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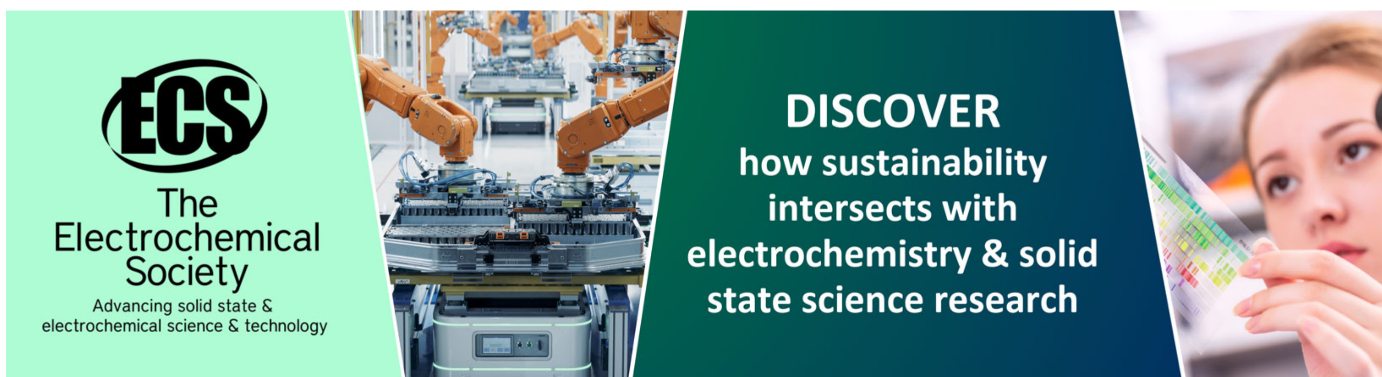

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Fabrication of polyimide micro/nano-structures based on contact-transfer and mask-embedded lithography

Cheng-Yu Chiu and Yung-Chun Lee[1]

Department of Mechanical Engineering, National Cheng Kung University, No. 1 University Road, Tainan, Taiwan

E-mail: yunglee@mail.ncku.edu.tw

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Abstract
Polyimide materials are well known for their excellent mechanical and chemical stability which, as an adverse consequence, makes their fabrication processes much more difficult, especially in micro- and nano-scales. In this paper, we demonstrate an innovative and powerful method for fabricating micro/nano-structures on polyimides. The proposed method first adopts an imprinting approach to transfer a patterned metal film from a mold to a polymer layer coated on a polyimide layer. The patterned double polymer layers are then dry etched using the transferred metal pattern as an etching mask. Finally, polyimide structures are obtained by lifting off the top polymer layer and the metal film through wet etching. Experiments have been carried out and important parameters to achieve high pattern-transformation fidelity are determined. Fine structures of polyimides with a feature size of 500 nm and a total patterned area of 8 × 8 mm^2 are demonstrated. Advantages of the proposed method include low-temperature, low contact pressure, small feature size, high throughput and ease of in implementation. Most importantly, it is applicable for a large number of tough polymers which are difficult to deal with by other methods in terms of micro/nano-fabrication.

(Some figures in this article are in colour only in the electronic version)

Introduction

Polyimides (PIs) are a class of high-performance polymers with a unique combination of many attractive material properties, such as excellent thermal and mechanical stability, high chemical and wear resistance, low dielectric constants, high breakdown voltage and good optical properties [1–5]. As a result, the polyimides have found a wide range of applications particularly in microelectronics and optoelectronics. Examples are flexible printed circuit boards, IC packagings, liquid crystal (LCD) alignment layers [6, 7], organic thin-film transistors [8], high-speed transmission lines [3], high-performance optical waveguides [4, 5], and so forth.

[1] Author to whom any correspondence should be addressed.

Due to their biocompatibility, polyimides are introduced in the bio-physic and bio-medical fields as the structure materials of bio-chips in microfluids and bio-chemical sensing [9, 10]. In many applications of polyimide materials, the capability of patterning and fabricating polyimides into micro-scaled or even nano-scaled structures plays a critical role and dominates the future developments of new polyimide-based devices. It is, however, a challenging issue still within academia and industry as well, owing to the mechanical and chemical stability of polyimides and the requirements for small feature size, precise dimension control, process compatibility, low-cost and high throughput.

There are many different ways of patterning and fabricating polyimide structures at the micro- and nano-scales depending on whether the polyimides are photosensitive

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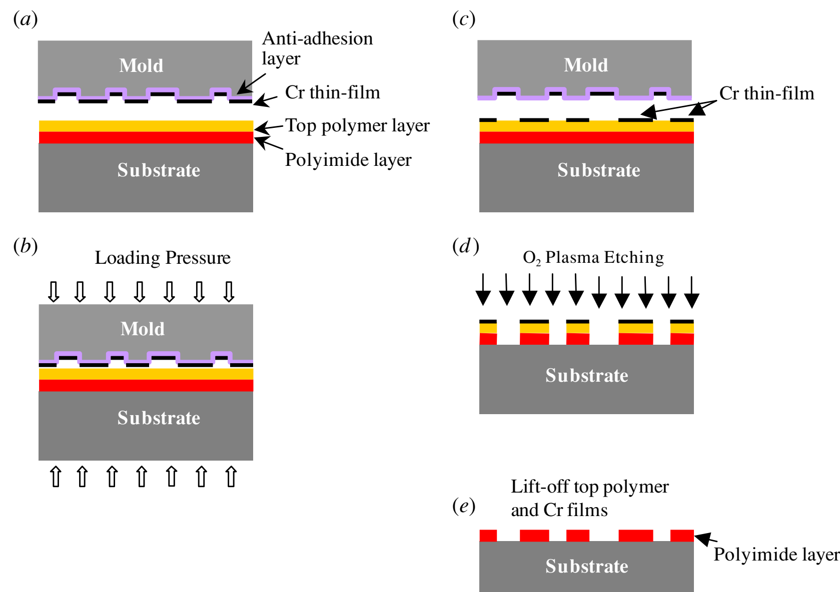

Figure 1. A schematic diagram of patterning polyimides based on double-layered contact-transfer and mask-embedded lithography (CMEL).

or non-photosensitive. Traditionally, polyimides are non-photosensitive and hence cannot be used as a photo-resist (PR) in photolithography. However, efforts have been made in the past few decades in synthesizing a variety of photosensitive polyimides (PSPIs) which have become popular now [11, 12]. Although patterning PSPIs with standard photolithography is easy and straightforward, several drawbacks and limitations still exist. First of all, the photolithography processes of PSPIs require thermal curing of uncured PSPIs, which usually results in dimensional changes and outgassing of water and solvent that may cause process contamination. Second, the smallest feature sizes are determined by the capability of photolithography systems in use and are typically limited to micro-scale only. Third, some favorable material properties of polyimides may be either sacrificed for the photosensitivity or altered and less controllable in the photolithography processes.

For patterning non-photosensitive polyimides, there are three different approaches but each one of them has encountered different problems. The first approach is basically a molding process which first shapes the uncured PIs in their soft state with a mold, and then followed by thermal treatment to cure the PIs [6, 7, 13, 14]. This method suffers the same problems as in patterning photosensitive PIs such as outgassing of water and solvent, dimensional change and shape deformation. The molding methods are typically for analog surface structures instead of digital ones. The second approach, also known as indirect photolithography, is to spin coat a photo-resist layer on top of the PI layer and then pattern the PR with standard photolithography [2, 11]. The process is then followed by wet or dry etching on PIs using the patterned PR as an etching mask. Quite often an inorganic layer such as SiO_2 in between the PR and PI layers is also needed as an intermittent etching mask since directly using a PR as the etching mask for PI can be very difficult [13]. Therefore, the indirect photolithography processes are quite complicated and not easy to implement. Finally, the last resort is direct imprinting or hot embossing on cured PIs using a mold to transfer the patterns [1, 13, 15, 16]. This direct imprinting process requires heating up PIs above their glass transition temperature, which typically ranges from 300 to 500 °C, and applying a high loading pressure on the mold/substrate. Obviously, direct imprinting PIs is not an easy job due to the thermal stability of the PI. High temperature and high pressure usually result in damage to the mold and its anti-adhesion coating, therefore shortening its life time [13].

In this work, we propose an innovative and powerful way for patterning and fabricating micro/nano-structures on PIs. The proposed method can solve all the currently existing problems in micro-/nano-fabrication of PIs as mentioned above. It is based on the authors' earlier work known as contact-transfer and mask-embedded lithography (CMEL) [17]. The basic idea of this modified CMEL method is to utilize the high distinguishable wet-etching rates between polymers, the target materials being polyimide material and a transition layer of PMMA, to obtain the nanostructures on the polyimide layer after the lift-off process of CMEL. The proposed CMEL method for patterning polyimide micro/nano-structures has many attractive advantages. First, it can be applied to all kinds of non-photosensitive and photosensitive polyimides since it works on fully cured PIs. The material properties of PIs are kept unchanged during the process. Second, it is a relatively low temperature process since heating is only required for soft baking of the top polymer (PMMA) layer. Third, the equipment required for this CMEL process are readily available and large-area and low-cost patterning can easily be achieved in ordinary environments. Finally, the feature size is not limited to optical diffraction of photolithography and therefore can easily reach micrometer, sub-micrometer and even nanometer scales.

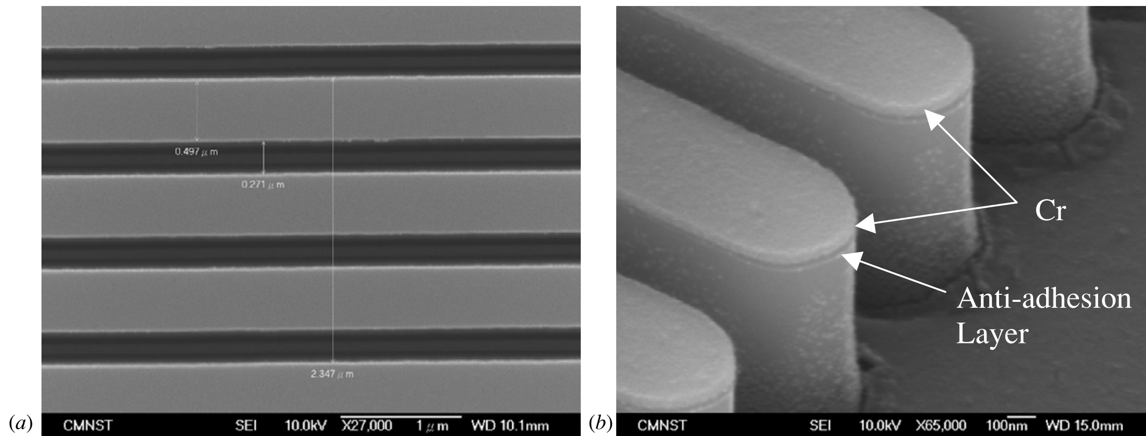

Figure 2. SEM images of a silicon mold of (*a*) linear grating features, (*b*) coated with a thin releasing layer and a 50 nm thick Cr film. The width, center-to-center pitch and the length of the linear gratings are 497 nm, 782 nm and 8 mm, respectively.

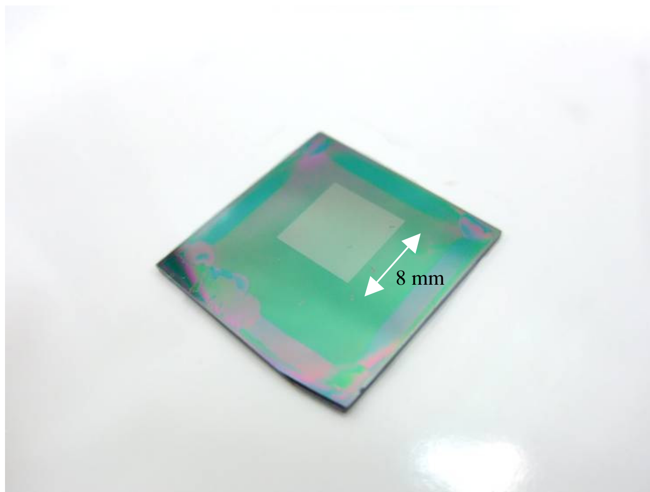

Figure 3. A photo of an imprinted area of 8 × 8 mm^2 on the PMMA/PI/Si substrate with a patterned Cr film.

Experimental details and results

In this section, experimental details of the proposed double-layered CMEL processes for fabricating micro/nano-structures on PIs will be discussed. The processing steps of the modified CMEL method for patterning PIs are schematically shown in figure 1. First of all, a commercially available polyimide precursor (Nissan RN-1349, Nissan Chemical Industries, Ltd, Tokyo, Japan) was spin coated on a silicon wafer with a speed of 2000 rpm to form a thin polyimide layer. The polyimide layer and the silicon substrate were then soft baked on a hot plate at a temperature of 100 °C for 90 s. The PI/Si sample was then moved into an oven for thermal imidization for 1 h at 250 °C. The measured thickness of this fully cured polyimide film is 100 nm. On top of the polyimide layer, a PMMA solution (PMMA 950 K A6, MicroChem Corp., Newton, MA) was spin coated at a speed of 4000 rpm, and a 340 nm thick PMMA layer is formed as shown in figure 1(*a*).

As for the imprinting mold, a silicon mold was prepared by standard photolithography. The silicon mold has continuous linear gratings on its surface and the total patterned area is 8 × 8 mm^2. Figure 2(*a*) shows one SEM image of the linear grating structures. The line width and the center-to-center pitch of the linear gratings are 497 nm and 782 nm, respectively, measured by SEM. These linear gratings go all the way across the patterned area and hence the length is 8 mm. After cleaning the mold, the mold surface was coated with an anti-adhesion layer of 1H, 1H, 2H, 2H-perfluorooctyl-trichlorosilane (F_{13}-TCS) by the thermal evaporation method [18]. On top of the anti-adhesion layer, a chromium film of 50 nm thickness was deposited by an E-beam thermal evaporator (VT1-10CE, ULVAC, Kanagawa, Japan). Figure 2(*b*) is a SEM image of the mold at the ends of the linear grating structures after coating both anti-adhesion and Cr films.

After preparing the mold and the substrate, the mold was placed on top of the PMMA/PI/silicon substrate as depicted in figure 1(*b*). A loading mechanism is utilized to apply uniform loading pressure on the mold/substrate assembly. Given the fact that the PMMA was only spin coated without any thermal treatment, a loading pressure of 1 MPa was applied, which was enough for the convex surface features of the mold to emboss in to the PMMA layer. As a comparison, typical loading pressure required in standard nano-imprinting lithography (NIL) is around 5 MPa. The compressed mold/substrate assembly was then thermally baked at a temperature of 95 °C for 5 min, which not only solidified the uncured PMMA but also guaranteed a complete transformation of the patterned Cr-film to the PMMA/PI/silicon substrate. The transferred and patterned Cr film can then serve as a hard mask for the subsequent dry etching. Figure 3 is a photo of the PMMA/PI/Si substrate after the imprinting process and one can see the patterned Cr film of an area of 8 × 8 mm^2. Further details of this Cr-patterned PMMA/PI/Si substrate are shown in figure 4. Figures 4(*a*) and (*b*) show detailed SEM images of the linear grating patterns of Cr on top of the PMMA layer. The surface structures are also scanned by a scanning probe microscope (SPM, SPA-400, SII NanoTechnology Inc., Tokyo, Japan) and

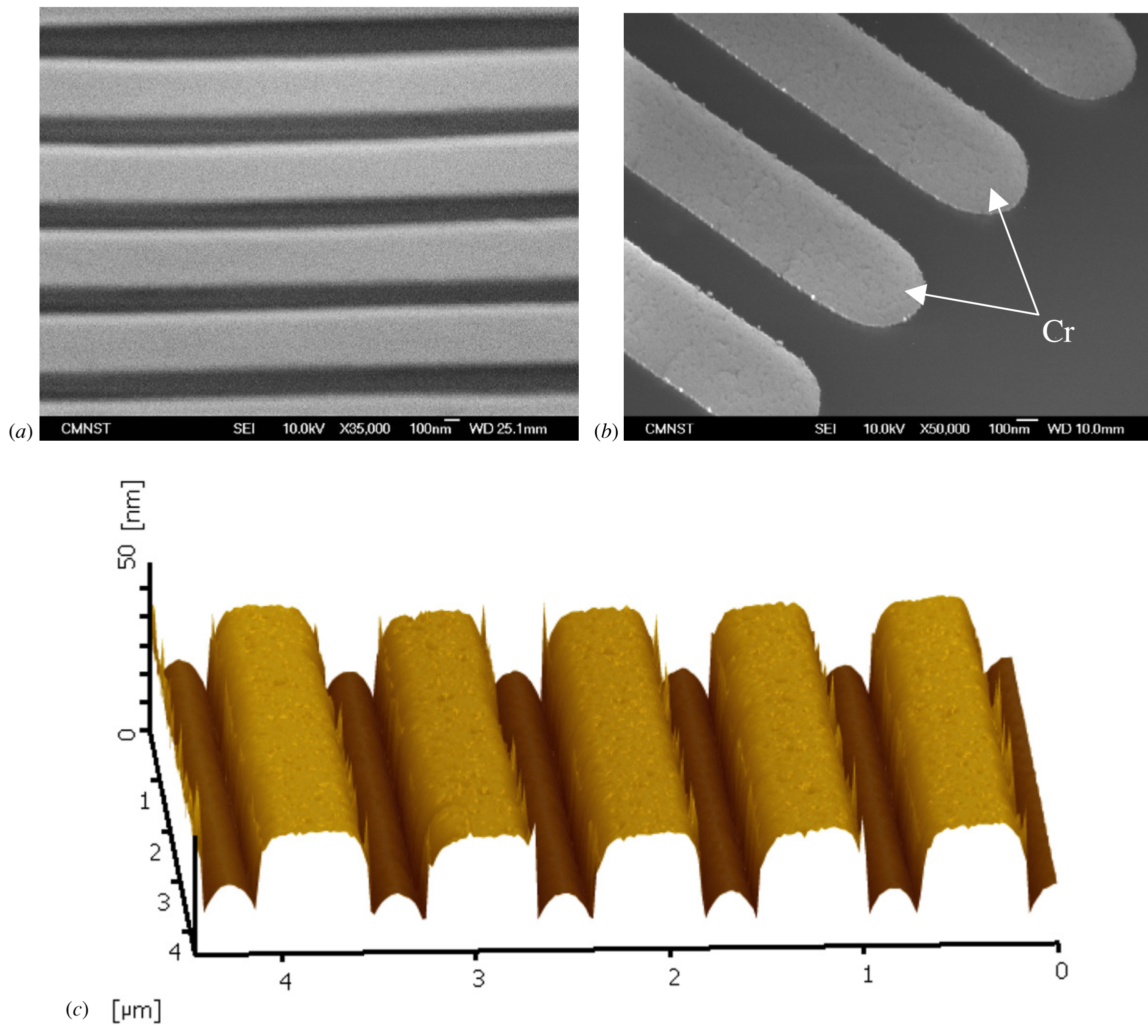

Figure 4. Linear grating structures of a Cr film embedded into the PMMA layer: (*a*) and (*b*) SEM images, and (*c*) SPM image.

the result is shown in figure 4(*c*). From figure 4(*c*), one can see the 50 nm thick Cr layer is about halfway embedded into the PMMA layer so that the remaining Cr above the PMMA surface is about 30 nm, and the PMMA material in between adjacent Cr layers is squeezed and bumped out a little bit due to the embedment of Cr layers. This is good evidence to show that the 1 MPa loading pressure and the thermal baking of PMMA at 95 °C are quite sufficient to transfer the patterned Cr layer from the mold to the PMMA/PI/Si substrate.

After the imprinting process, the Cr-patterned PMMA/PI/Si substrate was dry etched by O_2 plasma (RIE, OMNI-RIE, Duratex, Hsin-Chu, Taiwan) for 106 s to remove those PMMA and polyimide layers which were not covered by the Cr-film masks. The parameters of dry etching were as following: the power of RIE was set to 200 W, the pressure of the reaction chamber was 10 mTorr, and the flow rate of the reacting gas O_2 was controlled at 5 sccm. Figure 5 shows the SEM image of the sample after the O_2 plasma etching. It should be mentioned that the O_2 plasma etching is critical to the dimensional fidelity of pattern transformation. Therefore, we deliberately use low flow rates of reaction gases, low chamber pressure and higher RF power to minimize the side-etching effect and hence to obtain high accuracy of pattern transformation from the Cr mask to the polyimide layer [5]. Since a metal film is an excellent dry-etching mask for the CMEL process, we also patterned two kinds

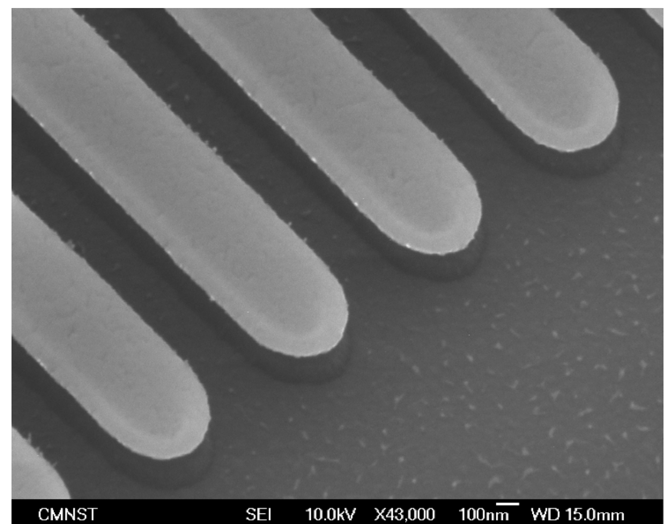

Figure 5. SEM image of the linear gratings of Cr/PMMA/PI/Si structures obtained after O_2 plasma etching for 106 s.

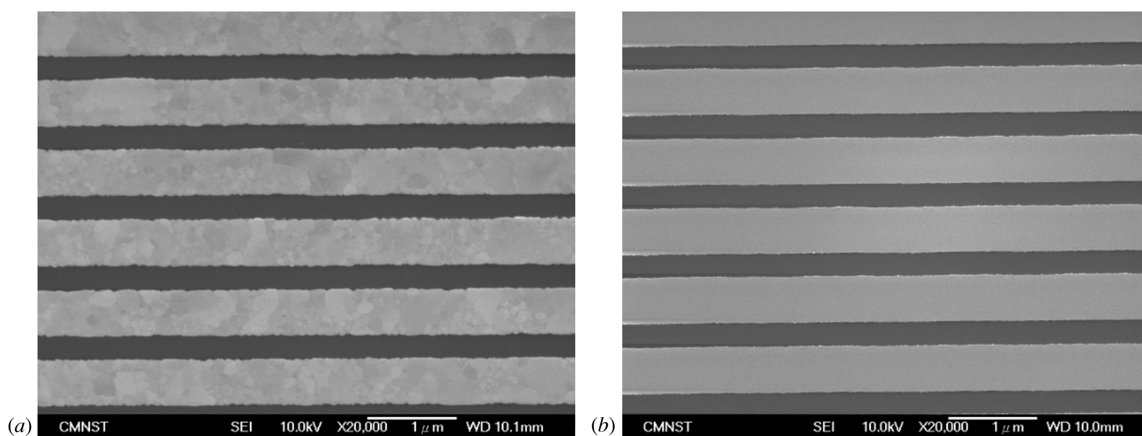

Figure 6. Linear grating structures of metal films embedded into the PMMA layer: (*a*) gold film and (*b*) nickel film.

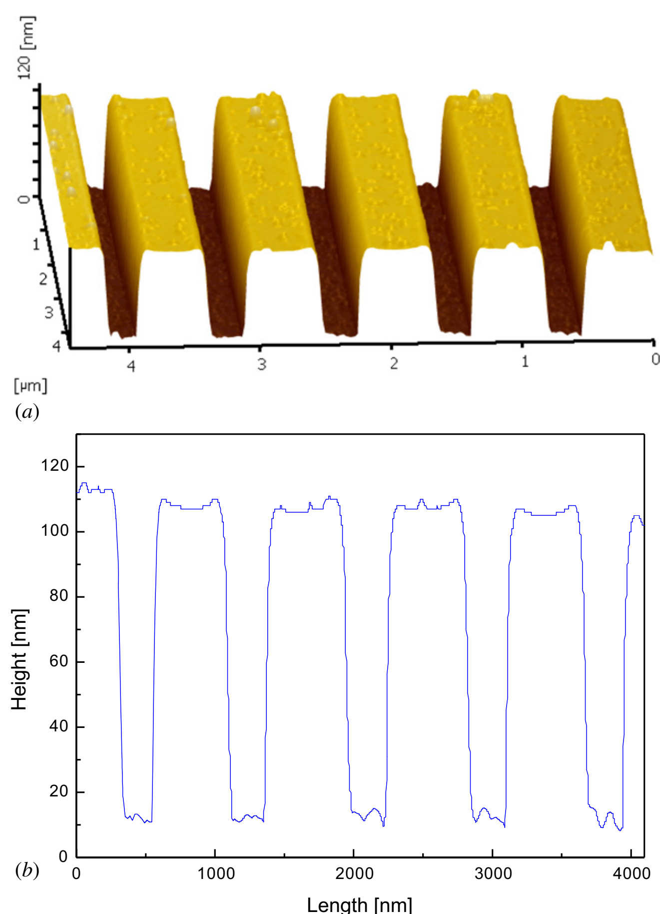

Figure 7. (*a*) SPM image and (*b*) a cross-sectional profile of the fabricated polyimide structure.

of metal films to demonstrate the variety of selection of metals as etching mask materials. Figures 6(*a*) and (*b*) show that gold and nickel films are successfully transferred into the PMMA layer as etching masks for the subsequent dry-etching process.

Finally, the structured PMMA/PI/Si sample was wet etched to lift-off the PMMA and Cr films and to obtain the final PI structures, as depicted in figure 1(*d*). Due to the chemical stability of PIs, it is not a problem to find etchants which can effectively remove PMMA but have very little or negligible effect on cured PIs. In this step, we use acetone as the etchant since we have found by experiments that the etching rate of acetone on PMMA is as high as 60 nm/s at 25 °C, while the acetone has no observable etching effect on the cured PI even after a few minutes. Therefore, the Cr-patterned PMMA/PI/Si sample was immersed in acetone for 30 s at room temperature. The PI structures on the silicon substrate were finally obtained. Figure 7 shows the PI structures scanned by SPM.

From figure 7, we measure the line width of the linear grating structures of PI to be 485 nm. The characteristic feature size is well matched to its counterpart of the silicon mold with a deviation of less than 3%. This indicates that this modified double-layer CMEL process indeed can fabricate PI micro/nano-structure with good accuracy. Furthermore, one can see from figure 7 that the fabricated PI structures have sharp corners and edges, as well as straight and vertical sidewalls. This is attributed to the powerful capability of O_2 plasma etching on polymer materials. Finally, we have examined the surface roughness on the top flat surface areas of the PI grating structures by SPM, and the average surface roughness is only 2 nm. This is because the surfaces are well protected by PMMA during the whole process until the final step of lift-off by acetone and acetone has almost no effect on PI during the wet etching. Good surface roughness on fabricated PI structures is critical to many optical applications of PIs.

Conclusions

We have successfully developed a new method for micro/nano-fabrication of polyimides. The key step in this fabrication process is the imprinting of a metal pattern from a mold to a polymer layer coated on polyimides. The pattern transformation is accomplished by cleverly mixing a few important elements including: (1) low surface energy of the coated anti-adhesion layer for metal film releasing, (2) soft state of an uncured PMMA layer for mold embossing and (3) thermal baking to solidify the PMMA layer and to secure the

embedment of metal patterns. It also relies on the superior etching capability of RIE, such as O_2 plasma, on polymers to form micro/nano-structures with precise dimension control and distinct surface profile. Finally, we take advantage of the high chemical stability of polyimides to lift-off the metal patterns and the sacrificial top polymer layer. A linear grating structure with a line width of around 500 nm and a patterned area of 8×8 mm^2 has been tested experimentally. Very good results are obtained.

Advantages of the proposed method are numerous and significant. It basically inherits all major strengths of nano-imprinting lithography such as small feature size, large area patterning, low-cost and less complicated equipment and ease of implementation. The proposed method also utilizes a much lower heating temperature and loading pressure so that the lifetime of the mold can be extended. Since it works on polymers that are fully thermal treated, the materials properties are preserved and unaffected by the processes. It is applicable to a majority of polymers and best suited for those high-performance polymers which have very stable material properties. It should be pointed out that the proposed method not only can work on polymer thin films deposited on a substrate, but also on stand-alone polymer layers or plates. In both cases, one can always control the depth of dry etching to obtain a variety of complex patterns and depths into the polymers. It is also very easy and straightforward to deposit other metals such as gold and nickel into the PMMA layer. Such a patterned metal/polymer composite structure with feature size in micrometer, sub-micrometer and nanometer scales can find a great deal of applications in microelectronics, optoelectronics, microwave engineering, bio-engineering, etc. In short, we have proposed and demonstrated a simple, effective and flexible way for patterning and fabricating micro/nano-structures on polymers with great future potential.

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References

[1] Youn S-W, Noguchi T, Takahashi M and Maeda R 2008 Dynamic mechanical thermal analysis, forming and mold fabrication studies for hot-embossing of a polyimide microfluidic platform *J. Micromech. Microeng.* **18** 045025-1–9

[2] Rubner R 2004 Innovation via photosensitive polyimide and poly(benzoxazole) precursors: a review by inventor *J. Photopolym. Sci. Technol.* **17** 685–91

[3] Yagi S, Itatani T, Kawanami H, Gorwadkar S, Uemura T, Fukushima T, Itatani H, Tomoi M and Tacano M 2003 Ultrafast active transmission lines with low-*k* polyimide integrated with ultrafast photoconductive switches *Japan J. Appl. Phys.* **42** L154–6

[4] Shioda T 2002 Fluorinated polyimide waveguide fabricated using replication process with antisticking layer *Japan J. Appl. Phys.* **41** 1379–85

[5] Agarwal N, Ponoth S, Plawsky J and Persans P D 2002 Optimized oxygen plasma etching of polyimide films for low loss optical waveguides *J. Vac. Sci. Technol.* A **20** 1587–91

[6] Chiou D-R and Chen L-J 2006 Pretilt angle of liquid crystals and liquid-crystal alignment on microgrooved polyimide surfaces fabricated by soft embossing method *Langmuir* **22** 9403–8

[7] Hah H, Sung S-J, Han M, Lee S and Park J-K 2007 Effect of the shape of imprinted alignment layer on the molecular orientation of liquid crystal *Mater. Sci. Eng.* C **27** 798–801

[8] Chou W-Y and Cheng H-L 2004 An orientation-controlled pentacene film aligned by photoaligned polyimide for organic thin-film transistor applications *Adv. Funct. Mater.* **14** 811–5

[9] Richardson R R Jr, Miller J A and Reichert W M 1993 Polyimides as biomaterials: preliminary biocompatibility testing *Biomaterials* **14** 627–35

[10] Rousche P J, Pellinen D S, Pivin D P, Williams J C, Vetter R J and Kipke D R 2001 Flexible polyimide-based intracortical electrode arrays with bioactive capability *IEEE Trans. Biomed. Eng.* **48** 361–71

[11] Fukukawa K-I and Ueda M 2008 Recent progress of photosensitive polyimides *Polym. J.* **40** 281–96

[12] Blach-Watson J A, Watson G S, Brown C L and Myhra S 2004 UV patterning of polyimide: differentiation and characterization of surface chemistry and structure *Appl. Surf. Sci.* **235** 164–9

[13] Cui B, Cortot Y and Veres T 2006 Polyimide nanostructures fabricated by nanoimprint lithography and its applications *Microelectron. Eng.* **83** 906–9

[14] Pai I-T, Leu I-C and Hon M H 2006 Nanostructures prepared on polyimide film by nanoimprinting with the assistance of residual solvent *J. Micromech. Microeng.* **16** 2192–6

[15] Youn S-W, Noguchi T, Takahashi M and Maeda R 2008 Fabrication of micro mold for hot-embossing of polyimide microfluidic platform by using electron beam lithography combined with inductively coupled plasma *Microelectron. Eng.* **85** 918–21

[16] Charest J L, Bryant L E, Garcia A J and King W P 2004 Hot embossing for micropatterned cell substrates *Biomaterials* **25** 4767–75

[17] Lee Y-C and Chiu C-Y 2008 Micro-/nano-lithography based on the contact transfer of thin film and mask embedded etching *J. Micromech. Microeng.* **18** 075013

[18] Beck M, Graczyk M, Maximov I, Sarwe E-L, Ling T G I, Keil M and Montelius L 2002 Improving stamps for 10 nm level wafer scale nanoimprint lithography *Microelectron. Eng.* **61–62** 441–8