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Role of Fluorinated Monomer for Simple Demolding in Nanoimprint Lithography

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ABSTRACT: In this study, we explored the effect of a fluorinated monomer on nanoimprint lithography (NIL) and determined the optimum amount of fluorinated monomer required in the formulation for better NIL. To estimate the role of the fluorinated monomer for demolding, NIL was conducted using copolymers of nonfluorinated silane monomers and fluorinated silane monomers. Epoxy ring-opening photopolymerization based on the cationic polymerization mechanism was utilized for the NIL process. The physical properties of the photopolymerized copolymeric materials, such as tensile strength, elongation, modulus, and impact strength, as well as surface characteristics such as the contact angle were reported. Aluminum deposition on the nanoimprinted pattern, which is instrumental in fabricating a wire grid polarizer, was also conducted. According to the study results, the use of a copolymer containing 20 mol % of the fluorinated monomer in NIL proved to be the best formulation for easy demolding and for ensuring optimum levels of the physical properties. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41317.

KEYWORDS: demolding process; epoxy; fluorinated monomer; nanoimprint lithography; photopolymerization

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INTRODUCTION

Nanoimprint lithography (NIL) has attracted much attention because of its ability to substitute photolithography, which is currently used to form nanopatterns in the electronics industry. NIL provides a simpler and less expensive route to nanometer-scale fabrication. Using NIL, nanoscale patterns can be duplicated by simple physical contact.[1–6] In the early stage of NIL, polymers were used directly.[7–10] The polymer was heated above the glass transition temperature (T_g) and placed on a mold on which a high pressure would be applied. After a certain period of time, the temperature is reduced and the mold is removed to produce a nanopattern that duplicates the surface of the polymer substrate from the mold.

Currently, several patterning strategies for NIL are being investigated.[1,2,11,12] One of the important representative nanoimprinting methods is that in which a monomer is used.[13,14] After coating the monomer on the substrate, it is brought in contact with the mold. Once the mold is in place, polymerization is conducted, and the mold is then removed to obtain the nanopattern on the surface of the polymeric substrate. One disadvantage of this process is the shrinkage that occurs during the polymerization. This shrinkage leads to a limitation in the pattern-size of several hundred nanometers in the NIL process. To avoid this shrinkage and obtain better nanopatterns, one of the improved methods utilizes prepolymers with a low molecular weight. Numerous research groups have used the prepolymer method to fabricate nanopatterns due to the ease of processing and the nonrequirement of high pressures. Even though this method has considerable advantages, it has several disadvantages that need to be addressed.

One of the most pertinent issues is that perfect demolding is very difficult to achieve in the demolding process.[15] To solve this problem, researchers have employed methods in which the surface of the mold is treated with a fluorinated surfactant; however, this route proved to be inefficient in fabricating nanopatterns of sizes 100 nm or less. Hence, most of the recent methods focus on mixing fluorinated monomers in the molding compound to form copolymeric materials.[16]

Previous research was directed at the use of the angled evaporation of aluminum on two sidewalls of the imprinted nanograting to produce a wire grid polarizer (WGP).[17,18] During this process, nanoimprinting was conducted using silane compounds containing a fluorinated monomer, which could aid demolding. It is known that fluorinated surfaces facilitate the demolding process. However, there is no clear knowledge on the extent to which this fluorinated compound aids demolding and on the

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optimum amount of fluorinated monomer to be used in the nanoimprinting process.

In this study, we investigate the effects of a fluorinated monomer on nanoimprinting by measuring the physical properties and contact angle of the fabricated patterns. The materials for nanoimprinting were synthesized with a fluorinated monomer and other silane compounds using sol–gel reaction, and nanoimprinting was conducted using epoxy ring-opening photopolymerization via the cationic polymerization mechanism.

Cationic polymerization was specifically chosen for this study instead of radical polymerization, as radical polymerization would be affected by atmospheric oxygen and hence could be harmful to the nanopatterned surface. However, the effect of oxygen is negligible in the case of cationic polymerization, and this type of polymerization has thus recently attracted much interest for improving NIL.

Figure 1. Chemical structures of monomeric silane compounds and mold release agent.

EXPERIMENTAL

Materials

Phenyltrimethoxysilane (PTMS), (3-glycidyloxypropyl)trimethoxysilane (GTMS), (tridecafluoro-1-octyl)triethoxysilane (FTES), cesium hydroxide (CsOH), and propylene glycol monomethyl ether acetate (PGMA) were purchased from Aldrich Chemical (St. Louis, MO). The photoacid generator (PAG) was purchased from Craig Adhesive and Coating Co. (Newark, NJ) under the name UV9390C. The PAG contains about 50 wt % of bis(4-dodecylphenyl)iodonium hexafluoroantimonate as an active ingredient. The mold release agent 1*H*,1*H*,2*H*,2*H*-perfluorododecyltrichlorosilane (FDTS) was purchased from Gelest (Morrisville, PA). Silquest A-187 Silane (GTMS as the main ingredient) was purchased from Crompton Co. (Lisle, IL). Poly(ethyleneterephthalate) (PET) film, with a thickness of 50 μm, was obtained from 3M Co. (St. Paul, MN).

Instruments

A Nanonex 2000 imprinting tool (Monmouth Junction, NJ) with vacuum capability and UV curing wavelength of 365 nm, or a light curing system (ELC-430) from Electro-Lite Corporation (Bethel, CT), was used for UV-NIL. Aluminum was deposited using electron-beam evaporation. Scanning electron microscopy (SEM) was performed using a Hitachi SU8000 scanning electron microscope (Tokyo, Japan). The modulus, tensile strength, and elongation of the film of the copolymeric material were measured using a materials testing machine (LS 5, Lloyd Instruments), and the impact strength of the copolymeric material film was measured using an Izod impact tester (IM-705C) according to ASTM D256. A minimum of six specimens were tested, and the average results were recorded. The contact angle was measured using a contact angle goniometer and tensiometer (Rame-Hart Model 250, Rame-Hart Instrument).

Synthesis of Silicate Copolymers (PPGF)

PPGF was synthesized by modifying a previously reported method.[14,17]. PTMS (0.30 mol, 59.5 g), FTES (0.20 mol, 102.1 g), GTMS (0.50 mol, 118.2 g), water (4.0 mol), and CsOH (1.0 mmol, 0.168 g) were added to methanol (180 g) in a 1-L three-necked round-bottomed flask, which was equipped with a mechanical stirrer, a Dean-Stark trap, and a condenser. The reaction was conducted at 65°C for 2 h under an N_2 atmosphere. During the reaction, the solvent and the byproduct were removed through the Dean-Stark trap, and an equivalent amount of toluene was added to replace the distilled material. The reaction temperature was then gradually increased to 110°C for 1 h. The remaining methanol and byproduct were removed while the reaction temperature was increasing. After completion of the reaction, more toluene (180 g) was added to the flask containing the product solution. CsOH (catalyst) was removed by a separatory funnel using acetic acid solution (6.0 g in 100 mL of water). The toluene layer was washed three times with 100 mL of water. The majority of the toluene was removed using a rotary evaporator, and the residual toluene was removed by evaporation under vacuum at 50°C for 10 h to obtain PPGF (171.3 g).

Nanoimprinting

The nanoimprint resist was prepared by dissolving the PPGF resin in PGMA, followed by the addition of PAG (1 wt % of the PPGF resin). The original silicon oxide master molds were vapor-coated with FDTS for easy mold release after the NIL process. The PPGF resin solution was spun on a flexible PET film substrate, which was previously surface-treated with O_2 plasma and then vapor-coated with Silquest A-187 silane as an adhesion promoter. Imprinting was performed under UV light exposure for a few seconds at room temperature. A Nanonex 2000 imprinting tool with vacuum capability for UV curing at 365 nm, or a light curing system (ELC-430) from Electro-Lite Corporation, was used for imprinting and curing. The imprinting pressure was typically 40 psi. NIL was performed on a flexible PET film. A nanograting with a period of 180 nm, linewidth of 60 nm, and height of 180 nm was imprinted using the PPGF material.

Aluminum Deposition

The rate of aluminum deposition in this study is 0.50 nm/s. To deposit aluminum on the sidewalls of the imprinted nanopattern while avoiding the base of the trench, the deposition

Table I. formulation of Compounds (PPGF) Used for Nanoimprinting (Unit: mole)

	FTES	PTMS	GTMS
PPGF 0	0	0.50	0.50
PPGF 5	0.05	0.45	0.50
PPGF 10	0.10	0.40	0.50
PPGF 15	0.15	0.35	0.50
PPGF 20	0.20	0.30	0.50
PPGF 25	0.25	0.25	0.50
PPGF 30	0.30	0.20	0.50

mount was tilted to 40°. The deposition process was repeated on the opposite side to ensure aluminum deposition on both sidewalls of the PPGF nanogratings.

RESULTS AND DISCUSSION

Synthesis of PPGF

In this study, PPGF used for nanoimprinting was synthesized by a sol–gel reaction with three types of silane compounds: PTMS, GTMS, and FTES. GTMS was used to provide an epoxy functional group to conduct the polymerization, and FTES was used for easy demolding. The chemical structures of these monomeric compounds and the mold releasing agent (FDTS) are shown in Figure 1, while the formulation of PPGF is shown in Table I. Because GTMS has an epoxy functional group that aids photopolymerization during NIL, the amount of GTMS was fixed as 50 mol % in the PPGF formulation. The amount of FTES was controlled from 0 to 30 mol % in the PPGF formulation.

Physical Properties of Films of Photopolymerized PPGF

To estimate the physical properties of the photopolymerized PPGF, photopolymerization was conducted using PPGF on a PET film that was surface-treated with FDTS. The modulus, tensile strength, elongation, and impact strength were measured using the photopolymerized PPGF film. The results are shown in Figure 2.

As can be seen in Figure 2, the modulus was 2.5 GPa when the FTES content was 0 mol %. An increase in the FTES content resulted in a continuous decrease in the modulus, which reached 0.9 GPa when the FTES content was 30 mol %. Similar results were observed in the case of the tensile strength. The tensile strength was 56 MPa when the FTES content was 0 mol

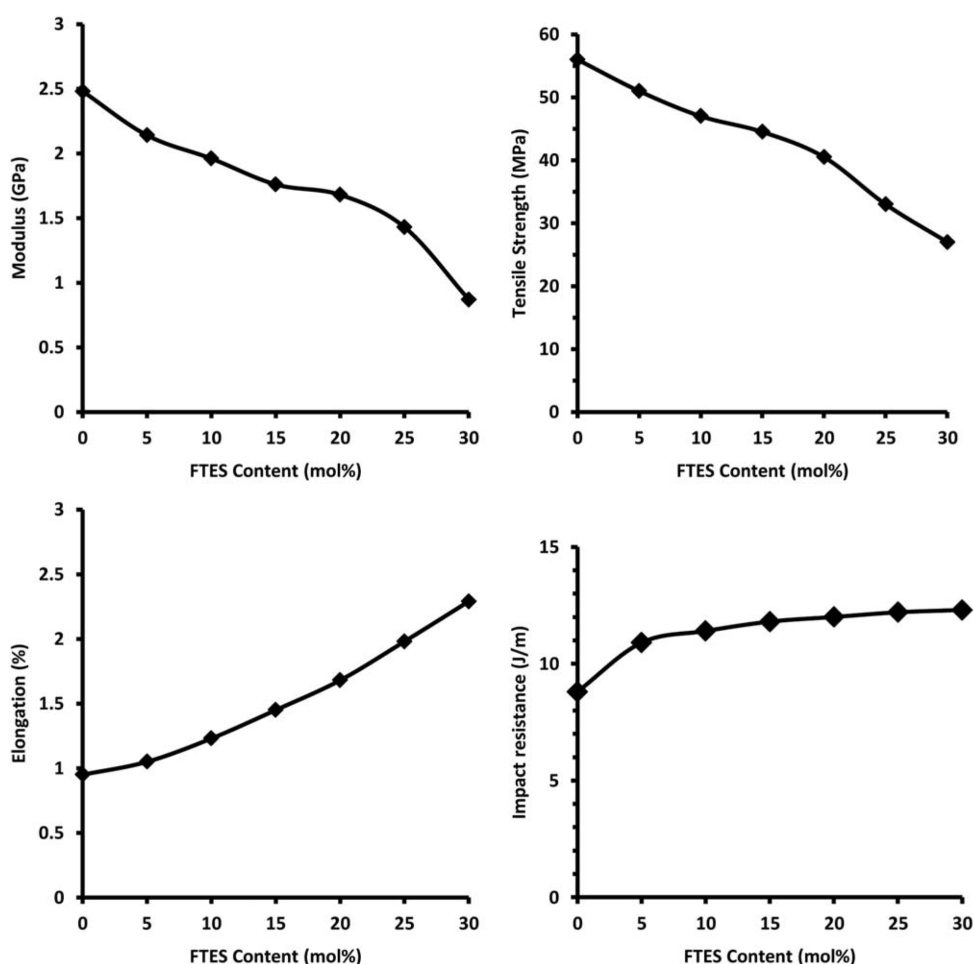


Figure 2. Physical properties of the copolymeric compounds.

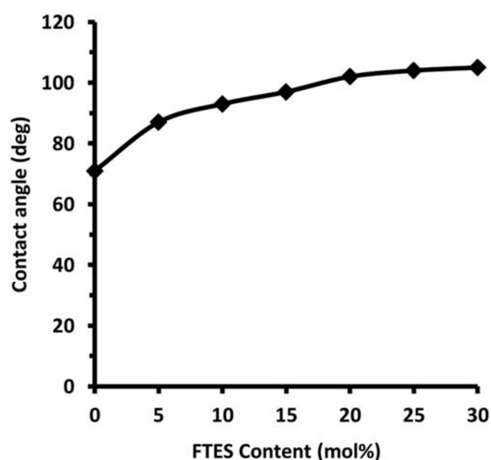


Figure 3. Contact angle of the surface with PPGF.

%, and reduced to 27 MPa when the FTES content reached 30 mol %. Further, the elongation was 1.0% when the FTES content was 0 mol %, and increased to 2.3% when the FTES content was 30 mol %. The impact strength was 8.8 J/m when the FTES content was 0 mol %, and increased to 12.3 J/m when the FTES content was 30 mol %. The impact strength increased sharply when the FTES content ranged from 0 to 5 mol %, but showed a plateau over the FTES content range of 10–30 mol %. In conclusion, an increase in the FTES content caused a decrease in the modulus and tensile strength, but an increase in the elongation and impact strength.

The contact angle was measured to estimate the surface characteristics of NIL materials because the contact angle could play an important role in the demolding process. Therefore, the contact angles of the films formed with PPGF were measured for various FTES contents. The results are shown in Figure 3. The surface of the film without FTES was hydrophilic, as shown in Figure 3. The hydrophobic character of the film increased with an increase in the amount of FTES in PPGF.

Nanoimprint Lithography

Using the prepolymer that was synthesized in this study, the NIL was conducted on the silicon mold by cationic ring-opening photopolymerization with the epoxy functional group, for various FTES contents. The SEM results are shown in Figure 4. In the case of PPGF0, which does not contain FTES, NIL was successful only when large amounts of FDTS were used. If small amounts of FDTS were used during the NIL process, the "demolding" produced imperfect patterns and was difficult to accomplish [Figure 4(a)]. In contrast, in the case of PPGF20, demolding could be carried out successfully. When using small amounts of FDTS, NIL was successfully executed using the large mold (2 $\times$ 2 cm^2) [Figure 4(b)]. We assume that the NIL was conducted successfully because the FTES in the formulation could stay on the surface of the substrate after the polymerization. Using the nanopattern formed in this study, a WGP was fabricated. The fabrication method shown in Figure 5 was reported previously.[17,18] This method has gained much attention because the period of the nanopattern can be reduced twofold.

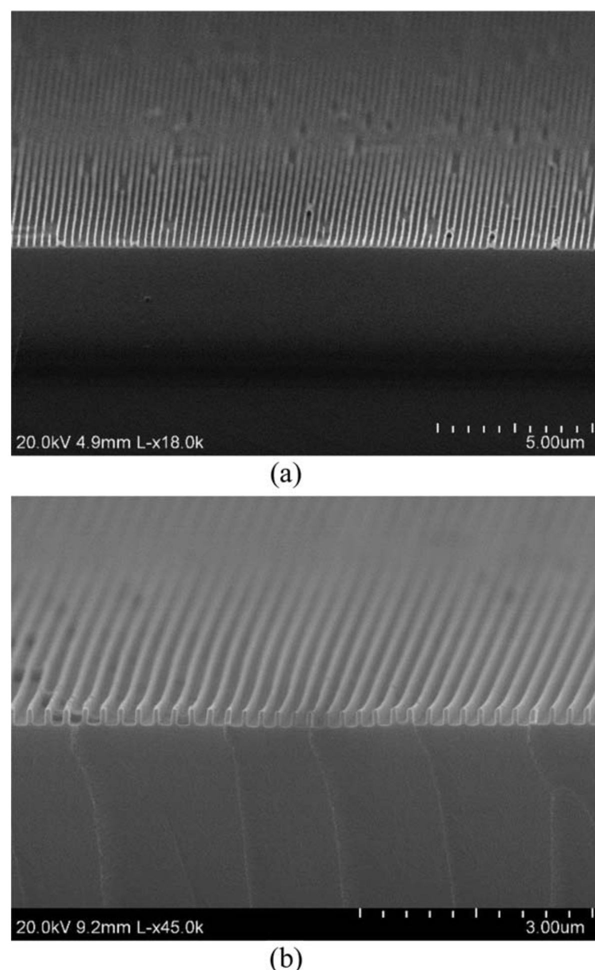


Figure 4. SEM images for NIL using (a) PPGF0 and (b) PPGF20.

WGP is one of the most attractive alternatives to the conventional polarizer, of which the optical performance cannot meet the requirements of some of the new optoelectronic systems currently under development. WGPs offer a large spectral range, are small in size, and can be integrated with other optical elements on the same chip. They can also be constructed as high-quality, integration-capable, and thin-film-type polarizers.[19–22]

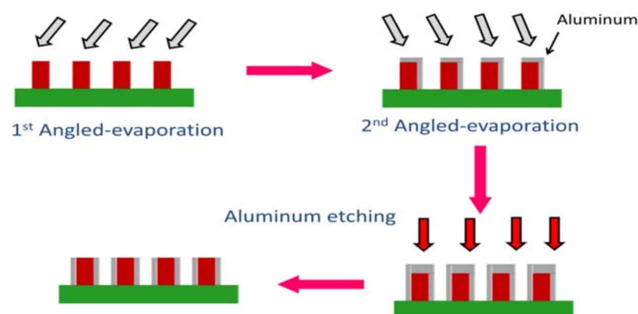
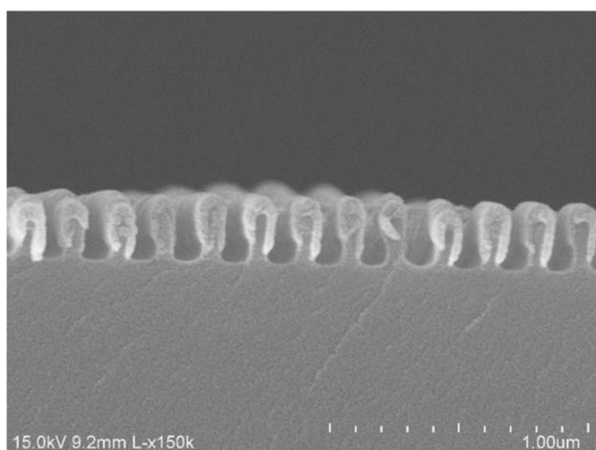
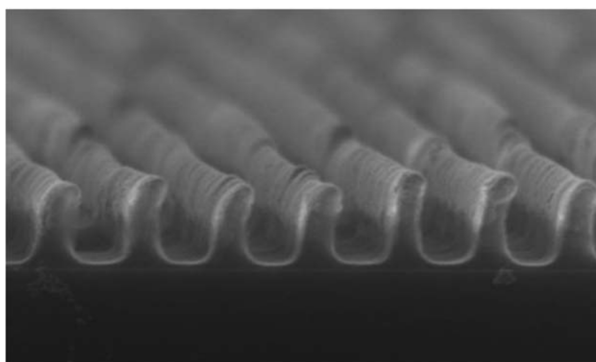


Figure 5. Fabrication of WGP using two consecutive angled aluminum evaporation steps. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



(a)



(b)

Figure 6. SEM images of nanopatterns (a) after two consecutive angled aluminum evaporation steps using PPGF20 and (b) after one angled aluminum evaporation step using PPGF30.

WGPs can be applied in various fields such as microscopy, imaging systems, and polarized beam splitters.

To obtain high performance in the visible-light range for WGPs, the nanopattern should have a period of less than 100 nm. Although a method to fabricate nanopatterns with a period of 100 nm by NIL has previously been developed, it is not practically applicable. Using the method shown in Figure 5, nanopatterns with a period of 90 nm can be fabricated from a nanopattern with a larger period of 180 nm, which can be more easily formed. The relative ease of operation of this method will attract more attention for developing WGPs. The most important step in producing WGPs involves the angled evaporation of aluminum on the nanopattern. Because the angle of the stacked aluminum is tilted, tension is exerted on the nanopattern. Hence, for superior performance, the nanopattern must be able to endure this tension. The SEM results for this process are shown in Figure 6.

The result for PPGF20 is shown in Figure 6(a); the SEM image shows that the two consecutive angled evaporation steps were successful, without causing deformation of the nanopattern. On the contrary, in the case of PPGF30, the SEM results after the first angled evaporation indicated that the nanopattern was displaced to a considerable extent [Figure 6(b)]. This result showed that the nanopattern could not endure the pressure from the stacked aluminum. We believe that this result is closely related to that shown in Figure 2, in which the modulus and tensile strength are seen to decrease with an increase in the FTES content. This result reveals that the physical properties of the substrate polymer must be seriously considered.

In conclusion, it was demonstrated that the optimum amount of FTES was 20 mol %, while 30 mol % FTES content had a negative influence on the NIL process.

CONCLUSION

The results of this study reveal that a fluorinated monomer plays a major role in the demolding process in NIL. However, an excessive amount of the fluorinated monomer, such as 30 mol %, may be detrimental to the NIL process because the desired physical properties of the substrate would be degraded. This problem is more prominent in the case of a tilted process such as angled evaporation. The recommended fluorinated monomer content for the NIL process is 20 mol %.

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REFERENCES

1. Guo, L. J. *Adv. Mater.* **2007**, *19*, 495.
2. Acilgoz, C.; Hempenius, M. A.; Huskens, J.; Vancso, G. J. *Eur. Polym. J.* **2011**, *47*, 2033.
3. Ahn, S. H.; Guo, L. J. *Adv. Mater.* **2008**, *20*, 2044.
4. Shin, Y. J.; Wu, Y. K.; Guo, L. J. *Nanotechnology* **2013**, *24*, 255302.
5. Pina-Hernandez, C.; Guo, L. J.; Fu, P. F. *ACS Nano.* **2010**, *4*, 4776.
6. Pina-Hernandez, C.; Fu, P. F.; Guo, L. J. *ACS Nano.* **2011**, *5*, 923.
7. Chou, S. Y.; Krauss, P. R.; Renstrom, P. J. *Science* **1996**, *272*, 85.
8. Choi, P.; Fu, P. F.; Guo, L. J. *Adv. Funct. Mater.* **2007**, *17*, 65.
9. Khang, D. Y.; Yoon, H.; Lee, H. H. *Adv. Mater.* **2001**, *13*, 749.
10. Khang, D. Y.; Kang, H.; Kim, T. L.; Lee, H. H. *Nano. Lett.* **2004**, *4*, 633.
11. Odom, T. W.; Love, J. C.; Wolfe, D. B.; Paul, K. E.; Whitesides, G. M. *Langmuir* **2002**, *18*, 5314.
12. Ahn, S. H.; Guo, L. J. *Nano. Lett.* **2009**, *9*, 4392.
13. Cheng, X.; Guo, L. J.; Fu, P. F. *Adv. Mater.* **2005**, *17*, 1419.
14. Pina-Hernandez, C.; Kim, J. S.; Fu, P. F.; Guo, L. J. *J. Vac. Sci. Technol. B* **2007**, *25*, 2402.
15. Amirsadeghi, A.; Lee, J. J.; Park, S. *Appl. Surf. Sci.* **2011**, *258*, 1272.

16. Pina-Hernandez, C.; Fu, P. F.; Guo, L. J. *J. Vac. Sci. Technol. B* **2008**, *26*, 2426.
17. Shin, Y. J.; Pina-Hernandez, C.; Wu, Y. K.; Ok, J. G.; Guo, L. J. *Nanotechnology* **2012**, *23*, 344018.
18. Shin, Y. J.; Wu, Y.-K.; Lee, K.-T.; Ok, J. G.; Guo, L. J. *Adv. Opt. Mater.* **2013**, *24*, 863.
19. Golden, J. H.; DiSalvo, F. J.; Silcox, J.; Thomas, M.; Elman, J. *Science* **1996**, *273*, 782.
20. Liu, X.; Deng, X.; Sciortino, J. P.; Buonanno, M.; Walters, F.; Varghese, R.; Bacon, J.; Chen, L.; O'Brien, N.; Wang, J. J. *Nano. Lett.* **2006**, *6*, 2723.
21. Pang, Y. T.; Meng, G. W.; Zhang, L. D.; Qin, Y.; Gao, X. Y.; Zhao, A.W.; Fang, Q. *Adv. Funct. Mater.* **2002**, *12*, 719.
22. Ahn, S. W.; Lee, K. D.; Kim, J. S.; Kim, S. H. *Nanotechnology* **2005**, *16*, 1874.