A non-fluorine mold release agent for Ni stamp in nanoimprint process

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ABSTRACT

This study presents a novel material as an anti-adhesive layer between Ni mold stamps and polymethyl methacrylate (PMMA) substrate in nanoimprint process. A polybenzoxazine ((6,6'-bis(2,3-dihydro-3-methyl-4H-1,3-benzoxazinyl))) molecule self-assembled monolayer (PBO-SAM) considering as anti-adhesive coating agent demonstrates that non-fluorine-containing compounds can be improve the nanoimprint process in Ni/PMMA substrates. In this work, the nanostructure-based Ni stamps and the imprinted PMMA mold are performed by electron-beam lithograph (EBL) and our homemade nanoimprint equipment, respectively. To control the forming of fabricated nanopatterns, the simulation can be analyzed their effect of temperature distributions on the deformation of PBO-SAM/PMMA substrate during hot embossing lithography (HEL) process. Herein the diameter of pillar patterns is 200 nm with and 400 nm pitch on Ni stamp surface. Based on the hydrophobic PBO-SAM surface in this conforming condition, the results of Ni mold stamps infer over 90% improvement in controlling quality and quantity.

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1. Introduction

Nanoimprint lithography (NIL) is the most potential for making ultra-fine patterning substrate technique to quantity productions [1,2]. In recent year, the fast development of NEMS/MEMS technologies that can be demanded for optoelectronic devices [3], quantum computing devices [4], biosensors [5] and the electronics devices [6]. Hence, the conventional photolithograph may not be the appropriate method for assignments [7]. In the case of X-ray, ion-beam, and electron-beam lithography, they are not suited to fabricate a large-area pattern production such as a light guide ultra-thin-film plate of LCD due to costly, time consuming, and hard to control. Based on some fabricated problems, the NIL process provides flexibilities in terms of material, pattern size, structures, and substrate topography [8].

Nowadays, the NIL fabricated method receives great attention that can open new doors for interdisciplinary nanoscale researches and the commercial products because of its combination of high patterning resolution in a low cost and high throughput. However, several application issues have to be solved before this nanoimprint technology is mature enough for industrial scale processes. Because the imprinted mold process is often carried out at high temperature (>100 °C about the glass transition temperature of polymer) and high pressure (>100 bar) that are obviously undesir-

able. The thermal cycle of heating and cooing processes can cause distortion of the mold and the imprinted substrate. One particular issue is control of an anti-adhesive layer treatment between the stamps and polymer to prevent the mechanical failure from being a critical pattern defect that can affect the imprint qualities and the stamps lifetime. Schift et al. demonstrated to employ fluorinated trichlorosilane as the anti-adhesive coatings on silicon in a micrometer regime [9]. In addition, Park et al. used a fluorinated silane agent to achieve a better anti-adhesive coating process for Ni mold stamps [10]. However, few attempts have so far been made at a non-fluoride material in NIL process of anti-adhesive coating treatment for Ni stamps. Our life environment is in need of non-fluoride materials to keep it. Furthermore, based on a soft characteristic of Ni-based material, the most important roller nanoimprint technique can be developed. The aim of this present study is to develop PBO-SAM as an anti-adhesive coating agent between Ni stamps and PMMA substrate that can improve nanofabrication technique, namely, NIL.

2. Experiment

Firstly, polybenzoxazines were prepared by reacting 4,4'-isopropylidenediphenol (bisphenol-A, BA-m), formaldehyde and methylamine. All chemical materials purchased from Aldrich chemical company, Inc. USA. In synthesis process was in need of benzoxazine monomers that were determination of the materials formaldehyde/dioxane and methylamine/dioxane at 10 °C for

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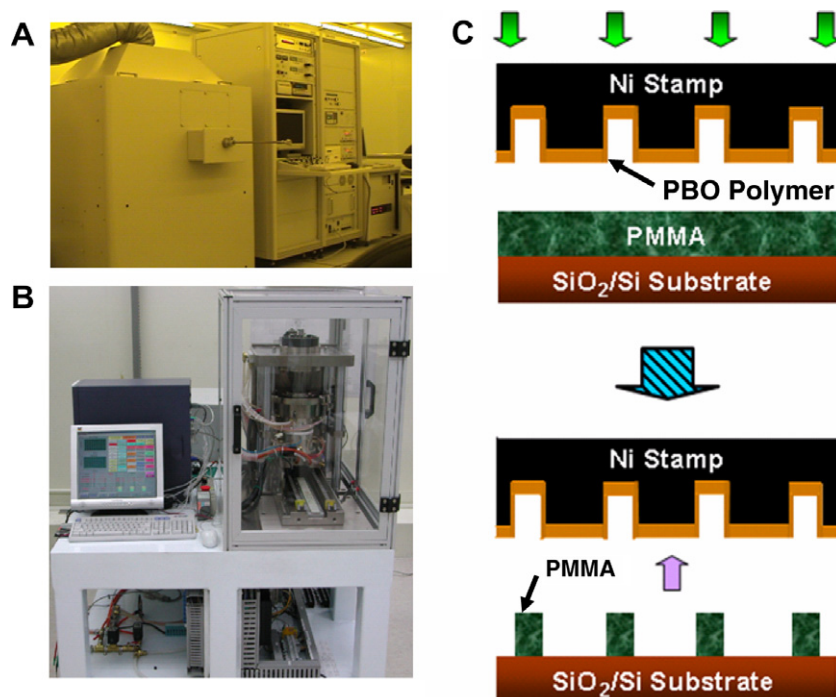E-mail address: tlchang@itri.org.tw (T.-L. Chang).

Fig. 1. Schematic diagram of nanostructures using NIL process: (A) EBL equipment for fabricated mold stamp. (B) HEL equipment for nanoimprint pattern with computer controlled electronics. (C) A nickel-based pillar mold can imprint into a PBO-SAM polymer resist layer; afterward, the mold removal and pattern transfer are based on anisotropic etching to remove reside.

10 min in a jar. After vaporizing diethyl ether, the benzoxazine precursors were done. By heating the benzoxazine precursors at 140 °C for 1 h, BA-m polybenzoxazines can be obtained. Next, a 4-in. p-type Si(100) wafers can be used in this study. For the preparation of SiO_2-based Ni (atomic weight 5.87 g/mole) substrate, a sequential deposition of Ti (5 nm), and SiO_2 (20 nm) was done and following by O_2-plasma treatment. A Ti interlayer was used to enhance the adhesive between Ni substrate and SiO_2 layer. After cleaning by using acetone, isopropanol, and deionized water, the sample was spin-coated by a photoresist (ZEP520A-7, Nippon Zeon Co., Ltd.). The master mold was fabricated using a Crestec CABL-8210 electron-beam direct write tool (30 keV, 100 pA) with reactive ion etching (RIE) of Ni film in Fig. 1(A). And then, the simulated results can provide the effect of mechanical failure with embossing pressure force in NIL process that can be beneficial for our desir-

able design and study of nanopatterns. The deformation of PBO-SAM/PMMA substrate model can be predicted via finite volume method (FVM) based on 3-dimensional approach. In Navier-Stokes equation [11], the coupling between pressure and velocity is achieved using the SIMPLE algorithm. The second-order upwind discretization scheme is implemented for convection flux and central-difference scheme for the diffusive flux in momentum, mass fraction of fluid. The typical values of under-relaxation factors are 0.5. The solution is considered converged when the residuals are less than 1×10^{-3} for all variables except continuity, for which the criterion of convergence is set to 1×10^{-5}. Here, the imprinted nanopatterns can be employed via HEL process that was performed
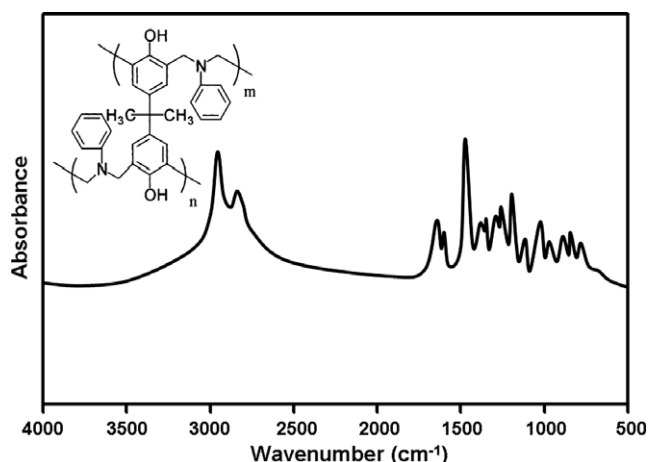

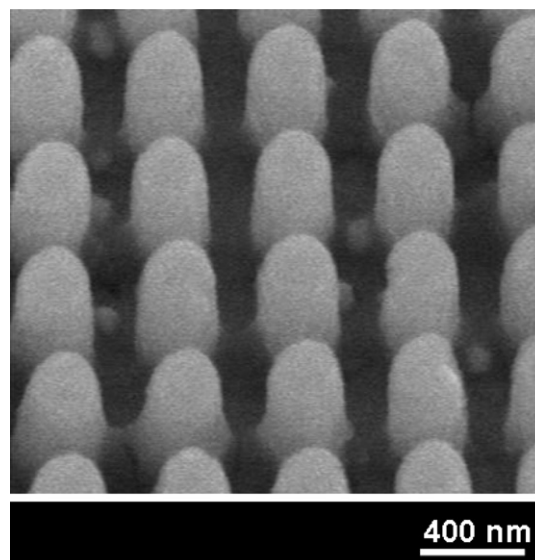**Fig. 2.** FTIR absorption spectrum of polybenzoxazines indicates the vibrational modes of molecular bonds.

Fig. 3. FE-SEM micrograph of Ni stamps before imprinted PMMA substrate. The pillar diameter is 200 nm, and its period is 400 nm.
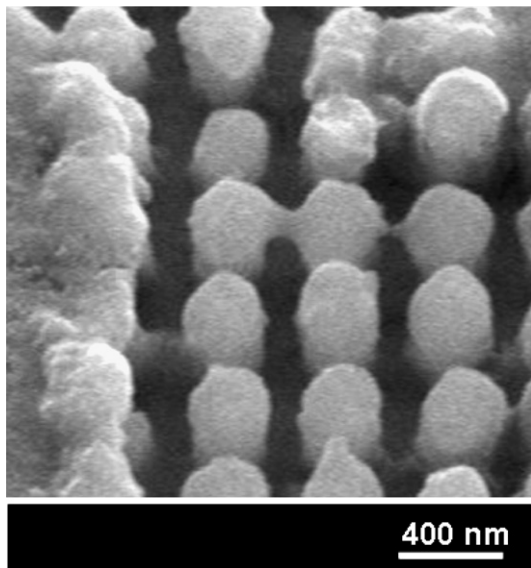
Fig. 4. FE-SEM micrograph of Ni-imprinted stamps after imprinted PMMA substrate that can not be via the anti-adhesive treatment process.
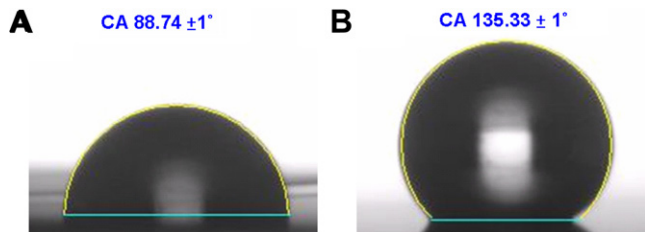

Fig. 5. Contact angles of water drops on (A) a PMMA polymer film surface, and (B) a smooth PBO-SAM coating film surface.
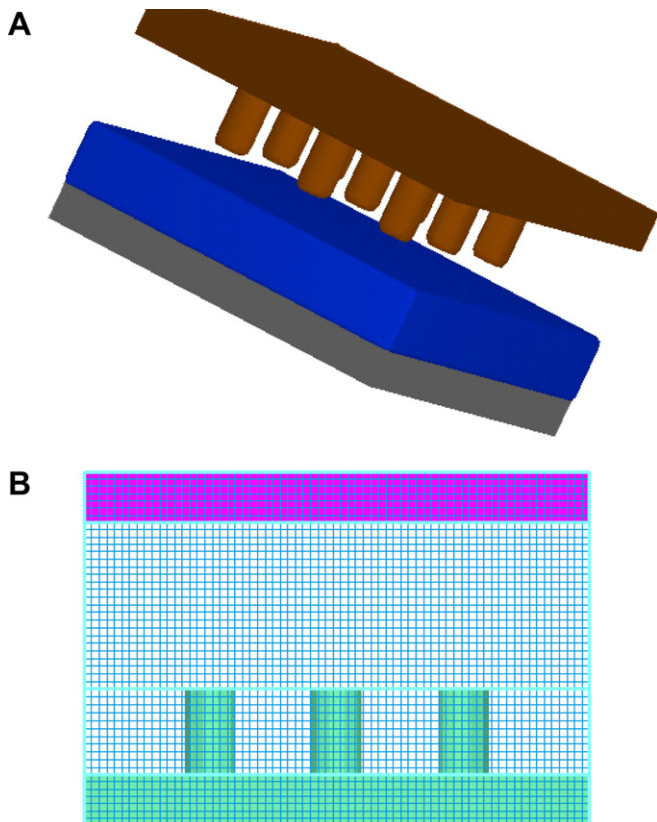

Fig. 6. Simulation of Ni stamps and PBO-SAM/PMMA substrate in NIL process: (A) A nanoimprint system geometry, and (B) its grid plot.

by our homemade equipment as shown in Fig. 1(B). The fabrication of nanopatterns utilizing HEL procedure with PBO-SAM coating method was schematically shown Fig. 1(C). A 200 nm thin PMMA film (molecular weight 15 kg/mole) was spin coated on a SiO_2 substrate, following by baking on a hot plate for 30 min at 160 °C. Furthermore, the PBO-SAM coatings as an anti-adhesive agent were deposited by CVD process. The master was replicated by embossing on the PBO-SAM/PMMA substrate film for 10 min at 150 °C and 50 bar. Finally, PBO-SAM/PMMA layer that remained on the bottom of embossed nanostructure was removed by RIE treatment. After each imprint the quality of stamps and substrates were fabricated, we can use a microscope to observe them, and the water contact angle (CA) measurements to find out their wetting and adhesive properties.

3. Results and discussion

In this study, the property of polybenzoxazines is investigated by a Fourier Transform Infrared Red Spectrometer (FTIR, model: FTS-40, MASS) as shown in Fig. 2. The absorption spectrum of polybenzoxazine solution occurs characteristic peaks at 1470 cm^{-1}, 1655 cm^{-1} and 2900 cm^{-1} that indicates the vibrational modes of
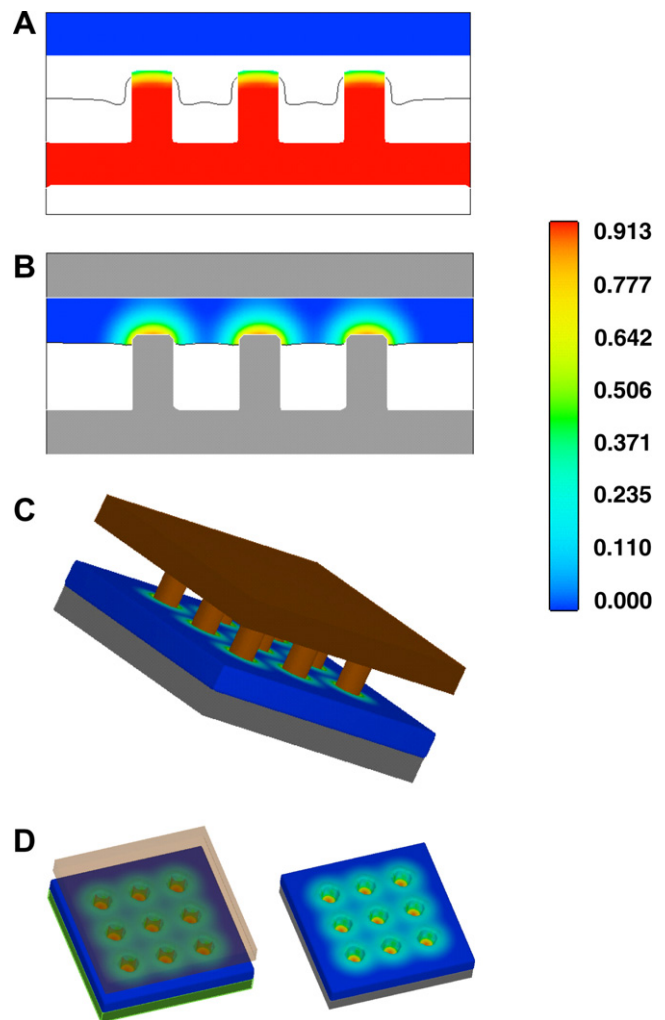

Fig. 7. Simulation results of temperature distribution between Ni stamps and PBO-SAM/PMMA substrate in NIL process: (A) stamp cross-sectional, (B) PMMA substrate cross-sectional, (C) 3-dimensional and (D) intrinsic 3-dimensional views, respectively. The study of computed condition in nanoimprint process is at 150 °C and 50 bar during 10 min. Note that for NIL experimental parameters, the simulated results have already decided before doing nanoimprint experiment.

molecular bonds. In addition, the structure of polybenzoxazines can be found by strong hydrogen-bounding interactions between the polymer chains, which act as chemical cross-links. The polybenzoxazines consists mainly of OH...N and O⁻...H⁺N intra-molecular hydrogen bonds. This material is like poly(tetrafluoro-ethylene) (Teflon) that is a low-surface-free-energy material as it combines water repellence with other desirable properties.

The master Ni nanopatterns including a diameter of 200 nm and a height of 340 nm with a 400 nm period that can be characterized using scanning electron microscopy (FE-SEM: JEOL, JSM-6500 F) as shown in Fig. 3. Herein if the nanopatterns are not done PBO-SAM coatings, we can find an adhesive problem leading to bad replication of nanostructures. The part of pillar nanopatterns without coating PBO-SAM can be difficult to peel off from the PMMA substrate due to the properties of hydrophilic/hydrophobic material as shown in Fig. 4. FE-SEM images of Ni stamp show some surface areas are hidden remaining PMMA layer. Theses fractures of Ni mold indicates that mechanical failure of duplication are caused by interfacial adhesion between the imprinted PMMA substrate and Ni mold stamp.

In this work, polybenzoxazines can be regarded as a novel material based on their unique properties that we discovered a non-fluorine, and low surface free energy to solve anti-adhesive treatment between PMMA substrate and Ni stamp. Here, the solution of polybenzoxazine is prepared by blending THF solution. Based on the chip immersing 0.1 wt% polybenzoxazine solution, the Ni samples with polymer molecules could improve the anti-adhesive properties in NIL process. The water CA measurements give a good idea of the density of hydrophilic groups at the surface of the substrates that shows a marked constant in the wetting behavior. After the chemical cleaning with polybenzoxazines and acetone, the measured results of water CA measurements for Ni stamp on PMMA substrate surface are compared between studies before and after PBO-SAM coating treatment, as shown in

Fig. 5(A) and (B), are $88.74 \pm 1^{\circ}$, and $135.33 \pm 1^{\circ}$ receptively. The contact angles of our samples are measured at 25 °C with a goniometer (model: GH-100, Kruss, Germany) interfaced image-capture software by injecting a 10 μL liquid drop. The measured results indicate that a Ni stamp with PBO-SAM coating treatment has low surface free energy ($\gamma = 16.43$ mJ/m^2). This surface free energy even lower than Teflon ($\gamma = 21.03$ mJ/m^2), nevertheless, the polybenzoxazine polymer material is cheaper and easier to prepare before an anti-adhesive experiment process.

The Pro/ENGINEER software is performed to build the solid model and to generate the structured, multi-block and body-fitted meshes. Grid-independent results can be obtained with total 100,000 cells as shown in Fig. 6. In nanoimprint process, the embossing pressure force for the results of mechanical failure can be from the heated temperature T (> T_g (glass transition temperature)) and keeping at this condition during a time in this system. The temperature distributions are analyzed thermomechanical mismatch between Ni stamps and PBO-SAM/PMMA substrate that can be significantly done before our NIL experimental process as shown in Fig. 7(A) and (B). This predicted process can prevent the effect of thermal stresses from being molding and demolding processes because of thermomechanical mismatch. In addition, the adhesion during demolding can be lead to Ni stamp separate from the substrate away the edge and fracture of imprinted line. Based on the characteristic of mechanical failure for nanostructure, a study of these thermal effects in HEL is needed to carry out and 3-dimensional phenomena simulation based on FVM can be adopted as shown Fig. 7(C) and (D).

The shape and size for Ni nanopattern mold with PBO-SAM coatings has good and uniform nanopatterns that can be verified by FE-SEM image in Fig. 8(A). Besides, the mold is characterized by atomic force microscopy (AFM, model: Autoprobe M5, Park Scientific Instruments) measurement in Fig. 8(B) and (C). A 3-dimensional AFM image of 2×2 μm^2 PBO-SAM coating square can be
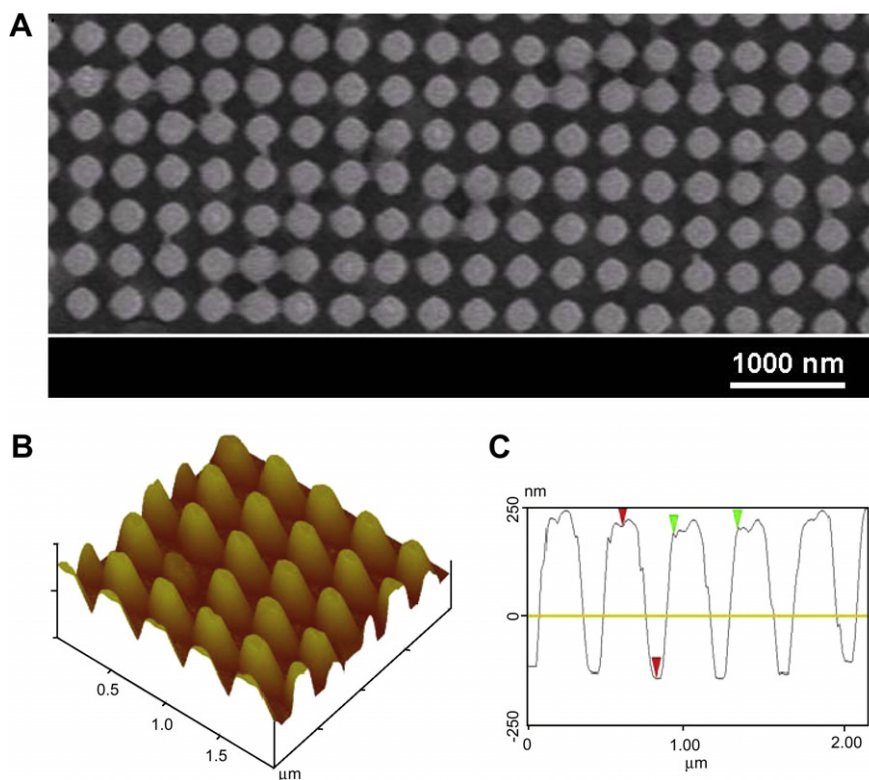
Fig. 8. (A) FE-SEM micrograph of Ni-imprinted stamp with anti-adhesive treatment process. (B) AFM image of master mold and (C) is its sectional profile view. Here, 3-dimensional AFM view indicates repeatedly a convinced surface characterization.

defined by NIL process. The image section clearly reveals an excellent homogeneity and fidelity of nanopatterns on this area.

4. Conclusions

A new chemical coating process without using fluorinated silane molecule material treatment has been successfully developed for using Ni stamps to imprint PMMA substrate. Besides, the measurement of water contact angle can be found to play an important role for quality after using a material coating treatment. Simultaneously, a simulated result can be easily to build the forming nanopatterns in nanoimprint process. Furthermore, this study successfully demonstrates PBO-SAM coatings to solve adhesive problem in NIL process; consequently, provides the capability and flexibility necessary for future optimization and development.

Acknowledgments

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