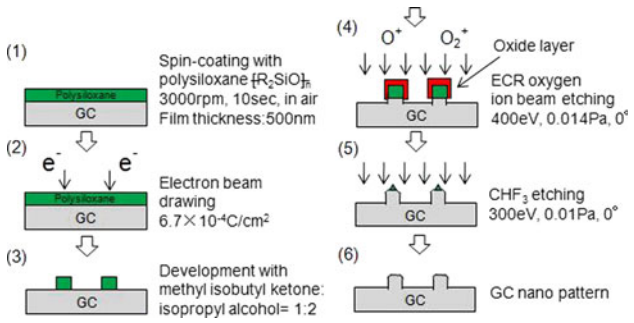

Fig. 1 The nanopatterning process for GC molds using polysiloxane oxide mask

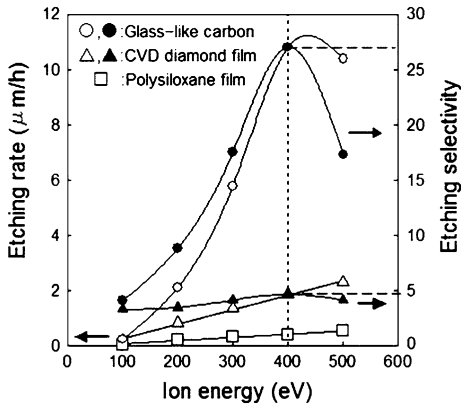

Fig. 2 The dependence of the etching rate, and etching selectivity of GC, CVD diamond film and polysiloxane film on ion energy (Ion incidence angle: 0°, Microwave power: 100 W, Gas pressure: 1.4×10^{-2} Pa, Stage temperature: 24 °C)

etching selectivity. (5) The remaining polysiloxane oxide mask on GC was removed with an ECR CHF_3 (trifluoromethane) ion beam. (6) Finally, the resulting GC mold was obtained.

2.2 Compact imprint apparatus

Figure 2 shows the appearance of compact imprint apparatus driven by a direct-current (DC) coreless motor (SIGUMA KOKI Co., Ltd., Japan, SOM-B13E) that we developed. The apparatus is 30 cm long, 30 cm wide and 47 cm high and has a mold mask holder (10 × 10 mm square) and a stage (60 × 60 mm square). The x–y-z positioning accuracy using the DC coreless motor had a resolution of 1 μm. The x–y-z axis stage was controlled by three DC coreless motors via a computer. The imprinting pressure measurements up to 1.2 MPa were performed with the aid of a strain-gage load cell (A & D Co., Ltd., Japan, LC1205-K020).

2.3 Optimum conditions for RT-NIL using GC molds

In order to obtain the optimum conditions for RT-NIL using GC molds that we fabricated, we investigated the dependence of imprint depth on pressure. The Si substrate (10 × 10 mm square, 0.5 mm thick) was first spin-coated with polysiloxane at 3,000 rpm for 10 s. The GC mold that we fabricated and a 0.5 μm thick polysiloxane coated substrate without curing were pressed for 5 min at the optimum imprinting pressure. Next, the GC mold was removed after curing. Then we have observed the imprinted polysiloxane patterns with an atomic force microscopy (AFM) (SII Nano Technology Inc., Japan, SPA-300).

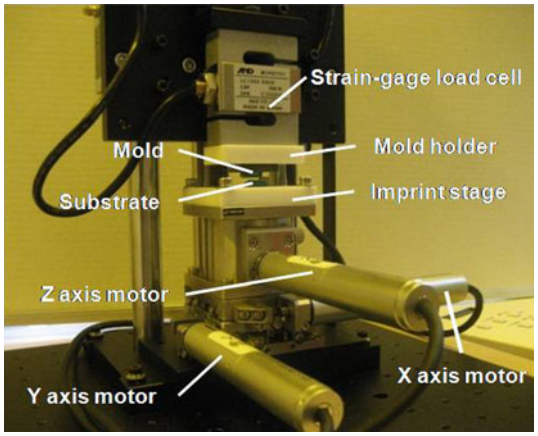

Fig. 3 Compact imprint apparatus driven by a DC coreless motor (30 cm long, 30 cm wide, 47 cm high)

3 Experimental results and discussion

3.1 ECR oxygen ion beam etching characteristics of GC

In order to obtain the optimum ECR oxygen ion beam etching conditions for GC, We investigated the dependence of etching rate and etching selectivity on ion energy. Figure 3 shows the dependence of the etching rates and the etching selectivity of GC, diamond and polysiloxane films on ion energy. With the ion energy ranging from 100 to 500 eV, the etching rates of GC, diamond and polysiloxane films increased linearly with increasing ion energy. The maximum etching selectivity of polysiloxane film against GC was 27, which was more than five times as high as that against the diamond film, which was obtained under the following ECR oxygen ion etching conditions : ion energy of 400 eV, ion incidence angle of 0°, microwave power of 100 W, gas pressure of 1.4×10^{-2} Pa and stage temperature of 24 °C.

3.2 Nanofabrication for GC molds

Figure 4a shows the scanning electron microscopy (SEM) (ELIONIX Co., Japan, ERA-8900FE) photographs of shaped tetragonal pyramid and cone dots, which are 500 nm in width and diameter, respectively, and were fabricated with etching time of 20 min. Figure 4b,c show the SEM photographs of enlarged tetragonal pyramid and cone, respectively, which dots with 4 μm pitch and a height of approximately 1 μm. As a result, the GC molds with high aspect ratio dots were fabricated, and the problems of diamond mold have been overcome. We carried out the RT-NIL process using the GC mold with dots with a height of approximately 1 μm, but we could not obtain imprinted polysiloxane pattern because dot patterns snapped. It was attributed to the height of dots, which was much higher compared to the polysiloxane film which was 0.5 μm in thickness film, as shown in Fig. 5a.

3.3 The control of height of dots according to the computer simulation of profile changes

We thought that the molds with dots which are 0.5 μm in height against the polysiloxane film (0.5 μm in thickness) are necessary for the imprinting process in which we transfer dot patterns from the mold to polysiloxane film in high accuracy, as shown in Fig. 5b. In order to obtain the optimum ECR oxygen ion beam etching time of GC, the

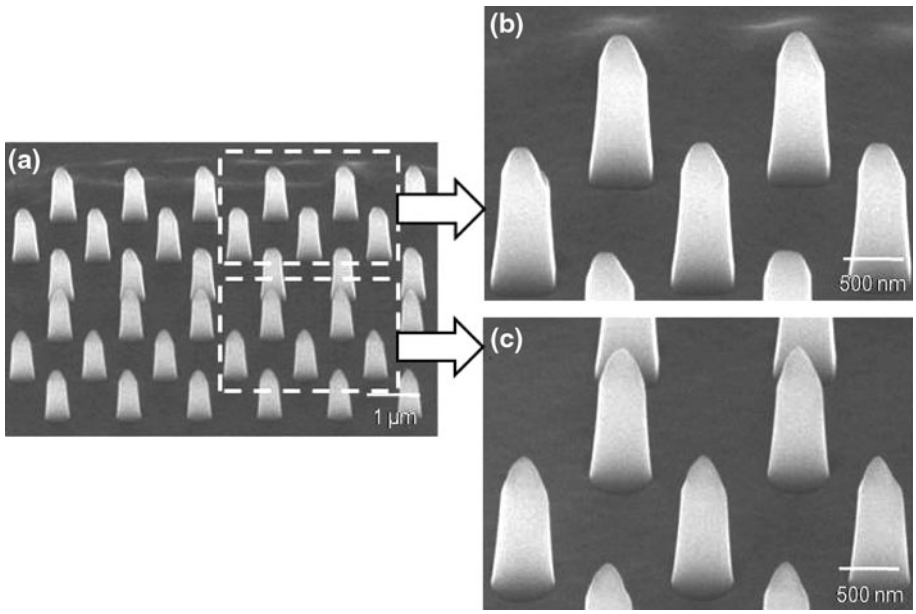

Fig. 4 SEM photographs of the GC mold with tetragonal pyramid and cone dots [width and diameter, 500 nm; pitch, 4 μm; height, approximately 1 μm] (**a**), SEM photographs (**b**) and (**c**) of enlarged tetragonal pyramid and cone dots, respectively

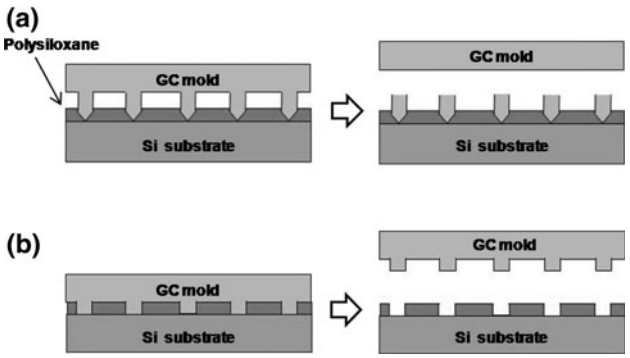

Fig. 5 Schematic illustration of the transfer of dot patterns from GC mold to polysiloxane film which is 0.5 μm in thickness: (**a**) the case of dots 1 μm in height and (**b**) the case of dots 500 nm in height

dependence of the height with dots on etching time were investigated by the computer simulation of profile changes that we developed.

Figure 6 shows the simulation results of under the following etching conditions, which are before etching and at the etching time of 5, 10, 15, 20 min, respectively, and the changing height of the dot. As a result, it was found that the optimum etching time to fabricate dots of 0.5 μm in height was 5 min.

Figure 7a,b show the SEM photographs of square pole and cylinder dots which are 500 nm in width and diameter, respectively, and are approximately 500 nm in height. Moreover, Fig. 8a shows the SEM photographs of the micro-gear patterns which were fabricated as an example of mechanical application. We fabricated the gear patterns in various sizes including the minimum one with the tip diameter of 3 μm and root diameter of 2 μm, as shown in Fig. 8b.

3.4 Optimum conditions for RT-NIL using GC molds

We have carried out the RT-NIL process using a GC mold with square pole and cylinder dots with 500 nm in width and diameter, respectively, which have height of 500 nm. Figure 9 shows the dependence of the imprint depth of polysiloxane film on imprinting pressure. The imprint depth of polysiloxane film increased linearly with the

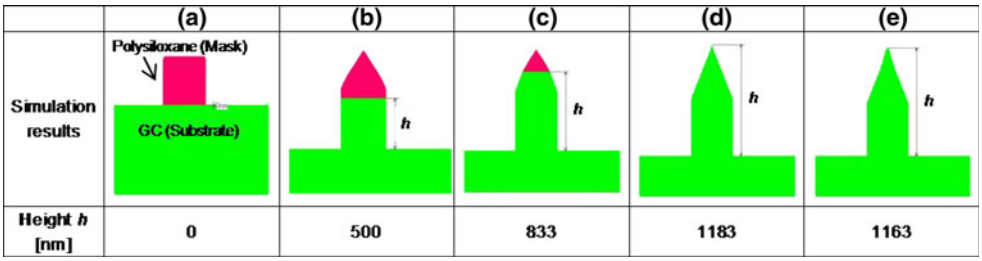

Fig. 6 The simulation results of profile changes of ECR oxygen ion beam etching time, before etching (**a**) and at the etching time of 5, 10, 15, 20 min (**b**), (**c**), (**d**) and (**e**), respectively

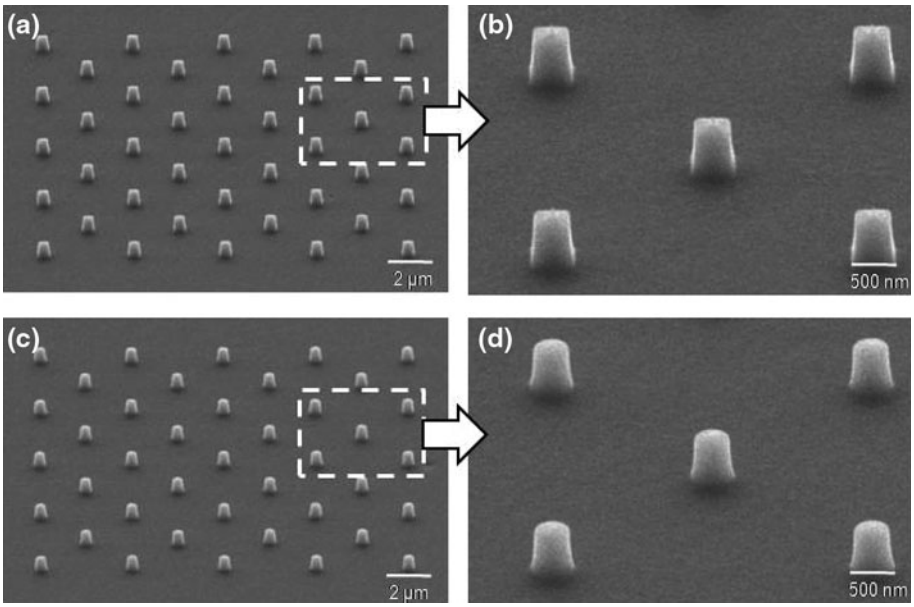

Fig. 7 SEM photographs of the GC mold (**a**) and (**c**) of square pole and cylinder dots, and enlarged SEM photographs (**b**) and (**d**) of square pole and cylinder dots, respectively [diameter and width, 500 nm; pitch, 6 μm; height, approximately 500 nm]

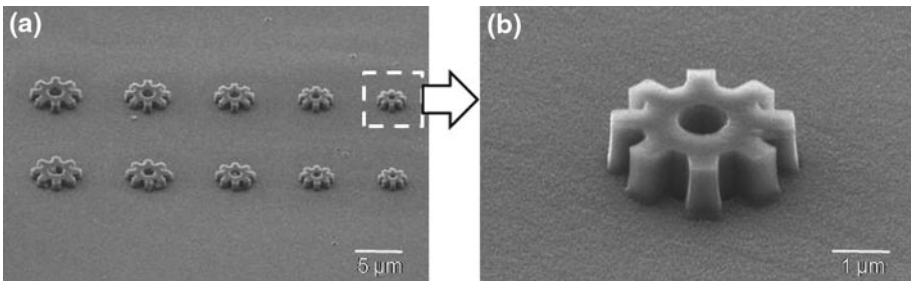

Fig. 8 SEM photographs of (**a**) the gear patterns in various sizes and (**b**) the minimum gear pattern [tooth numbers, 8; tip diameter, 3 μm; root diameter, 2 μm]

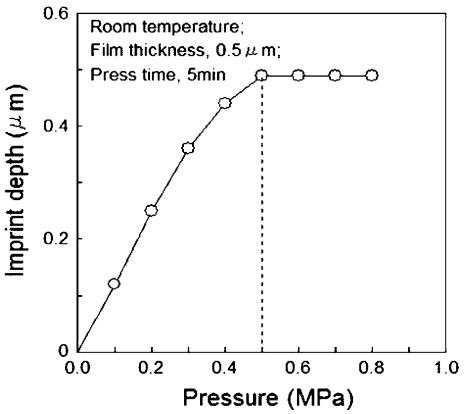

Fig. 9 The dependence of the imprint depth of polysiloxane film on imprinting pressure

increase of imprinting pressure up to 0.5 MPa because polysiloxane is in the state of sticky liquid at room temperature, and then, the imprint depth of polysiloxane film was in agreement with the film thickness of 0.5 μm from 0.5 to 0.8 MPa, where the same imprinted polysiloxane patterns were obtained, respectively. Therefore, we assume the minimum imprinting pressure of 0.5 MPa to be the optimum imprinting pressure from 0.5 to 0.8 MPa. Thus the optimum imprinting pressure and its depth obtained after the press for 5 min were 0.5 MPa and 0.5 μm, respectively.

Figure 10 shows the AFM images of (a) a GC mold [Square pole dots with a 500 nm width having height of 500 nm] and (b) an imprinted polysiloxane pattern [Press time, 5 min; Imprinting pressure, 0.5 MPa]. The width of an imprinted polysiloxane pattern was in good agreement with that of the GC mold, and the polysiloxane mask pattern was fabricated in high accuracy.

4 Conclusions

In this study we have investigated the nanofabrication of GC molds in ECR oxygen ion beam etching technologies using polysiloxane oxide mask. From the experimental results the following conclusions can be drawn. The maximum etching selectivity of polysiloxane film against GC was 27, which was more than five times as high as that against the diamond film. We have explored the optimum etching time to fabricate dots with the same height as film thickness of polysiloxane, which was 5 min according to the computer simulation of profile changes. The GC molds of square pole and cylinder dots with a height of 500 nm were fabricated with the etching time of 5 min, using polysiloxane oxide mask with EB lithography technology that we developed. The width of imprinted polysiloxane patterns was in good agreement with that of the GC mold, and the polysiloxane mask pattern was fabricated in high accuracy. The RT-NIL technology using the GC molds that

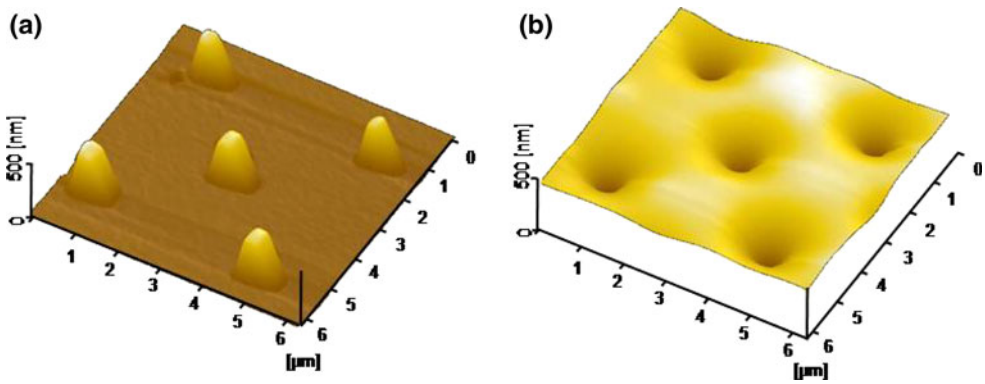

Fig. 10 AFM images of (**a**) the GC mold and (**b**) an imprinted polysiloxane pattern

we developed has been shown to be useful for the nanofabrication and is expected to enable applications for nano/micro electronics, optical and mechanical devices.

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