INSTITUTE OF PHYSICS PUBLISHING NANOTECHNOLOGY
Nanotechnology **17** (2006) 1212–1216 doi:10.1088/0957-4484/17/5/008

Low adhesive force of fluorinated sol–gel hybrid materials for easy de-moulding in a UV-based nano-imprint process

Woo-Soo Kim, Jung-Ho Jin and Byeong-Soo Bae

Laboratory of Optical Materials and Coating, Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea

E-mail: bsbae@kaist.ac.kr

Received 5 October 2005, in final form 5 January 2006
Published 7 February 2006
Online at stacks.iop.org/Nano/17/1212

Abstract
A fluorinated methacryl hybrid material, with low surface tension, was used as an imprinting material for easy de-moulding in a UV-based nano-imprint process. Specifically, a method to measure the adhesive force between the poly(dimethylsiloxane) (PDMS) mould and the imprinting material, using the force–distance curve of PDMS, was suggested to represent the de-mouldability of the PDMS mould in a UV-based nano-imprint process. The fluorinated methacryl hybrid material exhibited a low adhesive force to PDMS, as well as low surface tension, and could be nano-imprinted without using an anti-sticking treatment on the PDMS mould.

1. Introduction

UV-based nano-imprint [1] is a fundamentally new, inexpensive and smart technique, replacing photolithography in many areas of lithographic applications, e.g., optical application patterning [2], large area sub-micron scale structures of display panels [3], etc. In order to transfer patterns from a mould to imprinted materials by UV-based nano-imprint, the imprinting material used has to be chosen carefully by considering the surface property of the imprinting material. A major issue in UV-based nano-imprint approaches is the reproducibility of the imprinted results. Since UV-based nano-imprint is a contact process of the mould and the imprinting material, a de-moulding process is very important to fabricate reproducible imprints. An important prerequisite for reproducibility is to avoid sticking of the imprinting material to the surface of the mould after detachment. In the UV-based nano-imprint process, large area uniformity of the detached nano-imprinted pattern is essential [4].

Several polymer materials have been used as low cost mould materials [5, 6] including poly(dimethylsiloxane) (PDMS), polyurethane (PU) and amorphous fluoropolymer. Most soft lithography techniques, such as UV-based nano-imprint and capillary micro-moulding use PDMS for the mould [7]. However, a PDMS mould has some disadvantages for dense nano-pattern fabrication because of collapse caused by a relatively low modulus (1.8 MPa). Also, the surface tension of an elastomeric mould can cause rounding of sharp edges in the nano-pattern. To solve these problems, the modified hard PDMS (h-PDMS) with a high tensile modulus, which seems to replicate nano-structures well, has been used as a mould for nano-patterning by several groups [8].

Also, during UV-based nano-imprint, the PDMS mould is usually stuck to imprinted materials, which are UV curable polymers such as epoxy polymers, photoresists, photocurable oligomers etc. Thus, it is difficult to de-mould easily for reproducible nano-imprinting. In order to be applied to a large area UV-based nano-imprint, the imprinting materials need to have highly repellent surface properties. When general polymers such as PMMA are used as imprinting materials, however, an anti-sticking treatment is needed. For example, in [9], the surface of the polymer mould was functionalized by a liquid phase coating of trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane (97%, Aldrich) for 10 min to form a self-assembled monolayer (SAM), which has a functional unit, $-CF_3$, that gives it the high repellency required for it to act as a releasing layer. This treatment is an extra processing step for the realization of practical nanoimprint technology. This type of releasing layer is unnecessary if the imprinted material has highly repellent functionality.

Table 1. Surface tension of imprinting materials and the adhesive force of the PDMS mould to each material.

Imprinting materials	Surface tension (mN m^{-1})	Adhesive force (μN)	Adhesive force/unit area (nN nm^{-2})[a]
Fluorinated methacryl hybrimer	15.9–22.3	0.78–0.88	0.138–0.156
Methacryl hybrimer	28	2.45	0.435
PFCB	22.6	1.15	0.204
Tri(propylene glycol) diacrylate	30.3	2.5	0.43
PMMA	41.1	6.5	1.16

[a] Calculated result based on JKR model.

2. Hydrophobic behaviour of fluorinated methacryl hybrid materials

The organic–inorganic hybrid polymer (hybrimer) has been used in the UV-based nano-imprint process of optical device patterning [10, 11]. They are synthesized by sol–gel processing, which gives a large flexibility in material synthesis with variation of organically modified alkoxysilanes [12]. This flexibility makes hybrimers suitable for application in various applications. The fluorinated methacryl hybrimer has been synthesized to be used for the UV-based imprinting process for the fabrication of an optical waveguide [13]. The fluorinated methacryl hybrimer can be imprinted as a crack-free pattern without leaving any trace of solvent and without abrupt volume shrinkage. The fluorinated methacryl hybrimer can have high repellency, due to the long fluorine chain in the backbone structure. Thus, the PDMS mould can be de-moulded with the imprinting material of the fluorinated methacryl hybrimer without applying a surface treatment. If the imprinting material has high repellent characteristics to the PDMS mould, the surface treatment for a releasing layer is not necessary. Thus, it is necessary to understand the adhesive force between the mould and the imprinting materials to enhance easy de-moulding behaviour in UV-based nano-imprint. However, a quantitative analysis of the adhesive force of the PDMS mould with the imprinting material has not been reported. In this work, we suggest a new method to measure the adhesive force of the PDMS mould with the imprinting materials using a force–distance curve of AFM. Subsequently, we compare the adhesive force of several imprinting materials with the fluorinated methacryl hybrimer against the PDMS mould.

The fluorinated methacryl hybrimers used in this study were produced using the non-hydrolytic sol–gel process [14]. In order to investigate the effect of fluorine content on de-moulding behaviour during UV-based nano-imprint, the fluorine composition was modified from 10 to 20 mol% by changing the content of the perfluoro-group containing silane. Diphenylsilanediol (DPSD), composed of silanol groups, can react with the alkoxy group of organo alkoxysilane to form a siloxane bond. The alkoxysilane consists of perfluoro-alkylsilane (PFAS) and 3-(trimethoxysilyl)propyl methacrylate (MPTMS). The synthesized structure of fluorinated methacryl hybrimer is shown in figure 1(a). To fabricate a thin film of these hybrimers, the fluorinated methacryl hybrimer was spin-coated on silicon substrate and cured by UV-light (365 nm, 860 mJ cm^{-2}) in a N_2 atmosphere. Finally, the films were cured thermally at 170 °C for 3 h. More details on the material synthesis can be found in a previous publication [13].

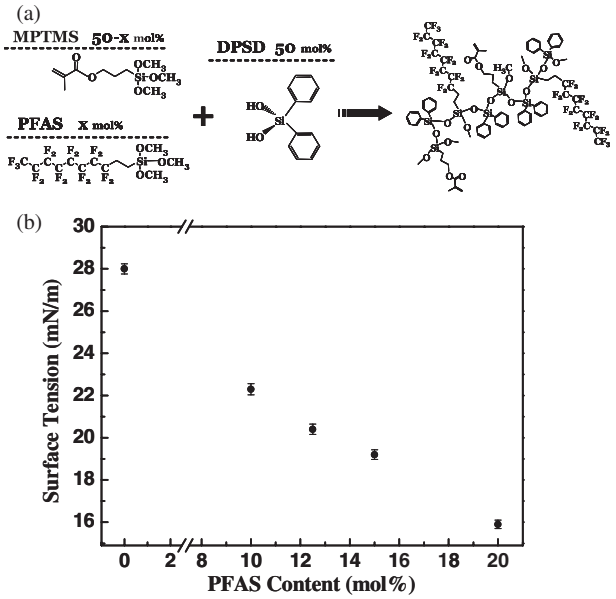

Figure 1. (a) A diagram of the fluorinated methacryl hybrimer's synthesized structure. (b) Fluorine dependence of surface tension of fluorinated methacryl hybrimers.

In this paper, we report on the result of hydrophobic behaviour of a fluorinated methacryl hybrimer on the UV-based nano-imprint process. At first, we observed the surface tension of the fluorinated methacryl hybrimer, with respect to fluorine content, by pendant drop shape analysis. Pendant drop shape analysis was carried out using the DSA 10 contact angle measuring system of Kruess GmbH Germany. The liquid was injected from a syringe tip so that it formed a drop on the tip of the needle. The shape of a drop of liquid hanging from a syringe tip is determined from the balance of forces, which include the surface tension of that liquid. Figure 1(b) shows the surface tension result with varying fluorine content, from 0 to 20 mol% of perfluoro-group containing silane. With increasing fluorine compositions to 20 mol%, the surface tension of fluorinated methacryl hybrimers is reduced from 28 to 15.9 mN m^{-1}. This value can be compared with that of other materials in table 1. The surface tension of the conventional perfluorocyclobutane (PFCB) polymer shows about 22.6 mN m^{-1}. Compared with PFCB, fluorinated methacryl hybrimer shows very low surface tension. Because of this low surface tension, the fluorinated methacryl hybrimer is expected to show very high hydrophobic properties, which will enhance the repellency with the PDMS mould.

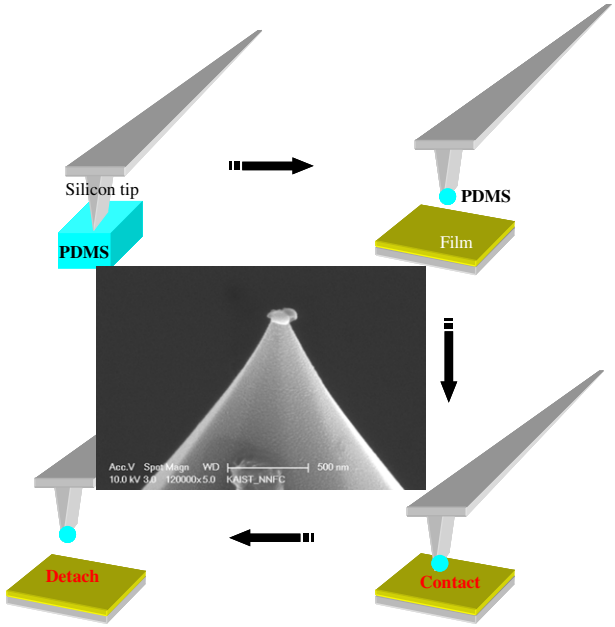

Figure 2. Force–distance experimental setup; a schematic diagram of the adhesion test of an AFM tip (covered with PDMS) to hybrimer film, and an SEM image of the PDMS-covered AFM tip.

(This figure is in colour only in the electronic version)

3. Experimental details of measuring the adhesive force

The AFM can record the amount of force felt by the cantilever as the probe tip is brought close to a sample surface and then pulled away. This technique can be used to measure the long range attractive or repulsive forces between the probe tip and the sample surface, elucidating local chemical and mechanical properties like adhesion [15, 16]. The force–distance curve typically shows the deflection of the free end of the AFM cantilever as the fixed end of the cantilever is brought vertically towards, and then away from, the sample surface. During retraction of an AFM tip pressed against the sample surface, it adheres to the surface until the spring force of the cantilever is higher than the attractive interaction force.

In this study, we show the adhesive force of fluorinated methacryl hybrimers to the mould material, poly(dimethylsiloxane) (PDMS), by using a PDMS coated silicon tip. The adhesive force of other imprinting materials can be compared with that of fluorinated methacryl hybrimers. Figure 2 shows the experimental procedure for the adhesive test using a PDMS coated AFM tip with several thin film samples. At first, the end of a silicon contact tip is covered by PDMS rubber, care is taken so that the spring force of the cantilever is not affected. The liquid PDMS was smeared onto the edge of the silicon tip, and this cover was cured at 50 °C for about 3 h. A scanning electron microscope (SEM) image of a PDMS-covered silicon tip is shown in figure 2. Then, the deflection of the PDMS coated silicon tip, as the z axis scanner extends the cantilever towards the sample surface and then retracts it again, is measured and plotted at many points. A key measurement of this AFM force–distance curve is the point at which the adhesion is broken and the cantilever comes free from the sample surface. This can be used to measure the adhesive force required to break the adhesion of the PDMS mould with several samples during UV-based nano-imprint.

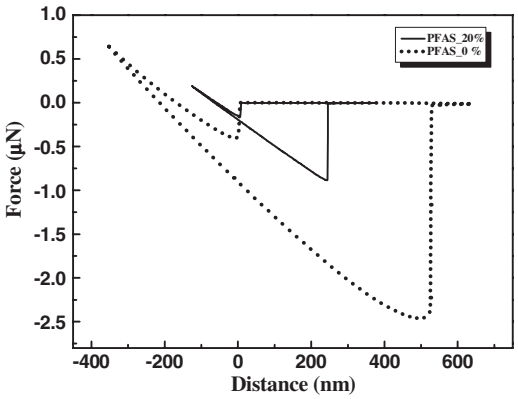

Figure 3. Force–distance curve for the fluorinated methacryl hybrimers by PDMS-covered silicon tip, which shows fluorine dependence of the adhesive force of hybrimers with PDMS-covered silicon tip.

Figure 3 shows the force–distance curve for fluorinated methacryl hybrimers with a variation in fluorine content. The horizontal axis denotes the distance of the PDMS-covered tip from the sample surface. The force signal is based on the spring constant of the AFM-cantilever which is taken from the data sheet of the manufacturer (silicon contact tip CSC12 from Mikromasch).

Because the shape of the PDMS-coated tip was not changed before and after the experiment, we assume that the tip is pulled off elastically from the hybrimer film samples. The influence of adhesion on a contact between solid surfaces was first considered by Johnson, Kendall and Roberts (JKR). In the JKR approximation only the adhesive force inside the contact area was taken into account. Thus, the JKR model is appropriate for our experiments. Accordingly, the contact radius is given as [17],

$$a^3 = \frac{d}{2K}\left[P + \frac{3}{2}W_{\mathrm{A}}\pi d + \sqrt{3\pi W_{\mathrm{A}}\,\mathrm{d}P + \left(\frac{3\pi W_{\mathrm{A}}d}{2}\right)^2}\right]. \tag{1}$$

Here W_{A} is the thermodynamic work of adhesion, d is the diameter of PDMS, and K is the composite Young's modulus given as,

$$K = \frac{4}{3}\left[\frac{1-\upsilon^2_{\mathrm{PDMS}}}{E_1} + \frac{1-\upsilon^2_{\mathrm{hybrimers}}}{E_2}\right]^{-1}. \tag{2}$$

In equation (2), E is the elastic modulus, υ is the Poisson ratio, and subscript 1 and 2 refer to the materials of the PDMS and hybrimer film substrate. The JKR model predicts that the force needed to remove the PDMS tip (the adhesive force) is given as

$$F^{\mathrm{JKR}}_{\mathrm{adhesive-force}} = \tfrac{3}{4}\pi W_{\mathrm{A}}d. \tag{3}$$

The contact radius at the separation is obtained by setting $P = -F^{\mathrm{JKR}}_{\mathrm{adhesive-force}}$ in equation (1). The corresponding contact radius is given by

$$a = \left(\frac{3\pi W_{\mathrm{A}}d^2}{8K}\right)^{\frac{1}{3}}. \tag{4}$$

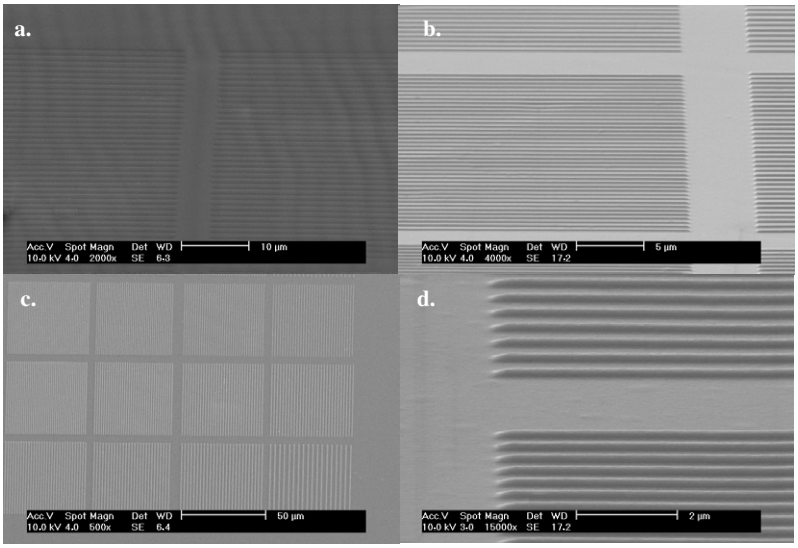

Figure 4. Scanning electron microscopy (SEM) image of line patterns with 200 nm pitch by UV-based nano-imprint of fluorinated methacryl hybrimer. (a) Concave line pattern of PDMS mould, (b) convex imprinted line patterns of hybrimer, (c) various pitch size of imprinted patterns, (d) 100 nm sized hybrimer line pattern.

According to equations (2)–(4), we calculated the adhesive force/unit area (nN nm^{-2}), as shown in table 1.

The sample of methacryl hybrimer containing 0% fluorine, see figure 3, shows 2.45 μN of adhesive force against adhesion with PDMS. Only if the formal distance reaches nearly 520 nm and the tensile force was more than 2.45 μN can the contact be broken and the force become zero. This tensile force, of about 2.45 μN, is the measure of the adhesive interaction between the PDMS-covered AFM tip and the methacryl hybrimer surface in this case. One could state that the adhesive force between PDMS and the methacryl hybrimer is 2.45 μN. In figure 3, a decreased adhesive force can be seen with the increased fluorine content of 20%. The fluorinated methacryl hybrimer shows drastically reduced adhesive force compared with the methacryl hybrimer. However, the increased fluorine composition is not significantly effective on the adhesive force of the fluorinated methacryl hybrimer. The adhesive force is slightly deceased from 0.88 to 0.78 μN by increasing the perfluoro-group containing silane from 10 to 20 mol%.

The surface tension, the adhesive force, and the adhesive force/unit area against adhesion with the PDMS mould, for several materials, are listed in table 1. For comparison, we present the same parameters measured for tri(propylene glycol) diacrylate [18, 19], polymetyl methacrylate (PMMA) [20] and per-fluorocyclobutane (PFCB) [21, 22], which are typically used in UV-based nano-imprint processes. The fluorinated methacryl hybrimers exhibit very low surface tension as well as low adhesive force. The low surface tension is consistent with a low adhesive force against the adhesion of the PDMS mould. Tuning of the surface parameters of the hybrimer film—such as surface tension—is achieved by adding long fluorine groups containing silane. Because the surface tension of fluorinated methacryl hybrimers is low enough, these hybrimers are one of the excellent imprinting candidate materials for easy de-moulding of imprinted pattern from any type of mould material. The high repellency of these materials also makes them useful for UV-based nano-imprint processes of large area patterning. By using an h-PDMS mould from a master fabricated by e-beam lithographic patterning, UV-based nano-imprint is carried out with the fluorinated methacryl hybrimer without any surface pre-treatment. A UV-moulded 100 nm width line pattern image which has various pitch sizes is shown in figure 4. Figure 4(a) shows a concave type h-PDMS mould pattern and figure 4(b) shows a convex type line pattern, which is imprinted by conformal contact of the h-PDMS mould. The PDMS mould has clearly detached without any remnants from the imprinted pattern. Figure 4(c) shows the imprinted hybrimer line patterns with various pitches (200 nm to 1 μm) and figure 4(d) shows 100 nm sized line pattern of imprinted hybrimer pattern.

4. Conclusion

In this study, we have suggested a method to measure quantitatively the adhesive force between the mould and the imprinting materials using an AFM. Then, we demonstrated that the fluorinated methacryl hybrimer, which has a low adhesive force, was a good candidate imprinting material to simplify de-moulding in the UV-based nano-imprint process, because it does not require surface treatment of the PDMS mould.

Acknowledgments

This work was supported by the sol–gel Innovation Project (SOLIP) of the Ministry of Commerce, Industry, and Energy of Korea.

References

[1] Chou S Y, Krauss P R and Renstrom P J 1996 *Science* **272** 85
[2] Lee B T, Kwon M S, Yoon J B and Shin S Y 2000 *IEEE Photon. Technol. Lett.* **12** 62

[3] Ziebarth J M, Saafir A K, Fan S and Mcgehee M D 2004 *Adv. Funct. Mater.* **14** 451
[4] Miller M, Doyle G, Stacey N, Xu F, Sreenivasan S V, Watts M and Labrake D L 2005 *Proc. SPIE* **5751** 994
[5] Kim Y S, Lee H H and Hammond P T 2003 *Nanotechnology* **14** 1140
[6] Xia Y and Whitesides G M 1998 *Annu. Rev. Mater. Sci.* **28** 153
[7] Xia Y and Whitesides G M 1998 *Angew. Chem. Int. Edn* **37** 550
[8] Odom T W, Love J C, Wolfe D B, Paul K E and Whitesides G M 2002 *Langmuir* **18** 5314
[9] Parikh A N, Allara D L, Azouz I B and Rondelezz F 1994 *J. Phys. Chem.* **98** 7577
[10] Kim W S, Lee J H, Shin S Y, Kim Y C and Bae B S 2004 *IEEE Photon. Technol. Lett.* **16** 1888
[11] Kim W S, Kim K S, Kim Y C and Bae B S 2005 *Thin Solid Films* **476** 181
[12] Eo Y J, Kim J H, Ko J H and Bae B S 2005 *J. Mater. Res.* **20** 401
[13] Kim W S, Kim K S, Eo Y J, Yoon K B and Bae B S 2005 *J. Mater. Chem.* **15** 465
[14] Eo Y J, Lee T H, Kim S Y, Kang J K, Han Y S and Bae B S 2005 *J. Polym. Sci.* B **43** 827
[15] Santner E, Meine K, Polaczyk C and Spaltmann D 2001 *Proc. Int. Tribology Conf.* p 681
[16] Polaczyk C, Schneider T, Schöfer J and Santner E 1998 *Surf. Sci.* **402** 454
[17] Johnson K L, Kendall K and Roberts A D 1971 *Proc. R. Soc.* A **324** 301
[18] Xu F *et al* 2004 *Proc. SPIE* **5374** 232
[19] Haisma J, Verheijen M, Heuvel K and Berg J 1996 *J. Vac. Sci. Technol.* B **14** 4124
[20] Chou S Y, Krauss P R and Renstrom P J 1996 *J. Vac. Sci. Technol.* B **14** 4129
[21] Bender M, Otto M, Hadam D, Spangenberg B and Kurz H 2002 *Microelectron. Eng.* **61** 407
[22] Smith J D W, Chen S, Kumar S M, Ballato J, Topping C, Shah H and Foulger S H 2002 *Adv. Mater.* **14** 1585