Iterative imprint for multilayered nanostructures by feeding, vacuum forming, and bonding of sheets

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The authors proposed an iterative imprint method for multilayered nanostructures. A thermoplastic sheet is fed onto a nanostructured mold and thermally imprinted by vacuum pumping between the mold and the sheet. Next, the imprinted sheet is thermally bonded onto a sheet that had been formed in the preprocess and that is held by an upper punch at the position opposite to the mold, and then the upper punch picks the sheet up from the mold. Repeating these processes realizes precision multilayered structures while maintaining horizontal positions of the upper punch and the vacuum-forming mold. This method will lead to the low-cost, high-accuracy fabrication of three-dimensional photonic devices. The authors formed $400 \times 400 \times 270\ \mathrm{nm}^3$ square hollows with an 800 nm pitch on the surface of a polymethyl methacrylate sheet of 1 μm thickness. The decrease in the light intensity diffracted by the mold surface as a result of the filling of the sheet was monitored in real time during the forming. The authors also successfully bonded another sheet and observed the hollows with 1 μm intervals in the thickness direction. [DOI: 10.1116/1.2982243]

I. INTRODUCTION

Three-dimensional (3D) photonic crystals,[1–5] which have periodic nanostructures of light-wavelength scale in 3D, are promising for optical devices or microelectronic devices. The conventional very large-scale integration (VLSI) process of deposition, lithography, and etching is not practical for the mass production of 3D photonic crystals. From the time nanoimprint lithography (NIL) was proposed and developed by Chou *et al.*,[6] many studies on the replication of polymer surfaces by pressing nanostructured molds have been carried out.[7–10] For fabricating multilayered nanostructures, some low-cost methods using NIL were reported. Bao *et al.*[11] proposed reversal imprint, in which polymer layers spun on a mold substrate immediately above the glass transition temperature (T_g) are stacked up, and demonstrated the stacking of three nanostructured polymer layers with different T_g. On the other hand, Nakajima *et al.*[12] proposed a repetition method for fabricating multilayered films in which a temperature gradient is created in the thickness direction of a 1.2-μm-thick polymethyl methacrylate (PMMA) layer sandwiched between the mold with higher temperature and the substrate with lower temperature. In these techniques, the positioning of the nanostructures on each layer is difficult because the mold must be released from the punch during spin coating of a polymer layer.

II. ITERATIVE IMPRINT

We propose, in this article, an iterative method without the need to release the mold from the press machine. Figure 1 shows a schematic of our iterative imprint process. First, (1) a thin thermoplastic sheet is fed onto the nanostructured mold. Second, (2) a pump evacuates the gap between the sheet and the mold, and then (3) the heated mold imprints the nanostructure onto the polymer sheet at a temperature higher than the T_g of the polymer. In the third stage, (4) the sheet held by an upper punch at the position opposite to the mold is bonded to the imprinted sheet by controlling the temperature of the whole system, and (5) the sheet is picked up after cooling. (6) Repeating steps (1)–(5) allows us to fabricate

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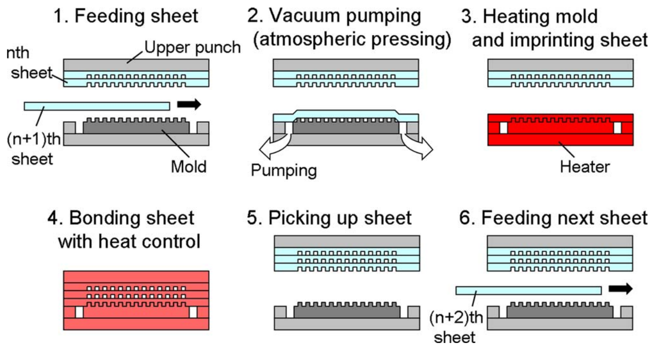

FIG. 1. Schematic of iterative imprint process.

multilayered nanostructures. Here, the vacuum forming, that is, atmospheric pressing, realizes imprinting in a large area because of its uniform pressure on a thin layer.

For steps (1) and (2), the following process can also be used; the sheet is fed onto the mold in vacuum, the edges of the sheet and the mold are sealed, and the equipment is exposed to air. At step (3), the imprinted sheet is uniformly cooled to room temperature (or a temperature lower than the bonding temperature) at a low cooling rate to suppress the residual stress in the imprinted sheet. At step (4), to avoid misalignment in the planar direction between sheets during bonding, the expansions of the nth sheet held by the upper punch and the $(n+1)$th sheet held by the mold must be the same. Both the upper punch and the mold are similarly heated to the bonding temperature to make the expansion of the bonded sheets equal. Of course, the coefficients of thermal expansion (CTEs) of the upper punch and the mold materials must be the same and hence, a material with low CTE should be selected. An advantage of this process is that the vertical movement of the upper punch allows the precise positioning of each layer because the upper punch can be devoted to the role of bonding and picking up the imprinted sheets. The detailed issues and their solutions will be described in Sec. IV.

III. EXPERIMENT

We obtained PMMA sheets of 1 μm thickness by spin coating. PMMA solution (10 wt %) in toluene was prepared by adding 1 g of the PMMA film (Acryplene HBS-005: Mitsubishi Rayon Co., Ltd.) into 10 ml of toluene. The solution was centrifuged at 8000 rpm for 3 min, and the top of the solution was dipped and spun at 4000 rpm on a polished chemical-vapor deposition-SiC substrate on which a lubricant (Durasurf HD-1101Z: Daikin Chemical) was coated before hand. The PMMA sheet was baked at 60 °C for 10 min. A perforated polyethylene terephthalate film (HS-75: Teijin DuPont Films Japan, Limited) and heat-resistant double-sided tape (9097: Sumitomo 3M Limited) were used to release the finished 1-μm-thick PMMA sheet.

The mold was fabricated by electroforming Ni using a master Si substrate with electron beam (EB) resist (ZEP-520A: Zeon Corporation) structures. A Ni thin film of 20 nm thickness was sputtered onto the master substrate as a seed

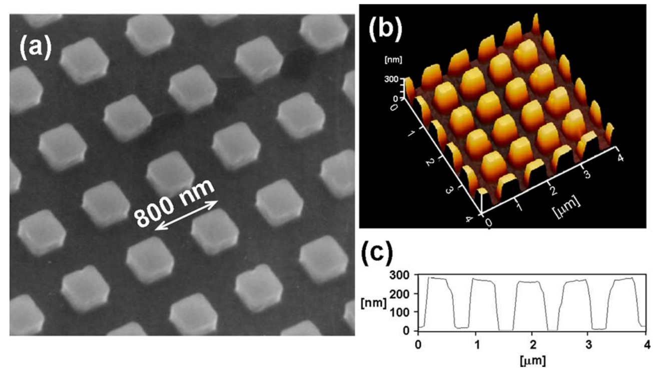

FIG. 2. (a) SEM image, (b) AFM image, and (c) surface profile of Ni mold.

layer for electroforming. Figure 2 shows (a) a scanning electron microscopy (SEM) (S-4160s: Hitachi) image and (b) an atomic force microscopy (AFM) image of the nanostructured Ni mold. The mold has $400\times400\times270\ \text{nm}^3$ square pillars with 800 nm pitch and in $8\times8\ \text{mm}^2$ area. A mold lubricant (Durasurf HD-2101Z: Daikin Chemical) was coated on the Ni mold before the experiment. Figure 3 shows a schematic of our experimental setup for demonstrating the vacuum forming of the sheet. The mold and a ceramic heater were placed in a vacuum flow channel. In our design of the mold with pillars, we could evacuate the air between the Ni mold and PMMA sheet in the entire area using this flow channel around the mold. However, in the case of a larger imprinted area of the mold or other nanostructure designs that disturb the evacuation of the gaps, the forming will be carried out in a vacuum chamber, as described in Sec. II. The heating for imprinting was started after sufficient evacuation. The temperatures of the PMMA film surface and heater were measured with thermocouples. We also monitored, in real time, the intensity of the diffracted wave with a spectroscope (USB2000: Ocean Optics, Inc.).[13] The mold surface reflects and disperses the light irradiated from an angle. In this study, we irradiated white light from an angle of 54° and monitored the intensity of the wave with 650 nm wavelength using the spectroscope set just above the mold. The intensity of the diffracted wave decreases owing to the progress of PMMA

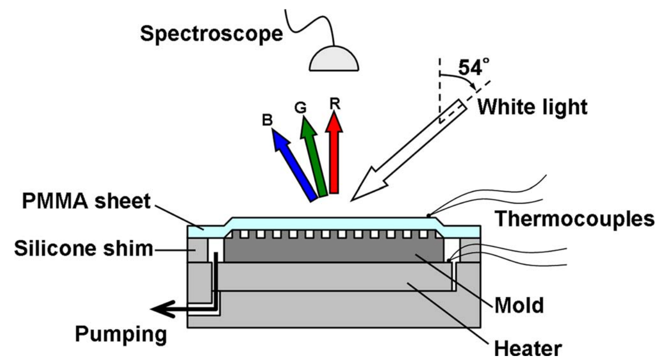

FIG. 3. Schematic of experimental setup for demonstrating vacuum forming of PMMA sheet, while measuring surface temperatures of the PMMA sheet and heater and monitoring the diffracted wave in real time.

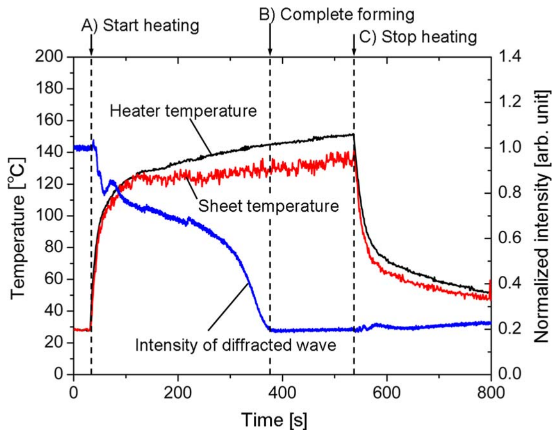

FIG. 4. Temperatures of PMMA surface and mold surface, and intensity of diffracted wave (650 nm wavelength).

filling. Furthermore, we bonded another PMMA sheet with nanostructures (corresponding to Fig. 1, step 4).

IV. RESULTS AND DISCUSSION

We vacuum formed a single PMMA sheet at 150 °C. Figure 4 shows the plots of the temperatures of the PMMA surface and the mold surface together with the intensity of the diffracted wave (650 nm wavelength), which is normalized by the initial intensity. The intensity of the diffracted wave decreased as the PMMA filled the mold during heating. The time of heating to 150 °C was 500 s (A–C); however, the intensity of the diffracted wave was saturated 350 s after the start of heating. The filling of the nanostructures was considered to be finished by this time. Figure 5 shows (a) an optical image of the replicated PMMA sheet and (b) a magnified SEM image and (c) an AFM image of the surface of the sheet. The PMMA sheet was evenly imprinted in the entire area and the nanostructures were completely formed. The average roughness (R_a) of the back of the sheet, as

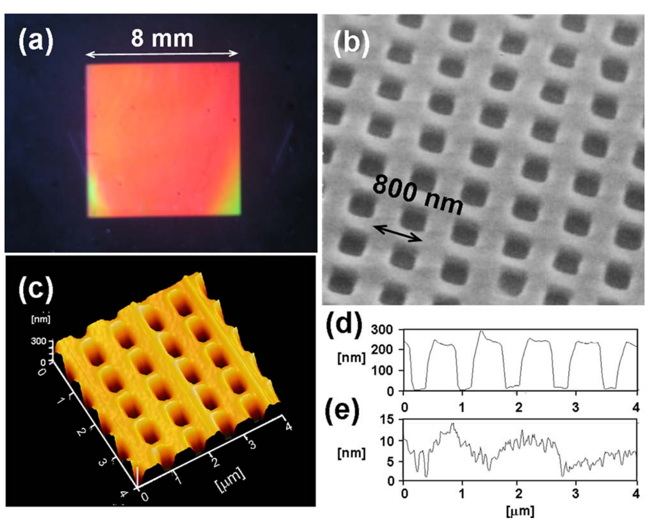

FIG. 5. (a) Optical image, (b) SEM image, (c) AFM image, (d) surface profile, and (e) back surface profile of vacuum-formed 1-μm-thick PMMA sheet.

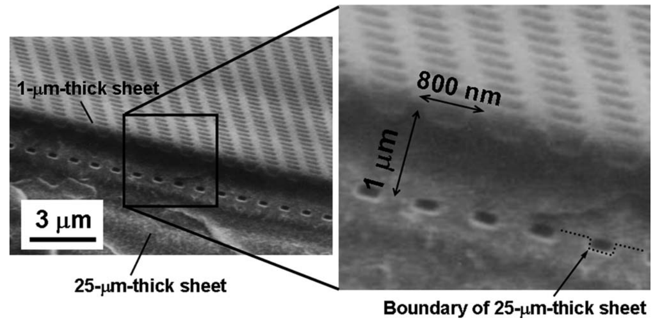

FIG. 6. SEM images of cross section of bonded sheets.

shown in Fig. 5(e), was about 6 nm. This flatness over a large area is realized by the uniform pressing using the vacuum pump. Hence, the effect of the cooling rate on the residual stress in the PMMA sheet will be investigated.

We bonded another PMMA sheet with nanostructures. The heater raised the temperature at the rate of 0.9 °C/s. Heating was stopped when 100 °C was reached and was followed by air cooling. The vacuum pumping prevented the occurrence of air bubbles during heating. Note that this bonding process does not require pressing by vacuum; normal punch pressing in vacuum can also be used. Figure 6 shows a SEM image of a cross section of the bonded sheet. The cross section was obtained by freezing in liquid nitrogen and breaking the sheet. No bonded boundary was observed and the shapes in the gap between the two sheets were not lost.

The mold and the polymer materials used in this study were Ni and PMMA, respectively. There are two main critical barriers to bonding alignment owing to thermal expansion. The first problem is the thermal strain between the mold and the polymer or that between the upper punch and the polymer. However, when the thickness of the mold or the upper punch is designed to be 1 mm, in contrast to ~10-μm-thick polymer layers (Young's moduli of Ni and PMMA are 200 and 3 GPa, respectively), the in-plane expansion of the polymer can be governed by that of the mold or the upper punch. The second problem is the difference in thermal expansion between the mold and the upper punch or each in-plane unevenness of thermal expansion. The CTE of Ni is about $13 \times 10^{-6}/°C$, thus, 100-mm-long Ni requires a temperature control accuracy of better than 0.03 °C for 50 nm alignment. When using quartz (CTE: $0.5 \times 10^{-6}/°C$) for the materials of the mold and the upper punch, for example, the temperature control is degraded to 1 °C. To align each layer during bonding throughout the entire area or to enlarge the area, the temperatures of the mold and the upper punch must be precisely controlled.

V. CONCLUSIONS

We have proposed a new imprint method for multilayered periodic nanostructures involving feeding, vacuum forming, and bonding of sheets. Our experiment demonstrated the imprinting of $400 \times 400 \times 270$ nm^3 square hollows with 800 nm pitch on the surface of a 1-μm-thick PMMA sheet. By real-time monitoring of a diffracted wave during forming, the completion of the filling of the sheet on the mold was confirmed. We bonded another sheet without losing the nanostructures in the gaps by heating at a rate of 0.9 °C/s and stopping at 100 °C. This iterative imprint method will lead to the low-cost, high-accuracy fabrication of 3D photonic devices or microelectronic systems.

ACKNOWLEDGMENTS

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