Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Microelectronic Engineering 83 (2006) 906–909
MICROELECTRONIC ENGINEERING
www.elsevier.com/locate/mee

Polyimide nanostructures fabricated by nanoimprint lithography and its applications

Bo Cui *, Yann Cortot, Teodor Veres

Industrial Materials Institute, National Research Council of Canada, 75 de Mortagne Blvd., Boucherville, QC, Canada J4B6Y4

Available online 31 January 2006

Abstract

Polyimides have attractive thermal, mechanical and electrical properties, and have found applications in fields ranging from spacecraft to microelectronics and optoelectronics. Patterning polyimide at nanoscale would open the window for many new applications. In this work, we developed three approaches to pattern polyimide using nanoimprint lithography (NIL): imprint at its uncured soft state and cure it afterwards; imprint another low Tg polymer, then transfer the pattern into polyimide by RIE; and direct imprint into polyimide at temperature higher than its Tg. Polyimide gratings with 200 nm period and 110 nm line-width were successfully fabricated by all the three approaches. Each approach has its advantages and disadvantages. The first method is relatively simple and fast, but some residual solvent and water may cause outgassing when subjected to temperature well above 200 °C for prolonged time. The second approach is more complicated, while the third approach needs very high temperature. Two applications of the nanostructured polyimide are demonstrated: as a flexible mould to structure PMMA by NIL and as a template for chemical sensor based on surface enhanced Raman spectroscopy (SERS). Both applications have taken advantage of polyimide's high temperature stability and excellent mechanical properties, and cannot be realized by other common thermoplastic polymers. We believe that NIL is an efficient technique to pattern polyimide with high throughput and low cost.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Polyimide; Nanoimprint lithography; Flexible mould; SERS; Nanofabrication; Grating

1. Introduction

Polyimides have many desirable properties, such as low dielectric constant, high breakdown voltage, chemical resistance, wear resistance, stability at elevated temperatures, low thermal expansion, as well as excellent mechanical and good optical properties [1]. As a result, polyimide has found many applications. For example, in microelectronics, polyimides are used for electronics packaging with reduced package delay compared to ceramics due to its relatively low dielectric constants [2]. For the same reason, together with its good surface planarization characteristics and low residual stress, polyimide is considered as one of the most attractive interlayer dielectrics [3]. In optoelectronics, polyimides are used for optical waveguide with moderate optical loss but superior thermal stability to stand chip joining temperature of ∼360 °C, which is too high for common thermoplastic polymers such as PMMA and polycarbonate [1,4]. More recently, polyimides were proven to be biocompatible [5], and they have found applications in the biomedical fields such as a flexible and implantable intracortical electrode array [6], and a microstructured substrate for contact guidance of osteoblast cell growth [7]. Their application could be further extended to other fields if they can be patterned at micro or nanoscale.

There are two types of polyimides (precursors): the traditional non-photosensitive ones based on poly(amic acid) precursors, and photosensitive ones based on poly(amic acid ester)s or salts precursors. Accordingly, polyimide microstructures are typically patterned either by direct photolithography for photosensitive type, or by lithography plus dry or wet etching for non-photosensitive type. In this work, we will investigate the nanopatterning of polyimide by nanoimprint lithography (NIL) [8], a low cost and high throughput process; and then take advantage of

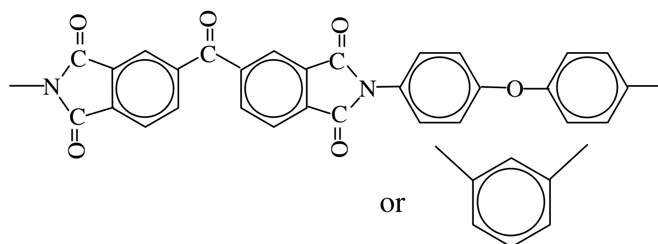
* Corresponding author. Tel.: +1 450 641 5231; fax: +1 450 641 5105.
E-mail address: bo.cui@nrc.ca (B. Cui).

0167-9317/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.mee.2006.01.014

its superior mechanical and thermal properties and use it as a flexible NIL mould and SERS template.

2. Experimental and results

Three different approaches were attempted to pattern polyimide using NIL: imprint it at its uncured state and complete curing afterwards, imprint another polymer resist having lower Tg then transfer the pattern into the underneath cured polyimide, and imprint cured polyimide at temperature above its Tg. The polyimide chosen in this study is non-photosensitive Pyralin® 2525 (HD Microsystems PI2525) having the following basic structure:



The polyimide was spun on a silicon wafer at 2000–6000 rpm, resulting in cured film thickness of 4.5–12 μm. Before spinning polyimide, the Si wafer was spin-coated with an adhesion enhancer (HD Microsystems VM651), without which the polyimide film was often found to peel off when subjected to wet chemicals.

The mould contains a grating structure over $\sim$5 cm^2 in thermal SiO_2 with period 200 nm and about 110 nm linewidth and 100 nm trench-depth, and was treated with an anti-adhesion layer. The imprint was conducted using an EVG-520 tool for the first two approaches, and a simple setup on a hot plate for the third approach as it requires temperature beyond the tool's specification.

2.1. Imprinting polyimide at its uncured state

For this approach, the as-spun polyimide was soft-baked at 100 °C for 1–5 min then 120 °C for 1 min on a hotplate to partly drive away the solvent. During NIL, the chamber was pumped to below 10^{-2} mbar and heated to 120 °C at 20 °C/min. At this point, pressure of 30 bar was applied and the temperature was ramped to 200 °C at 20 °C/min and held at 200 °C for 2 min before removing the pressure. The polyimide had been partly cured at this step because PI2525 has a relatively low imidization temperature of 150–180 °C. After NIL, hard-bake was carried out at 250 °C for 10 min on a hotplate, which completed the imidization and further drove away the solvent. Due to volume shrinkage, the feature edge was found slightly rounded after hard bake. The completed polyimide grating is shown in Fig. 1(a).

We found that inadequate soft bake cannot drive away most of the solvent (*N*-methyl-2-pyrrolidone, boiling temperature 202 °C), which, together with the generated water during imidization, caused un-imprinted bubbles. But too

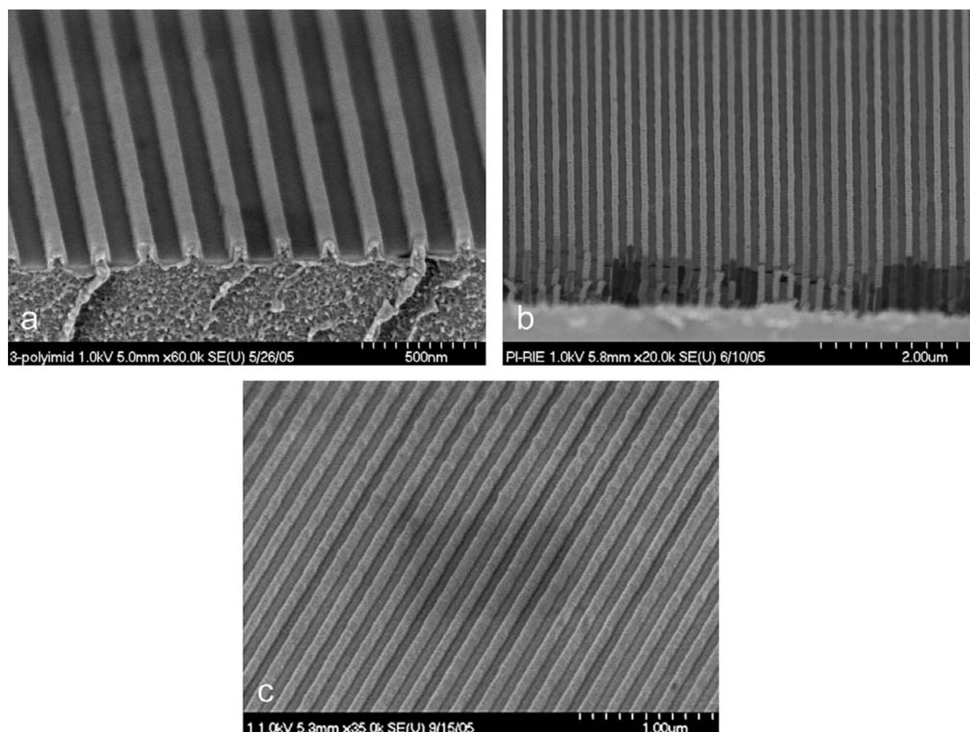


Fig. 1. Polyimide grating with 200 nm period fabricated by (a) imprint at its uncured state (before hard bake); (b) RIE pattern transfer from a NIL-defined PMMA grating (lines broken at edge, trench depth 100 nm) and (c) direct NIL at 360 °C. Polyimide film thickness was 4.5 μm for (a), and 12 μm for (b) and (c).

much soft bake hardened the film and led to incomplete imprint. As for NIL parameters, though low imprint temperature such as 150 °C can achieve faithful embossing, the pattern suffered significant shrinkage after hard bake. While more aggressive condition, namely imprinting at relatively high temperature for long time, such as holding at 200 °C for over 8 min, may cause the pattern to crack. The pressure is less significant than the temperature, with high pressure preferable, but not too high (>50 bar) to avoid possible mould damage. Lastly, de-embossing after cooling to 100 °C was found to result in slightly zigzagged grating lines.

2.2. Structuring polyimide by NIL and RIE pattern transfer

For this method, the polyimide film was hard-baked at 300 °C for 1 h to completely drive away the solvent and imidize. After coating polyimide with a thin etching mask of SiO_2, PMMA was spun on the film, patterned by NIL, and transferred into SiO_2 by CHF_3 RIE, then into polyimide by oxygen RIE, which also etched away the remaining PMMA. The polyimide grating fabricated by this method is shown in Fig. 1(b). Compared to the first approach, this approach is more complicated, and the RIE step may result in a rougher polyimide surface that is detrimental especially for optical waveguide device [9]. Nevertheless, this method is preferable for applications where nanostructured polyimide would experience temperature well above 200 °C for prolonged time and outgasing of residual solvent or water is very undesirable.

2.3. Direct imprinting polyimide at temperature above its Tg

Like other thermoplastic polymers, fully cured PI-2525 film is amorphous and flexible, with prominent and narrow glass transition near 325 °C. The NIL was carried out using a simple setup in air on a hotplate, and a grating structure imprinted at 360 °C is shown in Fig. 1(c). Compared to previous two approaches, the current one is more straightforward, but the high imprint temperature of >350 °C would lead to large thermal stress, large misalignment in case alignment is needed, and other unfavourable features. In addition, temperature over 500 °C would be required for embossing some other popular polyimides having a stiff backbone and semi-crystalline morphology [1].

3. Applications of nanostructured polyimide

Polyimides possess the desirable features necessary for a flexible imprint mould: excellent mechanical properties and high temperature stability. To demonstrate this, we coated the polyimide gratings fabricated by the first and second approach with an anti-adhesion layer, and carried out imprint into PMMA at 200 °C and 18 bar. Noticeably peel off was found when the anti-adhesion layer, 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl trichlorosilane, was applied directly on polyimide surface, so we coated a 10 nm SiO_2 layer on polyimide, which effectively eliminated the peel off. The imprinted PMMA structures are shown in Fig. 2, which indicates a faithful replication of the mould pattern. A second application of nanostructured polyimide could be a template for metal nanoclusters synthesis to be used for SERS sensor with improved sensibility for detecting and identifying various absorbate molecules [10]. Thus we patterned a pillar array with 200 nm period into polyimide by the first approach using a mould containing a hole array pattern, and sputtered silver on it at 250 °C (Fig. 3). Such an elevated temperature was found to favour the formation of Ag clusters (rather than a continuous film) that is necessary for sensitive SERS, and cannot be attained by other common thermoplastic polymers like PMMA or polystyrene.

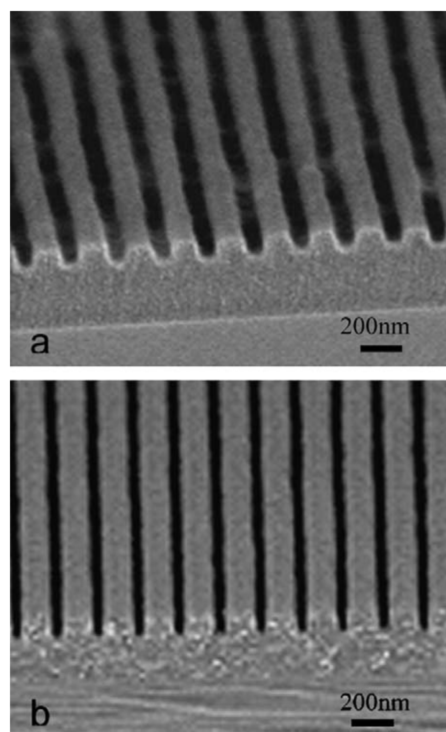


Fig. 2. PMMA grating with 200 nm period by NIL using polyimide moulds shown in Fig. 1. (a) Mould fabricated by imprint at its uncured state and (b) mould by RIE pattern transfer.

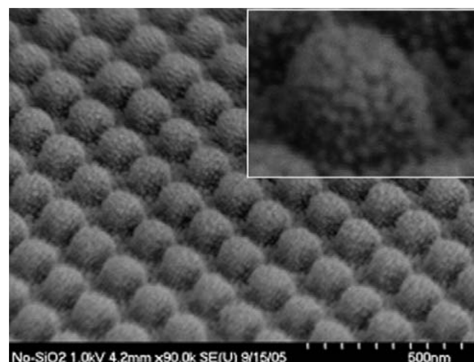


Fig. 3. Ag clusters with size ~20 nm on polyimide pillars by sputtering at 250 °C for 10 min.

4. Summary

Polyimide nanostructures have been patterned by three different approaches using nanoimprint lithography: imprint at its uncured soft state and cure it afterwards; imprint another low Tg polymer, then transfer the pattern into polyimide by RIE; and direct imprint into polyimide at temperature higher than its Tg. The first approach is relatively simple and fast, but some residual solvent and water may cause outgassing when the polyimide is subjected to temperature well above 200 °C for prolonged time. The second and third approach used polyimide cured at 300 °C for 1 h, thus no outgassing should occur. But the second approach is more complicated and the dry etching may increase the surface roughness that would lead to more loss for optical waveguide, while the third approach needs very high temperature of 350–550 °C depending on the type of polyimide. Finally, two applications using nanostructured polyimide have been demonstrated: as a flexible imprint mould and a template for SERS-based sensor.

References

[1] M.K. Ghosh, K.L. Mittal (Eds.), Polyimides: Fundamentals and Applications, Marcel Dekker Inc., New York, 1996.
[2] R.J. Jensen, in: D.A. Doane, P.D. Franzon (Eds.), Multichip Module Technologies and Alternatives: The Basics, Van Nostrand Reinhold, New York, 1993.
[3] T. Homma, Mater. Sci. Eng. R 23 (1998) 243–285.
[4] R. Reuter, H. Franke, C. Feger, Appl. Opt. 27 (1988) 4565–4571.
[5] R.R. Richardson Jr., J.A. Miller, W.M. Reichert, Biomaterials 14 (8) (1993) 627–635.
[6] P.J. Rousche, D.S. Pellinen, D.P. Pivin Jr., J.C. Williams, R.J. Vetter, D.R. Kipke, IEEE Trans. Biomed. Eng. 48 (3) (2001) 361–371.
[7] J.L. Charest, L.E. Bryant, A.J. Garcia, W.P. King, Biomaterials 25 (2004) 4767–4775.
[8] S.Y. Chou, P.R. Krauss, Microelectron. Eng. 35 (1997) 237–240.
[9] N. Agarwal, S. Ponoth, J. Plawsky, P.D. Persans, J. Vac. Sci. Technol. A 20 (5) (2002) 1587–1591.
[10] S. Chattopadhyay, H.C. Lo, C.H. Hsu, L.C. Chen, K.H. Chen, Chem. Mater. 17 (2005) 553–559.