



# A photo-polymerization resist for UV nanoimprint lithography

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## ABSTRACT

A novel liquid photo-polymerization resist was prepared for nanoimprint lithography on transparent flexible plastic substrates. The resist is a mixture of polymethylmethacrylate (PMMA), methylmethacrylate (MMA), methacrylic acid (MAA) and two photo-initiators, (2-isopropyl thioxanthone (ITX) and ethyl 4-(dimethylamino)benzoate (EDAB)). The resist can be imprinted at room temperature with a pressure of 0.25 kg/cm<sup>2</sup>, and then exposed from the transparent substrate side using a broad band UV lamp to obtain nano- and micro-scale patterns. Replications of high-density line and space patterns with resolution of 150 nm were obtained on a flexible indium tin oxide/poly(ethylene terephthalate) (ITO/PET) substrate. The liquid resist has low viscosity due to the liquid monomers, and low shrinkage due to the addition of PMMA as a binder.

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## 1. Introduction

Nanoimprint lithography (NIL) has been demonstrated to be a high volume and cost-effective patterning technique with sub-10 nm resolution and is regarded as a promising candidate for next generation lithography [1–6]. In the NIL process, a mold with nano-scale features is pressed into a thin resist film, deforming the shape of the film according to the features of the mold and forming a relief pattern in the film. Its progress is closely linked to the availability of suitable resists, which meet all the requirements of this technology [7–11].

Different approaches have been used in the NIL process. The most commonly used approach is hot embossing lithography (HEL). In the HEL, high pressures and high temperatures are usually required for the imprinting of thermoplastic resists. However, this may induce mechanical strain in the mold and resists. Also, the viscoelastic flow of polymer resist is a slow process that can limit patterning performances. Compared to the HEL, UV radiation curing technology has many advantages, such as high curing speed that reduces the cycle time, low energy costs as polymerization proceeds at room temperature, and no pattern shift due to the absence of mismatch of the coefficients of thermal expansion of mold and substrate. This led to a fast acceptance of UV curing in the nanoimprinting field. Step and flash imprint lithography (SFIL) is a representative example [12]. We have also reported back flash imprint lithography (BFIL) for UV curing resists [13].

The key element for nanoimprint lithography is the resist material. In this paper, we report a novel low viscosity and fast photo-polymerization resist system. The resist system was based on reac-

tive acrylate monomers mixed with a polymer and photo-initiators, but without any solvents. Acrylate-based monomers need an initiator, which decomposes into free radicals upon UV exposure and subsequently initiates the polymerization reaction. The focuses of this new resist system are on low viscosity, fast UV curing, low shrinkage, minimum residual layer thickness, good adhesion on different substrates, and sufficient thermal stability in subsequent processes. The resist system can be used on large area flexible indium tin oxide/poly(ethylene terephthalate) ITO/PET substrates for next generation display application.

## 2. Experimental details

### 2.1. Materials

Methylmethacrylate (MMA), methacrylic acid (MAA) were purchased from Fluka Co., without further purification. 2-Isopropyl thioxanthone (ITX) and ethyl 4-(dimethylamino)benzoate (EDAB) were obtained from Satomer Co., Poly(methyl methacrylate) (PMMA) was obtained from Aldrich Co., with a weight average molecular weight ( $M_w$ ) of around 15,000 g/mole.

### 2.2. Resist preparation

The preparation of the liquid resists was as follows: different amounts of PMMA were first mixed with MMA and MAA monomers. The mixtures were stirred by a mechanical stirrer until all PMMA was dissolved in the MMA and MAA, and became clear, homogeneous solutions. To the solutions, the photo-initiators, ITX and EDAB, were added and stirred until the initiators were totally dissolved in the solutions. The compositions of the resists are listed in Table 1. The compositions of the resists varied with the

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E-mail address: [lchs@mail.ncku.edu.tw](mailto:lchs@mail.ncku.edu.tw) (S. Lien-Chung Hsu).

**Table 1**  
Formulations of the photo-polymerization resists.

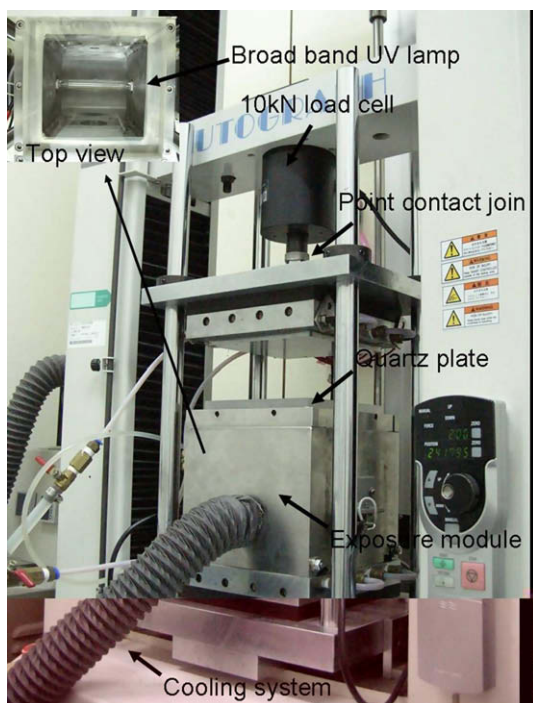
	Composition				
	PMMA (g)	MMA (g)	MAA (g)	ITX (g)	EDAB (g)
Resist-A	0	73	27	1.4	4
Resist-B	28	45	27	1	2.9
Resist-C	39	34	27	0.86	2.5
Resist-D	50	23	27	0.7	2

amounts of MMA and PMMA, but the sum of these two components remained the same. The amount of MAA was kept constant throughout the compositions.

### 2.3. Imprint experiments

Imprint experiments were performed on an imprint machine, which was assembled from a Shimadzu AG-IS universal testing machine and a home-designed exposure module (Fig. 1). We used a “point contact” technique to improve the uniformity between the two imprint plates. With the auxiliary tool, we can perform either hot embossing or UV back flash imprint lithography at the same time. The broad band UV exposure unit cooled by air has an intensity of 43 mW/cm<sup>2</sup> in the wavelength range of 220–450 nm. The platform is UV transparent quartz with 3 cm thickness for back flash imprinting. The maximum pressure was determined by the load cell of the universal testing machine, which was changeable.

Two different resolution molds were used in this experiment. One was the nanoscale mold, which was fabricated by an e-beam writer and inductively coupled plasma etching (ICP) on a silicon wafer with a depth of 250 nm. The other was the micro-scale mold, which was fabricated by optical lithography and reactive ion etching (RIE) on a silicon wafer with a depth of 5 μm. The minimum feature sizes of the molds were 150 nm and 6 μm, respectively. In order to reduce the sticking problem between the resist and mold, both molds were pretreated with a mold release agent,



**Fig. 1.** The imprint machine assembled from the Shimadzu AG-IS universal testing machine with a custom designed pressing module.

octadecyltrichlorosilane (OTS). Due to its long alkyl chain, the OTS can form a self-assembling layer during the pattern transfer, avoiding incomplete pattern transfer. A commercial poly(ethylene terephthalate) (PET) film with transparent conductive layer of indium tin oxide (ITO) from Join Well Technology Co., (Taiwan, ROC) was used as the substrate. The thickness of the ITO sputtered PET is 0.12 mm.

We used back flash imprint lithography technique in the experiment. The low viscosity liquid resist was first dispersed on the PET/ITO substrate using a syringe. We used a single droplet instead of multiple droplets in order to avoid the formation of bubbles in the resist layer. Then a silicon mold was pressed into the photo-polymerization resist to fill cavities of the mold. An UV light was applied from the transparent substrate side to polymerize the liquid resist. The mold was then separated from the cured resist. The imprinted patterns were inspected by the Phillips XL-40FEG high resolution field emission scanning electron microscopy (FE-SEM).

### 2.4. Characterization of the photo-polymerized resists

The viscosity of the liquid resist was measured by a Brookfield Viscometer DV-II+Pro. The IR spectra were recorded on a Jasco 460 FTIR spectrometer. The glass-transition temperature was measured by TA Instruments Differential Scanning Calorimetry (DSC) 2920 at a heating rate of 5 °C/min. The stability was analyzed with a TA Instruments Thermogravimetric analyzer (TGA) 2050 at a heating rate of 10 °C/min from 50 to 800 °C under nitrogen. The decomposition temperature ( $T_d$ ) was determined at the temperature of 5% weight loss. The molecular weight and molecular weight distribution of the photo-polymerized resist were determined on a Waters Breeze GPC System in THF using polystyrene as the standard for calibration. The adhesion of the resist to the PET/ITO substrate was evaluated by a Scotch tape peeling test according to ASTM-3359B.

## 3. Results and discussion

In conventional hot embossing lithography, the polymer resists are usually dissolved in an organic solvent. After spin-coating, the resists need to be softbaked to eliminate the solvent. In our case, our photo-polymerization resist systems contain ITX and EDAB photo-initiators, which do not allow softbaking to be used. Our approach was to use liquid monomers MMA and MAA to dissolve the PMMA polymer to prepare the solvent-free liquid resists. The viscosities of the resists could be adjusted by changing the amounts of the liquid monomers added. The lower the viscosity the liquid resist has, the lower the pressure is needed for imprinting. However, in this study, we tried to add as much PMMA as possible to reduce the shrinkage caused by the photo-polymerization of the acrylic monomers. Although the viscosities of the resists were increased, we still kept the resists in a liquid state with viscosities suitable for nanoimprint at room temperature. Fig. 2 shows the function of the resist viscosity versus the weight ratio of PMMA in the resist (the weight ratio did not include photo-initiators). The viscosities of resist A (weight ratio = 0), resist B (weight ratio = 0.28), resist C (weight ratio = 0.39) and resist D (weight ratio = 0.5) were 3 cP, 28 cP, 51 cP and 6300 cP, respectively, which were measured by a Brookfield viscometer at 25 °C. The viscosity remained low when the weight ratio was below 0.39, but increased dramatically at 0.5. The abrupt increase of viscosity at high PMMA loading is due to the onset of chain entanglement in the resist. The low resist viscosity is desirable in nanoimprinting, because it renders low imprint pressure with thin residual layer thickness due to the high flow ability [14].

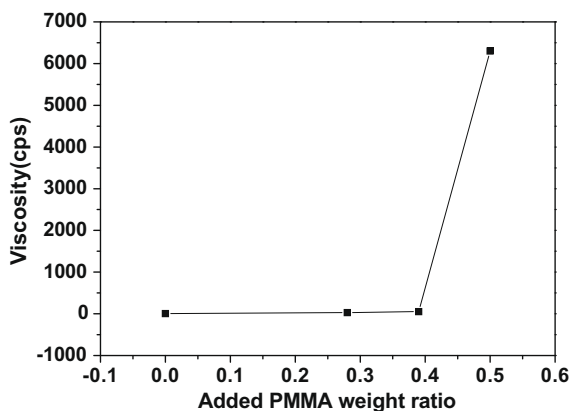


Fig. 2. Viscosity as a function of the pre-added PMMA weight ratio in the resists.

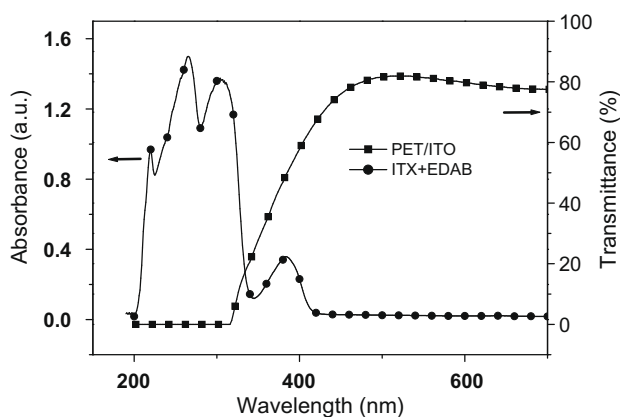


Fig. 3. UV-vis absorption spectrum of ITX plus EDAB in methanol ( $c = 2.03 \times 10^{-5}$  M) and UV-vis transmittance spectrum of ITO/PET substrate with 0.12 mm in thickness.

After imprinting, the resists were subjected to UV exposure. The liquid resists were solidified due to the photo-polymerization of MMA and MAA monomers to form poly(MMA-co-MAA). The final resists are a polyblend of the pre-added PMMA and poly(MMA-co-MAA). In given experimental conditions, a good choice of the photo-initiating systems could help reach a good performance in photo-polymerization. The ITX/EDAB (used at a wt% ratio of 1.4/4 relative to the resist), a classical UV initiation system, has proved to be very efficient in industrial irradiation conditions regardless of the light intensity and the type of lamp. The electron transfer from the EDAB to ITX creates free radicals. The two photo-initiators were selected to satisfy the rapid polymerization requirement and exploit UV energy from a wide range of UV-vis wavelengths. The UV-vis absorption spectrum of the initiating system ITX/EDAB in methanol (concentration =  $2.03 \times 10^{-5}$  M) and the UV-vis transmittance spectrum of ITO/PET substrate with 0.12 mm in thickness are shown in Fig. 3. The ITX/EDAB has UV absorption up to 420 nm and the ITO/PET substrate has enough transparency above 360 nm so that the photo-polymerization resist can be exposed from the substrate side by a broad band UV exposure as reported in our previous paper [13].

The formation of the poly(MMA-co-MAA) copolymers after photo-polymerization was confirmed by the IR spectra, as shown in Fig. 4. The double bond ( $-\text{CH}_2$  twist) absorption at  $810 \text{ cm}^{-1}$  for acrylate monomers disappeared after photo-polymerization. The poly(MMA-co-MAA) exhibited an absorption band at  $3400\text{--}3100 \text{ cm}^{-1}$  due to the OH group on the MAA moiety, and an

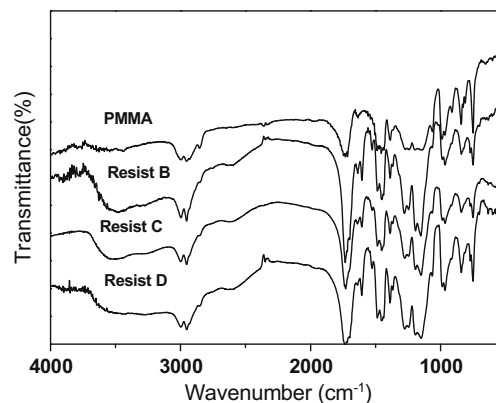


Fig. 4. IR spectra of the pre-added PMMA and the photo-polymerized resists.

Table 2

Molecular weights and polydispersities of the pre-added PMMA and the photo-polymerized resists.

	$M_n$ (g/mole)	$M_w$ (g/mole)	Polydispersity
PMMA (added)	5700	13,000	2.3
Resist-A	11,700	24,000	2.0
Resist-B	4600	14,000	3.0
Resist-C	4600	12,000	2.6
Resist-D	6200	13,500	2.2

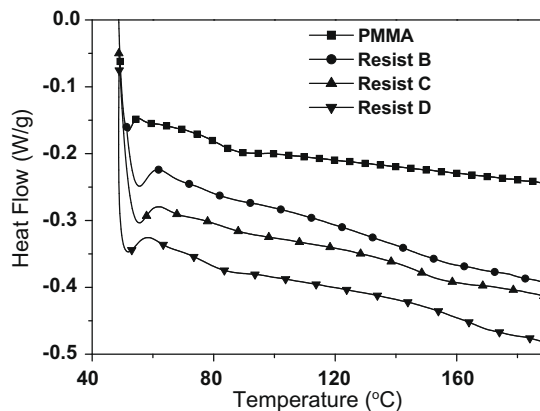


Fig. 5. DSC thermograms of the pre-added PMMA and the photo-polymerized resists.

absorption band at  $1605 \text{ cm}^{-1}$  due to the aromatic rings on the ITX/EDAB initiators.

The photo-polymerized resists were subjected to GPC analysis. The GPC data are shown in Table 2. The number average molecular weights ( $M_n$ ) were around 4600–11,700 g/mole, and the weight average molecular weights ( $M_w$ ) were around 12,000–24,000 g/mole. Their polydispersities were around 2.0–3.0. The molecular weight and polydispersity of the pre-added PMMA was similar to the photo-polymerized resists.

Fig. 5 shows the DSC thermograms of the pre-added PMMA and the photo-polymerized resists at a heating rate of  $5 \text{ }^\circ\text{C}/\text{min}$  from 50 to  $200 \text{ }^\circ\text{C}$  under nitrogen flow. The pre-added PMMA exhibits a glass-transition temperature ( $T_g$ ) at  $82 \text{ }^\circ\text{C}$ . On the other hand, two  $T_g$ 's were detected on the photo-polymerized resists. One is from the pre-added PMMA at around  $82 \text{ }^\circ\text{C}$  to the other is from the poly(MMA-co-MAA) copolymers. The  $T_g$ 's of poly(MMA-co-MAA) copolymer in resist B, resist C and resist D are  $143 \text{ }^\circ\text{C}$ ,  $149 \text{ }^\circ\text{C}$  and

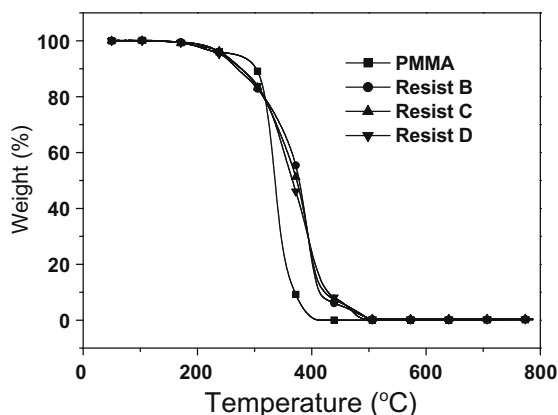


Fig. 6. TGA thermograms of the pre-added PMMA and the photo-polymerized resists.

168 °C, respectively. The  $T_g$ 's of the poly(MMA-co-MAA) copolymers increase with the increasing of MAA to MMA weight ratio. The higher the MAA to MMA weight ratio, the higher the increase in the amount of OH groups can be found on the backbone of poly(-MMA-co-MAA), which produce the intra- and intermolecular hydrogen bonds to increase  $T_g$ .

In the TGA analysis, a sample of 5–10 mg was put in a platinum pan and preheated at 100 °C in the TGA instrument for 5 min to remove any water absorbed from the atmosphere during sample loading. The experiment was carried out in a nitrogen atmosphere. Fig. 6 shows TGA thermograms of the pre-added PMMA and the photo-polymerized resists. The 5% weight loss temperature of these resists occurs at 260 °C, which is similar to that of the pre-added PMMA. From the TGA results, the thermal stability of these resists is good before 260 °C. The good thermal stability of the resists is required during the dry etching pattern transfer process. The imprinted etch barriers were etched using plasma collision in a chamber (OMNI reactive ion etch equipment from Duratek Inc.). Etching was carried out using a power of 100 W. The inlet gas was a mixture of oxygen (40 sccm) and argon (4 sccm) at a pressure of 58 mTorr, and the etching rate was calculated from the depth-profile changes at a constant time interval. The etching rate of the resists is around 110 nm/min, which is similar to the commercial PMMA.

In general, the shrinkage of acrylic monomers after photo-polymerization is about 14–15%, which is due to the double bond conversion [15,16]. Due to the addition of PMMA as the binder, the liquid resists have a low shrinkage of 3%, which was calculated from the original mold to the transfer patterns, as shown in

Fig. 7a and b. Lower shrinkage allows faithful pattern replication during the nanoimprinting process.

In this research, we chose resist C as the major imprinting resist due to the low viscosity and high amount of pre-added PMMA, which could effectively decrease the shrinkage after photo-polymerization. BFIL experiments were performed under air. The resist was dispersed on the ITO/PET substrate, and then covered by the silicon mold immediately to prevent oxygen diffusion. The filling of the mold cavities proceeded very fast due to the low viscosity of the resist C. The resist was UV-exposed immediately after the imprint pressure was reached. The UV exposure only took 50 s, which was equivalent to a UV dose of 1150 mJ/cm<sup>2</sup>. Using a higher intensity UV lamp could further reduce this exposure time. A short cycle time of ~1 min could be achieved, making the resist promising for industrial applications. Fig. 8a shows a scanning electron microscopy image of 150/150/250 nm (line/space/height) imprinted patterns from resist C. The patterns show well-defined edges and are compliant with the mold definition. From the insert highlighted picture on Fig. 8a, the patterns show very thin residual layer thickness. Without particular precaution, no voids or bubbles are observed on the imprinted samples. Fig. 8b is the overall area of the nanoscale patterns. Fig. 9a shows the micro-scale patterns transferred onto a 4-inch flexible ITO/PET substrate through the imprinting lithography. Fig. 9b shows no visual damage on the surface after distortion and bending of the substrate.

Due to the resist containing the MAA moiety, the polar carboxylic acid group in MAA enhances the adhesion of the resist to the PET/ITO substrate. The tape peeling test shows that the resist has the highest adhesion rating of 5B according to ASTM-3359B. We have also completed the adhesion test of a similar resist without adding MAA. That resist showed a very poor adhesion to the PET/ITO substrate. Its adhesion rating was 0B. Meanwhile, due to the incorporation of the MAA moiety into the resists, the resists can be removed by an aqueous NaOH solution at the final stripping step instead of using an organic solvent or reactive ion etching (RIE).

#### 4. Summary

In summary, a novel liquid photo-polymerization resist for nanoimprint lithography has been prepared from the mixture of PMMA, acrylic monomers, ITX and EDAB. The resist is solvent-free and is liquid at room temperature. It has low viscosity during the back flash imprint lithography process, and allows for the simultaneous replication of micrometer- and nanometer-scaled patterns. The shrinkage of the photo-polymerized resist is low due to the addition of a large amount of PMMA as a binder. The material could be a good resist for UV nanoimprint lithography.

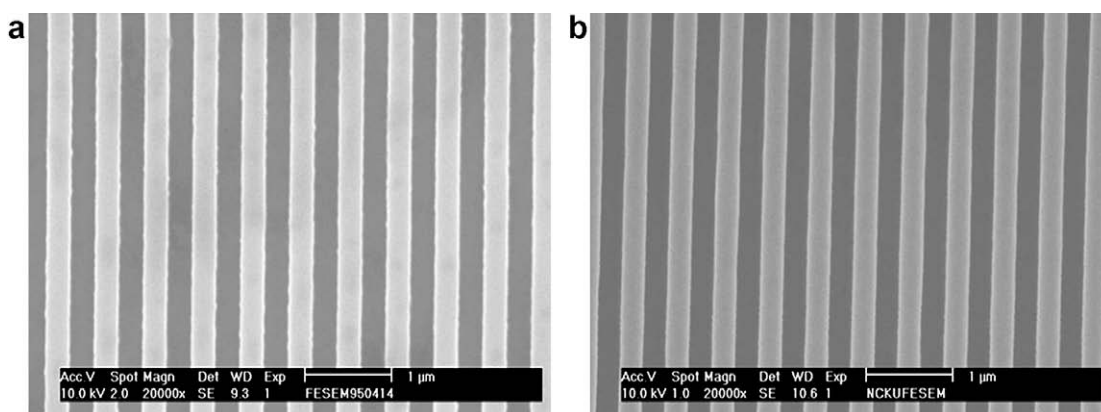


Fig. 7. The mold fabricated by an e-beam writer and ICP on silicon wafer (a) and the imprinted patterns on an ITO/PET substrate (b).

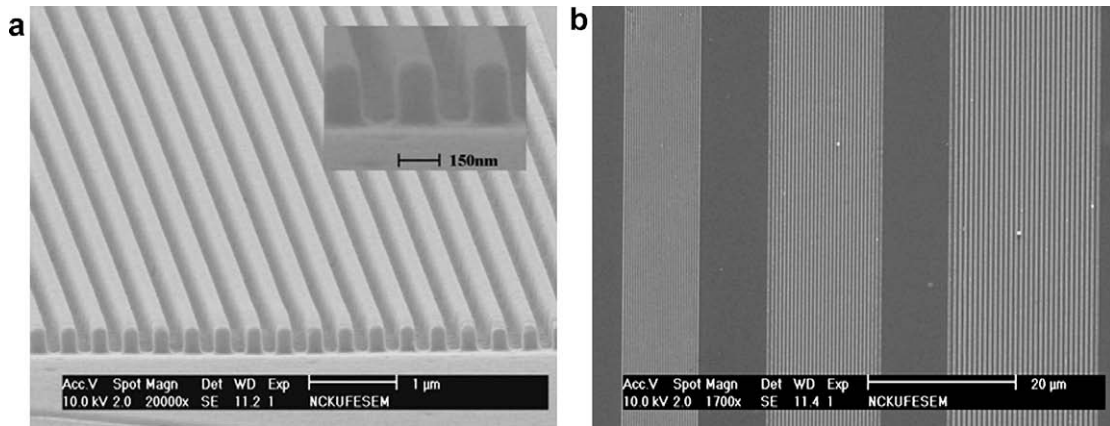


Fig. 8. FE-SEM image of 150/150/250 nm (line/space/height) imprinted patterns (a) and the overall area of the nanoscale patterns (b).

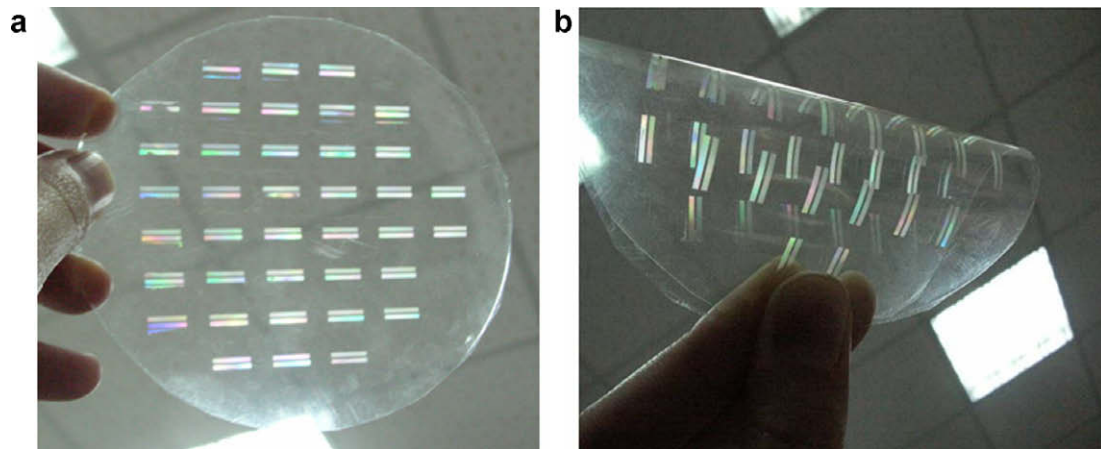


Fig. 9. The patterns transferred on a flexible ITO/PET substrate through the imprinting lithography (a). No visual damage on the surface after distortion and bending of the substrate (b).

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