



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 cooling 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. Schiff 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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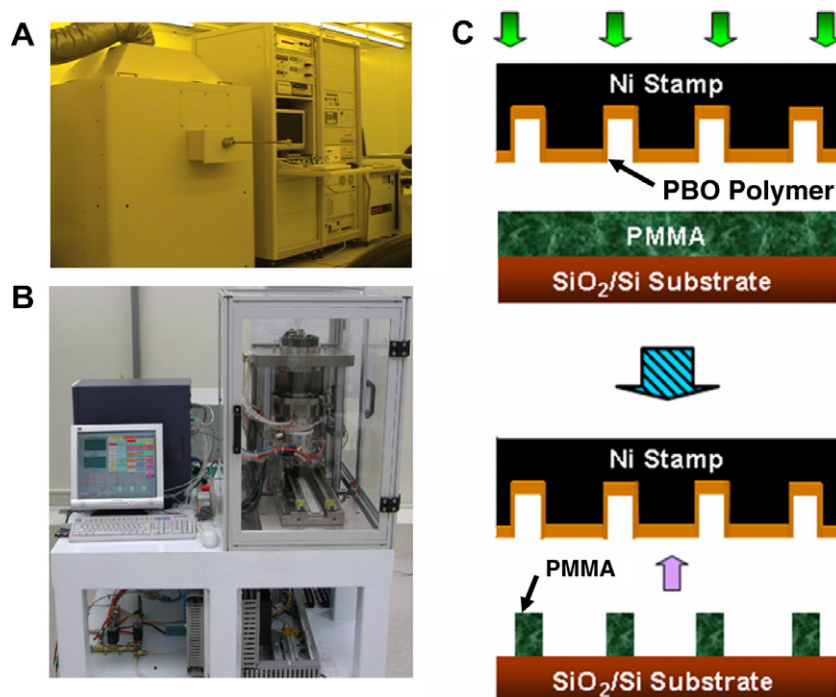


Fig. 1. Schematic diagram of nanostructures using NIL process: (A) EBL equipment for fabricated mold stamp. (B) HEL equipment for nanoimprint pattern with computer controlled electronics. (C) A nickel-based pillar mold can imprint into a PBO-SAM polymer resist layer; afterward, the mold removal and pattern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

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 SiO₂-based Ni (atomic weight 5.87 g/mole) substrate, a sequential deposition of Ti (5 nm), and SiO₂ (20 nm) was done and following by O₂-plasma treatment. A Ti interlayer was used to enhance the adhesive between Ni substrate and SiO₂ 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

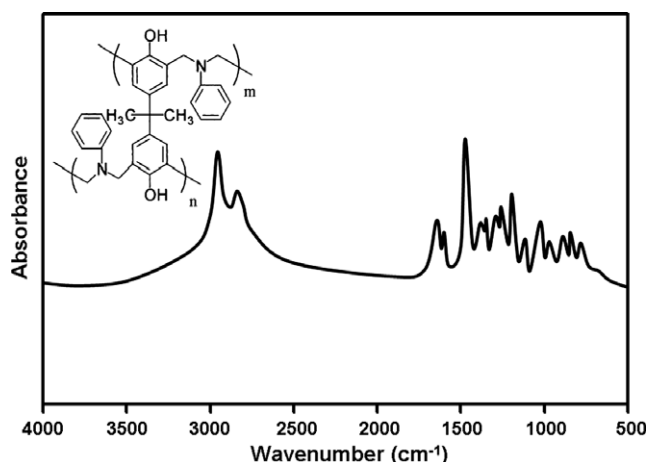


Fig. 2. FTIR absorption spectrum of polybenzoxazines indicates the vibrational modes of molecular bonds.

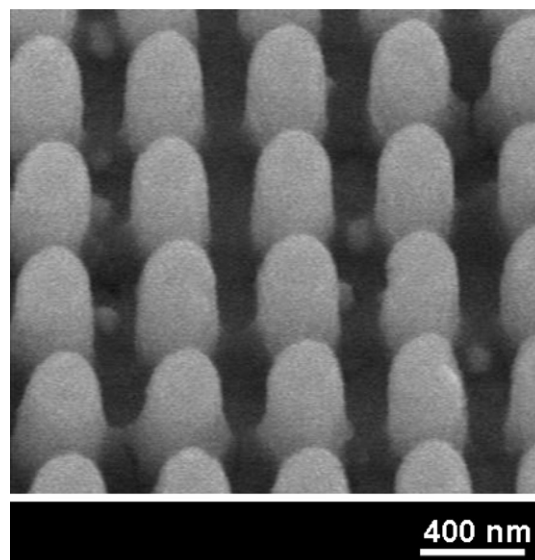


Fig. 3. FE-SEM micrograph of Ni stamps before imprinted PMMA substrate. The pillar diameter is 200 nm, and its period is 400 nm.

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