

# Photoreversible Resists for UV Nanoimprint Lithography (UV-NIL)

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**ABSTRACT** We designed a novel photoreversible resist for UV-NIL that comprises a photoreversible cross-linker (2-[(4-methyl-2-oxo-2-h-1-benzopyran-7-yl)oxy] ethyl ester, AHEMC). Under exposure of 365 nm UV light, this photoreversible resist can form a cross-linked network via radical polymerization of acrylate groups and photodimerization of coumarin moieties. The formed polymer networks containing coumarin dimer moieties could be degraded via illumination of point light source (254 nm). The reversibility of cross-linked system was helpful to refresh mold easily and release the adhered curing resist at room temperature.

**KEYWORDS:** photoreversible • UV-curable resist • UV nanoimprint lithography (UV-NIL)

## INTRODUCTION

Over the past decade, ultraviolet nanoimprint lithography (UV-NIL) has attracted much attention as a next-generation patterning technique that allows the fabrication of nanostructures with high resolution and complements an alternative to traditional photolithography. This process is performed at room temperature and low pressure using low-viscosity, photocurable resists and a transparent, rigid template (1–3). UV-NIL does not require temperature cycling, leading to higher throughput than thermal NIL. Further more, the transparency of the template offers the possibility for easy optical and high-precision alignment. Especially, the low viscosity of photocurable resist also beneficially influences the imprint force and compression time.

One of major challenges in UV-NIL is the repeatability of the imprinted results. As the expensive mold is susceptible to contamination from debris or residual resist left in its recesses, the important issue for UV-NIL is to avoid sticking of the resist to the surface of the mold after detachment. Recently, numerous UV-NIL techniques focused on the development of the new soft mold (4, 5), fluorinated agent modified SiO<sub>2</sub> mold (6, 7) and specifically additive fluorinated agent in resist (8, 9), aiming at improving the efficiency of the mold to reduce the cost in mass production. However, there are few publications dealing with UV-curable resist for UV-NIL. To fully explore the potential of UV-curable resist and increase its versatility, it is desirable to develop new resist materials that are reversible. Ogino's work demonstrates the feasibility of the tertiary ester structure as a thermally degradable material (10). Grant Willson and co-workers develop an acid-catalytic thermal degradable cross-linker for S-FIL NIL (11).

In the traditional photoresist for UV-NIL, the cross-linker is a very important component, and the high cross-linked degree means high mechanical and chemical resistance and good tailored property (12–14). However, the formed dense structure leads to difficulty in stripping polymers in UV-NIL (15, 16). On the contrast, the linear polymer exhibits better soluble in solvent (17, 18). By designing a UV-NIL resist in which the structure of the polymer easily converts reversibly between linear and network, the photoreversible coumarin derivative as degradable cross-linker was introduced in our system. The intermolecular reversible photodimerization and photocleavage of coumarin derivatives have been well-employed in the sol–gel transformation of polymers and other intelligent materials (19–21). As shown in Scheme 1, the photoreversible linkage can be cleaved by irradiation of UV light (254 nm). Photocleavage of the coumarin dimer makes the network transfer into linear structure, resulting in the improved solubility of cured photoresist. In this contribution we reported a novel, low-viscous, photoresponsive degradable resist system for UV-NIL. The reversibility of coumarin moiety helps to refresh mold easily to release the adhered curing resist at room temperature.

## EXPERIMENTAL SECTION

**Materials.** 7-Hydroxyl, 4-methylcoumarin, 2-bromoethanol, acryloyl chloride (AC), 3-methacryloyloxy propyltrimethoxysilane (MAPTES), and tridecafluoro-1,1,2,2-tetrahydrooctyl trichlorosilane (TDFOCS) were purchased from Aldrich. Monomer phenoxy ethyleneglycol acrylate (AMP-10G) was provided by Shin-Nakamura Chemical Co., Ltd. Photoinitiator I-907 was obtained from Tronly. (Changzhou, China). Other chemicals were obtained from China National Pharmaceutical Group Co. (Shanghai, China). All the reagents were used as received except as noted.

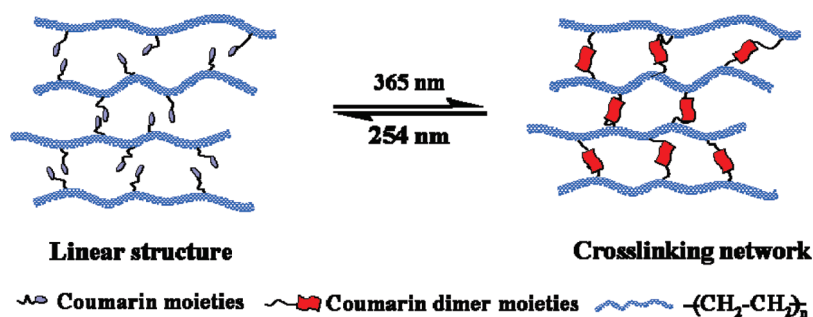
**Synthesis of AHEMC.** To a solution of 7-hydroxyl 4-methylcoumarin (10.0 g, 56.7 mmol) in acetone (450 mL), 2-bromoethanol (100 mmol) and potassium carbonate (120 mmol) were added. The mixture was refluxed for 3 h, and was then filtrated. The solvent was removed by rotary-evaporation, and the residue was recrystallized from ethanol to get 7-2(hydroxyethoxy)-4-methyl-coumarin (HEMC).

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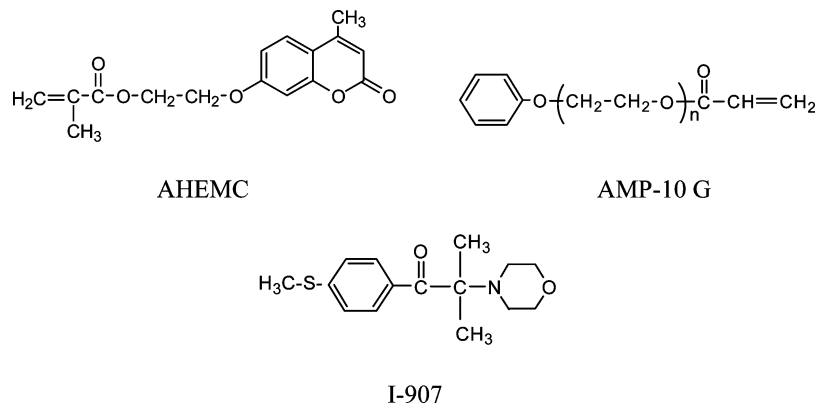
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### Scheme 1. Concept of Photoreversible UV-NIL Material with Coumarin Derivative Containing Acrylate As Degradable Cross-Linker



### Scheme 2. Chemical Structure of Each Component of Our Novel UV-NIL Photoresist



To a solution of HEMC (2 g) in  $\text{CHCl}_3$  (40 mL) was added TEA (triethylamine) as catalyst. The mixture was stirred at  $0^\circ\text{C}$ , and AC was added by dropwise. The mixture was stirred at  $0^\circ\text{C}$  for 2 h and then for 6 h at room temperature. The chloroform layer was washed with water, and was then dried by aqueous magnesium sulfate. Chloroform was removed by rotary-evaporation to get AHEMC (18).

**Characterization.**  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury Plus-400 nuclear magnetic resonance spectrometer (400 MHz) using  $\text{DMSO-d}_6$  as deuterated solvents. UV absorption spectra were recorded on an SHIMADZU UV-2550 UV-vis spectrophotometer. Atomic force microscope (AFM) images were taken with a Nanoscope III AFM Multimode camera (Digital Instruments, USA) under ambient conditions. The AFM was operated in the tapping mode using silicon cantilevers with a force constant of 40 N/m. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope operating at 20 kV.

**Mold and Substrate Modified.** The molds were modified with the fluorinating agent TDFOCs by vapor deposition. The silicon substrate was cleaned in a 1:3 mixing solution (30%  $\text{H}_2\text{O}_2$ : 98%  $\text{H}_2\text{SO}_4$ ) at  $150^\circ\text{C}$  for 3 h. After washing and drying, the silicon substrate was soaked inside 0.2 wt % MAPTES in toluene for 4 h. After the substrate was removed from the solution, it was cleaned thoroughly with fresh toluene in an ultrasonic bath and dried in nitrogen gas.

**Thin-Film Resist Preparation and UV-NIL Process.** The components of photoreversible resist are shown in Scheme 2 and Table 1. Filtration through a  $0.2\text{-}\mu\text{m}$  filter was performed before spin-coating. The resists employed for NIL were prepared on the Si substrate by spin-coating at 3000 rpm for 20 s. The thickness of the film was nearly 300 nm. The resist layer was covered by quartz mold, and then the sandwich sample was put in vacuum chamber to expel the trapped air bubble. The sample was exposed under UV-light for 15 min after a pressure of 0.2 bar was applied for 30 min. The sample was then removed from the nanoimprinter and the mold was detached

**Table 1. Components of the Photoreversible Resist and Their Functions**

component	proportion (wt %)	function
AMP-10G	79.2	low-vapor-pressure linear monomer, provides higher resistance and low-viscosity
AHEMC	19.8	reversible cross-linker
I-907	1.0	photoinitiator, generate free radicals upon exposure to UV radiation

from the substrate (Figure 1). The photoresist was imprinted by our independently developed IL-NP04 imprinter.

**Photoreversibility of Resist.** The coating film of photoresist covered by flat quartz was irradiated by 365 nm light source, and the light intensity is  $30\text{--}50\text{ mW/cm}^2$ . After curing, the polymer film was irradiated by 254 nm light with intensity of  $0.6\text{--}1\text{ mW/cm}^2$ . The light source for photoreversibility process is the USHIO SP-9 UV point light source.

**Lithographic Transfer Process.** The imprinted resist was etched by the RIE method with  $\text{SF}_6$  gas: gas flow, 20 sccm; RF power, 40 W; work pressure, 60 mTorr. The etching time was 120 s. The process of etching was carried out on the Nextral 100 reactive ion etcher of Alcatel.

## RESULTS AND DISCUSSION

**Preparation of Reversible Photoresist.** Despite their potential photoreversible property, many cross-linked system designs might cause compatible and soluble issues in NIL formulation, and the need for low viscosity limits many of the candidates in UV-NIL process. The photoreversible AHEMC exhibits good compatibility with our formulation. Table 1 lists the optimal component of resist with the functions. As one of main ingredients, AMP-10G monomer

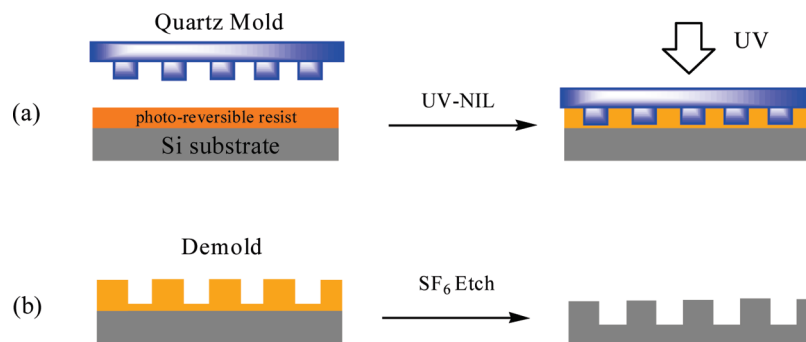
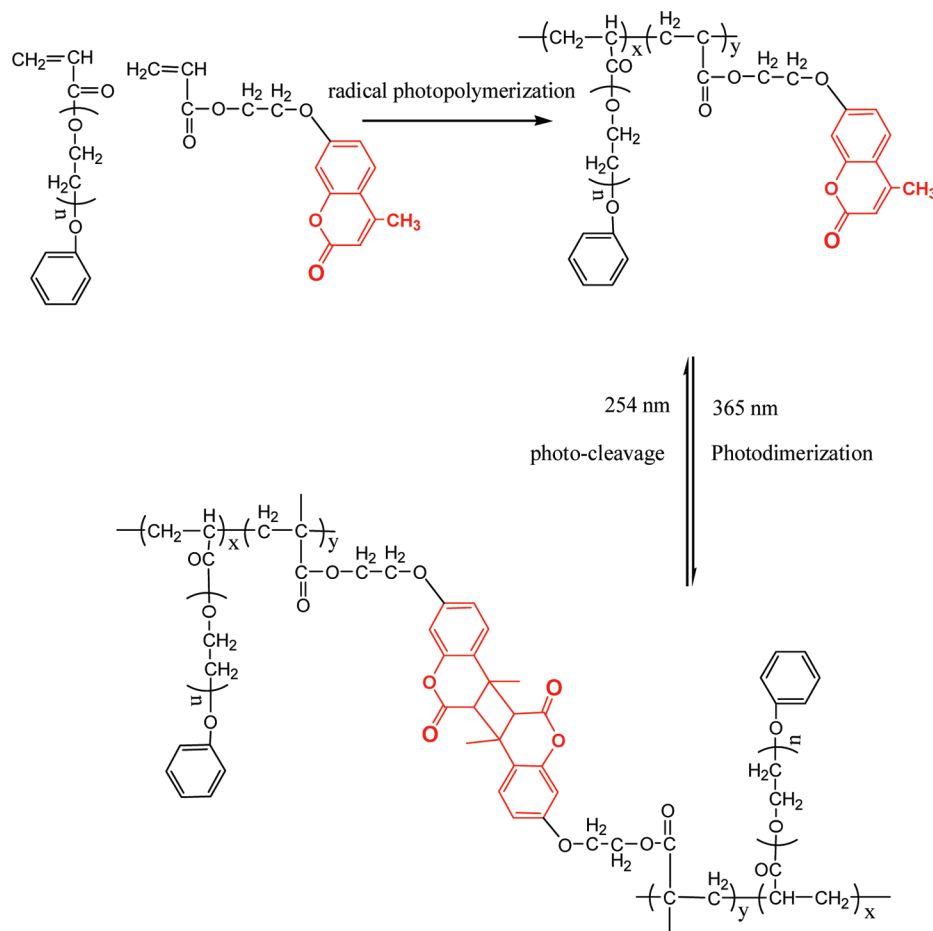


FIGURE 1. Schematic illustration of (a) UV-NIL of photoreversible resist, (b) pattern transfer to Si substrate.

### Scheme 3. Process of Photodimerization and Photocleavage of the Dimer-Coumarin-Bridged Polymer



is traditional acrylate monomer to reduce viscosity (22, 23). The viscosity of our photoreversible resist was less than 15 cPs, almost the same to that of the AMP-10G monomer. The whole photo-cross-linked mechanism is illustrated in Scheme 3 and involved two kinds of cross-linking reactions: radical photopolymerization of acrylate groups and photodimerization of coumarin moieties. Photopolymerization of acrylate groups generated linear structure of polymer chain rapidly in a few minutes under irradiation of UV light (18). The photodimerization of coumarin moieties led to the formation of polymer network, and the reaction rate is relatively slower. The detailed parameters will be discussed in the following text. Formulation study was conducted to

determine the optimal concentration of the AHEMC with good stripping and etching selectivity.

**Photoreversibility of Resist.** The UV absorption spectra of monomer AMP-10G, cross-linker AHEMC, and initiator I-907 are shown in Figure 2. The absorption maximum at 325 nm in spectrum of AHEMC is the characteristic absorption of coumarin moieties. The photoreversible process was monitored by UV spectra (Figure 3). With the increasing time of 365 nm UV-light exposure, the absorption peak of coumarin moieties around 325 nm decreased obviously (Figure 3a), which should be ascribed to photodimerization of coumarin moieties. After exposed by 254 nm UV-light, the absorption peak around 325 nm increased gradually

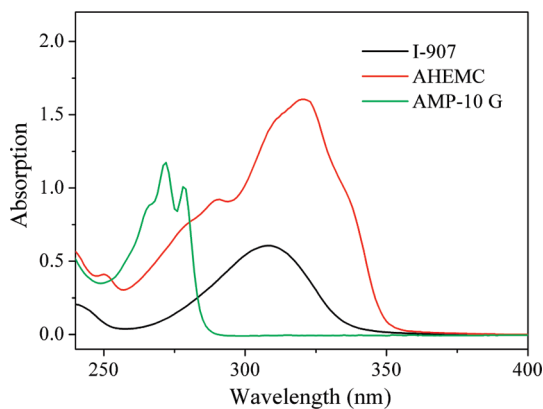


FIGURE 2. UV-vis absorption spectra of AMP-10G, AHEMC, I-907 in chloroform with a concentration of  $1 \times 10^{-5}$  mol/L.

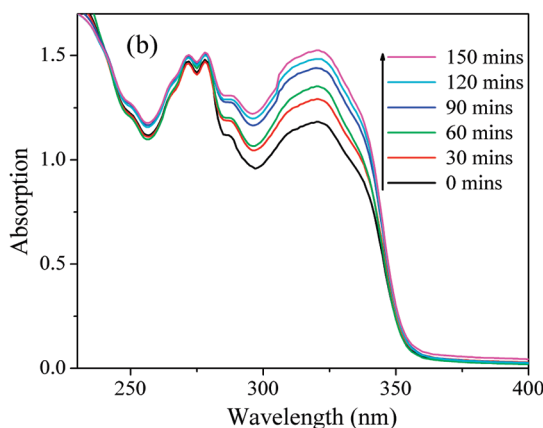
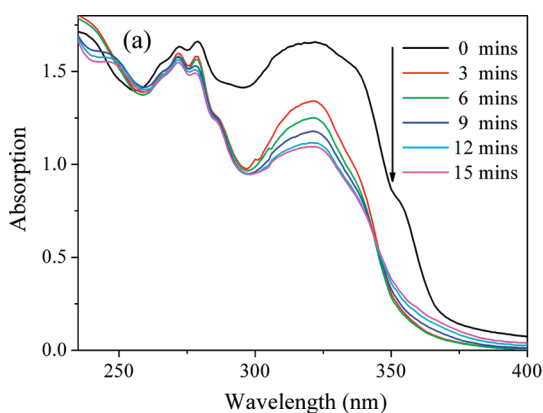


FIGURE 3. UV spectra of (a) AHEMC-AMP-10G resist during irradiation of UV light (365 nm), (b) cured AHEMC-AMP-10G resist after photodimerization film during irradiation of UV light (254 nm).

(Figure 3b), indicating the photocleavage of coumarin dimer. According to UV-vis spectra shown in Figure 3, the designed UV-NIL resist possessed photoreversibility to some extent. Because of low light intensity at 254 nm, the time of reversible process was relatively long.

Coumarin dimer moieties were the cross-linking point of network in the designed UV-NIL resist. To demonstrate the overall degradation profile for coumarin dimer, we monitored the changes in solubility of cured films, which were immersed in chloroform before and after irradiation of UV light (254 nm), by UV detector. As Figure 4a shows, the absorption intensity of the typical peak owing to coumarin

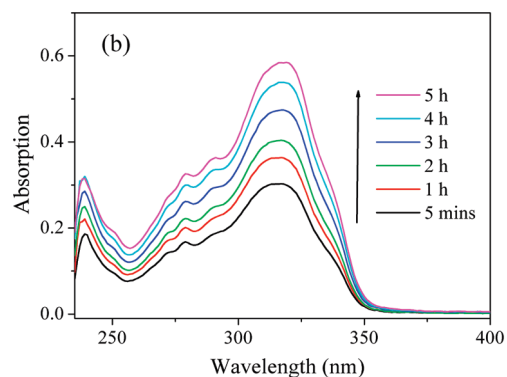
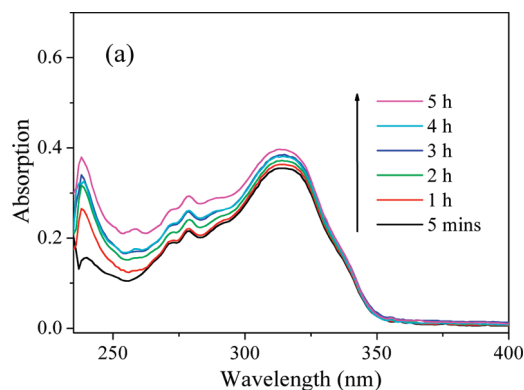


FIGURE 4. UV spectra of AMP-10G-AHEMC polymer (a) before and (b) after irradiation of UV light (254 nm) in  $\text{CHCl}_3$ .

Table 2. Etch Rate and Selectivity of Different Photoresists by  $\text{SF}_6$  Gas

	photoresist polymer			Si substrate
	AMP-AHEMC	watershed	NIL 6000 resist	
$V$ (nm/s)	$7.6 \pm 0.1$	$4.4 \pm 0.1$	$8.1 \pm 0.1$	$14.2 \pm 0.1$
etching selectivity ( $V_{\text{Si}}/V_{\text{resist}}$ )	1.9	3.2	1.7	

increases slightly, indicating that the cured polymer film of resist is almost insoluble in chloroform. This phenomenon is similar to other high concentration cross-linked system (8). The initial superior absorption of 5 min is ascribed to uncured resist nearly nanolayer on the surface, caused by the partly dissolved oxygen upon the surface of the resist, which could prevent polymerization of conventional acrylate monomer (24–26). After UV light (254 nm) exposure for 3 h, as shown in Figure 4b, the gradual increasing absorption at 320 nm shows that the concentration of coumarin moieties increases gradually in solution, suggesting a degradation process of the cured polymer film. After several hours, the cured polymer film completely dissolved in chloroform solution. The photocleavage reaction of coumarin dimer is assumed to proceed simultaneously throughout the bulk film rather than a surface erosion process.

**UV-NIL Process and Lithographic Transfer.** As shown in Figure 5, our photoreversible resist could be easily imprinted over large areas with pattern features in a variety of shapes and length scales. The emergence of nanoscale uniform pits on the surface (Figure 6) is probably due to the absorbed trace water of monomer AMP-10G. According to the sectional profile of AFM in Figure 6, the resulting pattern



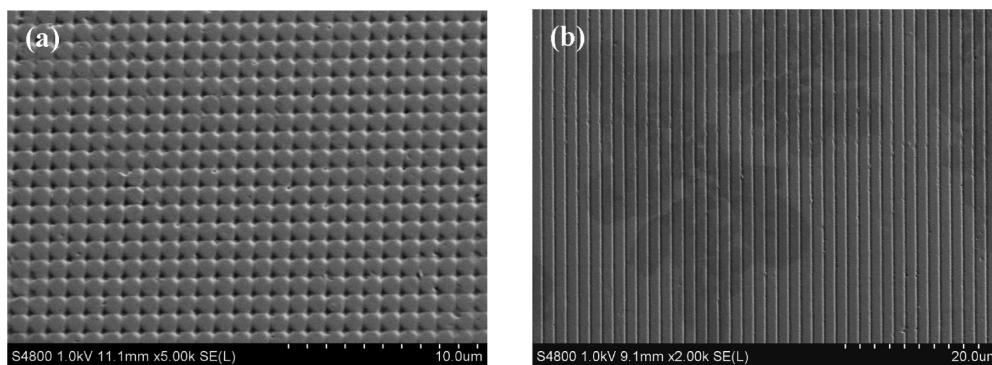


FIGURE 5. SEM images of NIL AMP-10G-AHEMC resist film: (a) 700 nm lattice ( $1.4 \mu\text{m}$ ), (b) 850 nm grating ( $1.7 \mu\text{m}$ ).

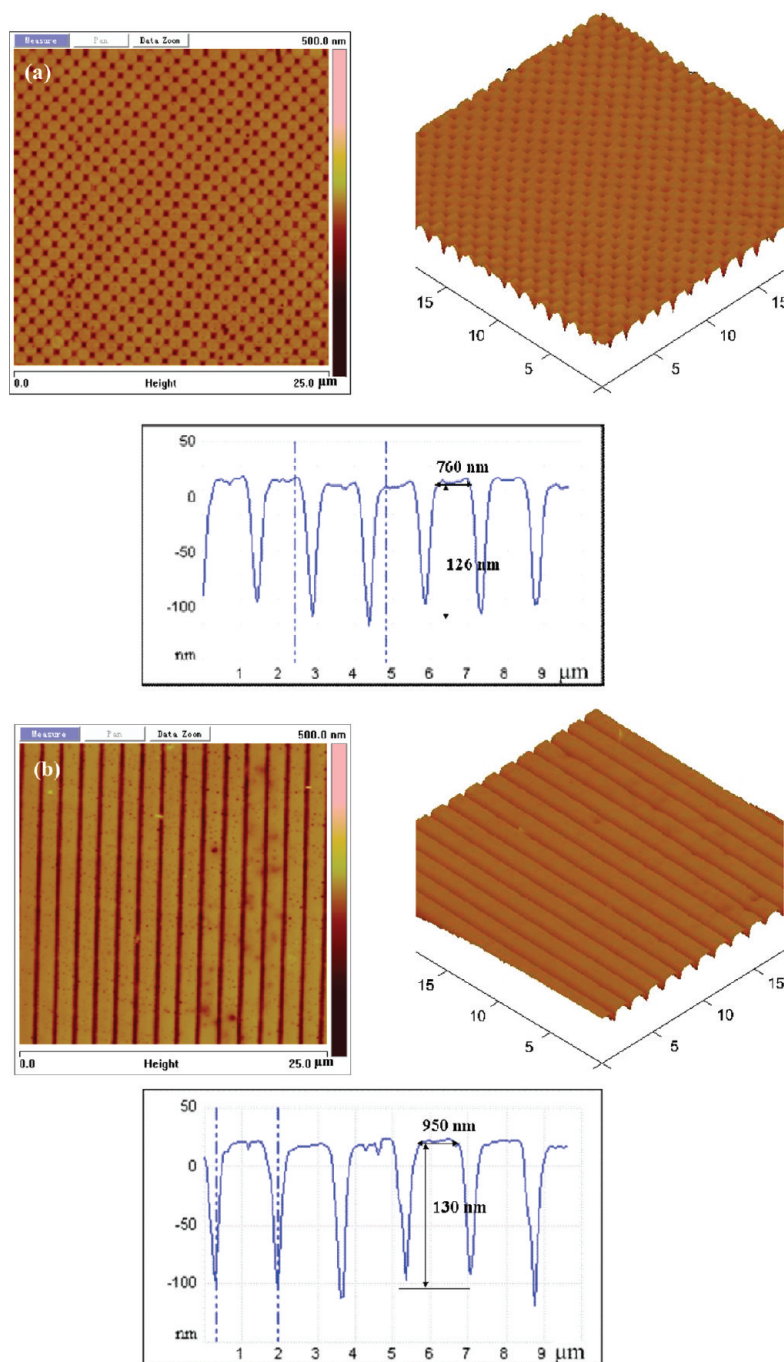


FIGURE 6. Perspective AFM and corresponding sectional profile images of NIL AMP-10G-AHEMC resist film: (a) 700 nm lattice ( $1.4 \mu\text{m}$ ), (b) 850 nm grating ( $1.7 \mu\text{m}$ ).

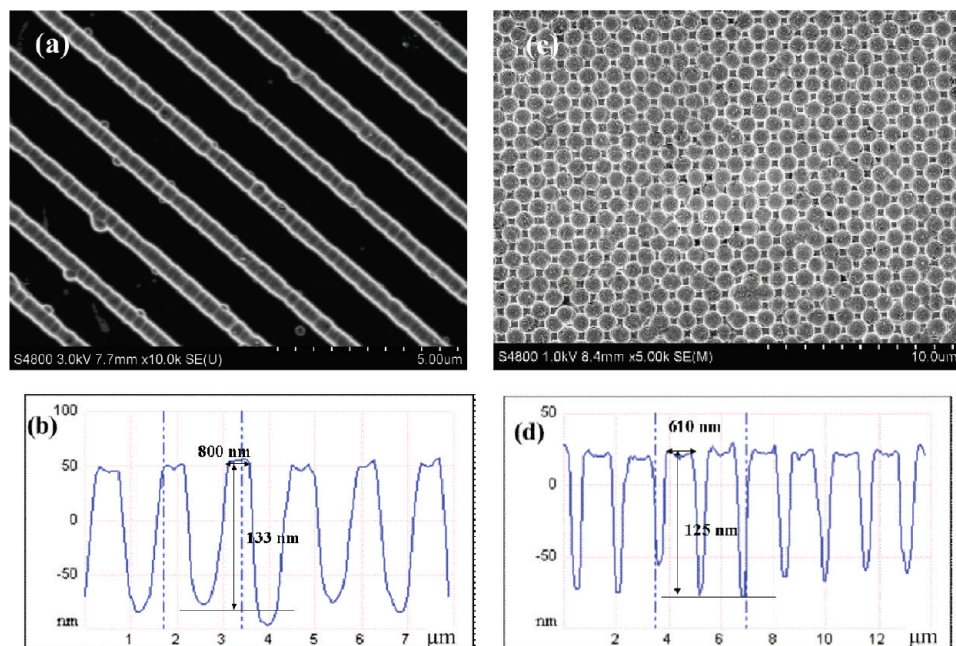


FIGURE 7. Perspective SEM and sectional profile images after pattern transferring into Si with (a, b) grating structure, (c, d) lattice structure.

height (about  $130 \pm 5$  nm) is smaller than that of the master pattern (200 nm), which might be due to the applied pressure of 0.2 bar not being high enough to completely fill the resist in the channel. In addition, the period of structure without obvious changes suggests no shrinkage and swell of the cured polymer film, indicating the resist could be potential to UV-NIL. Because the component of the reversible resist does not contain any long polymer chains and solid particles, the resolution generally is limited by the mold design but not by the resist polymer system.

To confirm the pattern transfer ability of the designed photoreversible resist for UV-NIL, we also investigated the etching rate and selectivity of other commercial NIL photoresists. As shown in Table 2, the etch selectivity between silicon and reversible resist was found to be 1.9, which is between two commercial NIL photoresists. The higher selectivity of the photoreversible resist indicates a suitable nanofabricated layer during transfer steps. Figure 7 shows the good results of pattern on silicon, and there is no any latent residual layer. The EDS (energy-dispersive X-ray analysis) of the same sample showed a clear silicon substrate with very low carbon content, indicating that the nanopattern has successfully transferred on Si surface. As for the original NIL patterns, the resulting structure parameters of the Si pattern decrease slightly. The width of the square-lattice structure (ca. 610 nm) is smaller than that of the NIL pattern (ca. 760 nm); the width of the grating structure (ca. 950 nm) also decreases to 800 nm. This might be caused by incomplete anisotropic etching in the RIE process, which was also observed by other groups (27–30).

## CONCLUSIONS

A novel photoreversible resist based on coumarin acrylate derivative was successfully developed for UV nanoimprint lithography. Through photodimerization of coumarin moi-

eties under 365 nm UV light, the photoreversible resist can be photocured to generate the cross-linked network, which can be further photocleaved by 254 nm UV light. This photoreversible resist offers a versatile and cost-effective way to fabricate nanopattern in large scale with good strip-able ability and etching selectivity.

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