Nanoimprint Graphoepitaxy for Molecularly Oriented Nanofabrication

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Nanoimprint graphoepitaxy is a simple way of fabricating molecularly oriented nano/microstructures. This paper describes our studies of the mechanism of the nanoimprint-graphoepitaxy-induced molecular orientation of P6CAM, a photo-cross-linkable liquid crystalline polymer. We describe the dependence of the molecular orientation of P6CAM on the nanoimprint process and the unique molecularly oriented patterns formed by nanoimprint graphoepitaxy.

Keywords: Nanoimprint process, Nanoimprint graphoepitaxy, Molecularly oriented nano/microstructure

1. Introduction

Nanoimprint lithography [1–8] is a suitable and straightforward process for nano/microfabrication. The resolution of the transferred pattern depends on the pattern of the mold, and the reverse pattern is fabricated on the replication material. There has been recent progress in nanoimprint lithography for high-volume semiconductor manufacturing [9,10]. There are two types of nanoimprint processes for the fabrication of devices. In one, the nano/microstructures of the replication material are used for the device, for example, for anti-reflection films. In the other, the resist pattern is used as a mask and the substrate is etched in several etching processes. Finally, the nano/microstructured substrates are applied as devices. It is important to choose the correct nanoimprint process to obtain the required device. However, the key common feature of both nanoimprint processes is that the replication material is patterned by the nanoimprint process without the need for any etching processes, although heating, cooling, and ultraviolet (UV) irradiation are required to cure the resins. We believe that there is an advantage to using the nanoimprint process for fabricating nano/microstructured functional materials because it causes less damage compared with conventional lithography processes, such as photolithography and electron beam lithography, which require an etching process to obtain the pattern.

Oriented crystal growth can be induced by using an amorphous substrate with relief features [11-13]. This technique is known as graphoepitaxy and has been applied to many inorganic and organic materials [14-18]. In nanolithography, the graphoepitaxy process has been used to create long-range order in block copolymers (BCPs) [19-21]. Molecular orientation can be also induced by nanoimprinting, and many studies have been reported [22]. The molecularly oriented nano/microstructures are formed through nanoimprinting, although the oriented films are obtained by a graphoepitaxy process. Chou’s group reported that gratings of polymethylmethacrylate with 4-(dicyanomethylene)-2-methyl-6-(julolidin-4-ylvinyl)-4H-pyran (DCM2) [23], a red fluorescent dye molecule, with periods of 200 and 300 nm were fabricated by thermal nanoimprinting [24]. From the polarized photoluminescence and absorption results, they concluded that the long axes of the DCM2 molecules were oriented parallel to the direction of the grating line. Direct thermal nanoimprinting of a BCP results in induced ordered-microphase separation of the BCP [25]. A sub-10-nm Si pattern has also been transferred from s polystyrene-block-poly(dimethylsiloxane) pattern aligned by thermal nanoimprinting [26]. Jonas’s group reported that the molecular orientation of
polyvinylidene fluoride (PVDF) depends on the residual layer thickness [27]. An ordered PVDF pattern was formed by nanoimprinting on a thin PVDF film, whereas a random molecular orientation was induced on a thick PVDF film. Kim and coauthors fabricated a flexible heterojunction organic photovoltaic cell and used nanoimprinting to increase the interface area between the donor and acceptor [28]. The resulting nanoimprinted device had an additional improvement in charge transport, and the authors suggested that the conjugated polymer was ordered by nanoimprinting. Cui and coauthors reported that the mobility of an organic thin-film transistor based on an imprinted poly(3-hexylthiophene) [P3HT] grating was higher than that of a control device without chain orientation [29]. In addition, Aryal and coauthors used out-of-plane and in-plane grazing incidence X-ray diffraction measurements to investigate the molecular orientation of a P3HT grating and pillar fabricated by nanoimprinting [30]. The photo-polymerizable liquid crystalline oligomer was reoriented by UV nanoimprinting and the pattern was used as a liquid crystal (LC) alignment layer in a LC cell [31].

We have previously found that a photo-cross-linkable liquid crystalline polymer (PLCP) [32-34] is reoriented by thermal nanoimprinting. P6CAM [35,36] is a PLCP material, and the molecular orientation of P6CAM is usually controlled by linearly polarized UV (LPUV) and heat treatment [37]. In the thermal nanoimprint process, the P6CAM molecules are oriented without LPUV irradiation and molecularly oriented nanostructures are formed. As described above, the nanoimprint process can easily produce molecularly oriented nano/microstructures on various materials. We refer to the nanoimprint process that induces molecular orientation as “nanoimprint graphoepitaxy”, and we expect this technique to have the potential to generate new characteristics from the combination of molecular orientation and nano/microstructure properties. In this paper, we describe nanoimprint graphoepitaxy for the molecularly oriented nanofabrication of P6CAM.

2. Experimental

Figure 1(a) shows the chemical structure of P6CAM, a polymethacrylate derivative with a side chain that contains a hexamethylene spacer group terminated with a 4-oxycinnamic acid moiety, which is side-chain-type LC polymer. P6CAM was diluted with a solvent and the solution was spin-coated on a substrate to form P6CAM films. We then carried out nanoimprint graphoepitaxy on the P6CAM films. The molds were fabricated by electron beam lithography (EBL, Elionix ELS-7500) and reactive ion etching (RIE, Samuco RIE-10NR). We mainly used a thin polydimethylsiloxane layer as the antisticking layer [38]. A Meisyo Kiko NM-0901HB instrument was used as the nanoimprint apparatus. We observed the obtained P6CAM patterns by polarized optical microscopy (POM) under crossed Nicols conditions, which means that the analyzer and the analyzer are crossed at 90°. Bright fields in the POM images generally indicate that the P6CAM molecules are unidirectionally oriented, whereas random molecular orientation of P6CAM leads to dark fields in the POM images. Atomic force microscopy (AFM, Hitachi Hitech Science, E-sweep/NanoNavi station) was also used to confirm the patterns on the P6CAM film and mold.

We examined the molecular orientation of P6CAM in the imprinted pattern by measuring the diffraction efficiency using 633-nm linearly polarized (LP) light over a range of angles of incidence from 0° to 180° [39]. The diffraction efficiency is defined as the ratio of diffracted to incident light intensity. Figure 1(b) shows a schematic diagram of the optical measurement. The polarization of the incident laser light was adjusted by using a λ/2 plate. The first-order diffraction efficiency (±) is at its highest when the molecular orientation of P6CAM and the incidence direction of the LP light are the same. In contrast, if there is
no angular dependence of the first-order diffraction efficiency, the P6CAM molecular orientation is not unidirectional.

3. Results and discussion

Figure 2(a) shows the POM image of the P6CAM line and space (L&S) pattern fabricated by nanoimprint graphoepitaxy. The nanoimprint pressure, temperature, and time were 15 MPa, 150 °C, and 5 min, respectively.

The orange arrows indicate the directions of the polarizer and analyzer. The yellow arrow shows the direction of the L&S pattern. The L&S pattern area became bright-field in the POM image, although the imprinted 2-μm-linewidth (4-μm-pitch) L&S pattern was much larger than a P6CAM molecule. In contrast, the imprinted flat area remained dark-field. These results indicate that the P6CAM molecules in the L&S pattern area were reoriented only by nanoimprint graphoepitaxy. We measured the diffraction efficiency of the P6CAM pattern, as shown in Fig. 2(b). In this case, the LP light direction was parallel to the L&S pattern at incident LP light rotation angles of 0° and 180°. We confirmed from the measurement results that the P6CAM molecules were oriented parallel to the imprinted L&S pattern because the first-order diffraction efficiency (±) was highest at 0° and 180°.

We compared the molecular orientation of P6CAM induced by thermal nanoimprinting (nanoimprint graphoepitaxy) to that induced by the graphoepitaxy process because the two processes are similar; they require a heating process and use a patterned substrate [40]. Figure 3 shows a schematic illustration of these processes.

![Fig. 3. Schematic illustration of thermal nanoimprinting (nanoimprint graphoepitaxy) and graphoepitaxy processes.](image)

A positive-tone mold (patterned substrate) with L&S widths of 2 μm and a pattern depth of 200 nm was used. In the graphoepitaxy process, P6CAM was spin-coated on a patterned quartz substrate and heated at 165 °C for 10 min. We confirmed from diffraction efficiency measurements that the orientation of P6CAM was more strongly induced by thermal nanoimprinting (nanoimprint graphoepitaxy) than by graphoepitaxy. Additionally, dependence of the molecular orientation of P6CAM on the nanoimprint pressure and temperature was not observed between 10 and 30 MPa at 125–165 °C in thermal nanoimprinting (nanoimprint graphoepitaxy).

We also examined the depth profile of the P6CAM molecular orientation induced by nanoimprint graphoepitaxy [41]. We repeated the RIE treatment with O₂ and performed further diffraction efficiency measurements for the P6CAM L&S pattern. Figure 4(a) shows the POM images of the L&S pattern on a 300-nm-thick P6CAM film before and after O₂ RIE for 4 min. The L&S pattern area became dark-field. In contrast, the L&S pattern on a 500-nm-thick P6CAM film after 4-min O₂ RIE treatment remained bright-field, as shown in Fig. 4(b).
These results suggest that the depth of the P6CAM molecular orientation on the 500-nm-thick film was deeper than that on the 300-nm-thick film. Using diffraction efficiency measurements, we then confirmed that the initial P6CAM film thickness affected the depth of the molecular orientation induced by nanoimprint graphoepitaxy.

The nanoimprint process can be carried out on a fabricated material pattern if the material is able to soften. This means that we can perform nanoimprinting on the imprinted P6CAM pattern, and, as a result, the reorientation of P6CAM may be induced twice. In addition, the molecular orientation of the P6CAM pattern fabricated by the first nanoimprinting may be reset by a second nanoimprinting using a flat mold. Thus, we demonstrated double nanoimprint graphoepitaxy using molds with L&S and flat patterns, as shown in Fig. 5 [42].

The L&S pattern was fabricated on the P6CAM film by the first nanoimprinting [Fig. 5 (1)]. After the first nanoimprinting, the P6CAM molecules were oriented parallel to the imprinted line pattern. Then, the second nanoimprinting was performed on the fabricated L&S pattern [Fig. 5 (2)], and this removed the pattern [Fig. 5(3)].
The POM image of the obtained P6CAM pattern is shown in Fig. 6. The top of the POM image shows the L&S pattern area fabricated by the first nanoimprinting. This area remained bright-field because it was not pressed by the second nanoimprinting. In contrast, the flat area formed by the second nanoimprinting (bottom of the POM image) became dark-field, even though the L&S pattern was present in this area before the second nanoimprinting. This result suggests that the P6CAM molecules aligned in the first nanoimprinting became randomly oriented by the second nanoimprinting with a flat mold. We continue to investigate this phenomenon.

We also carried out nanoimprint graphoepitaxy using molds with a unique pattern. Figure 7(a) shows the AFM image of the bidirectional line pattern on the mold [43]. The linewidth was 2 μm. (We digress from this paper: Fig. 3 (b) in Ref. 43 is an AFM image of the pattern on the mold. It is not the P6CAM pattern.) We observed the imprinted P6CAM pattern using POM under open Nicol condition, in which a polarizer is used [Fig. 7(b)], and crossed Nicols conditions [Fig. 7(c)]. A bidirectional line pattern was formed on the P6CAM film with pattern heights of 200 and 100 nm. We then evaluated the molecular orientation of the pattern by measuring the diffraction efficiency.
LP light was parallel to the direction of the 200-nm-height line pattern at incident LP light rotation angles of 0° and 180°, whereas it was parallel to the direction of the 100-nm-height line pattern at a rotation angle of 135°. Figure 8(b) shows the diffraction efficiency of the P6CAM bidirectional line pattern. The diffraction efficiency of the 200-nm-height line was highest at 0° and 180°, and that of the 100-nm-height line was highest at 135° and lowest at 45°. These results indicate that the P6CAM molecules were oriented parallel to each line and that a bidirectional molecularly oriented structure is easily fabricated by nanoimprint graphoepitaxy. Furthermore, these results suggest that the direction of the P6CAM molecular orientation is determined by the direction of the imprinted line.

We fabricated a pattern depicting Himeji castle on a mold using EBL and RIE. The original picture was downloaded from the Himeji Photo Bank on Himeji city’s official website [44]. We made a striped Himeji castle bitmap file from the original picture, and then carried out EBL in raster-scan mode using the bitmap file on the EB resist-coated substrate. After development and RIE, the Himeji castle pattern was formed on the mold. Figure 9(a) shows the scanning electron microscopy (SEM) image of the striped Himeji castle pattern. We used a mold with a bigger Himeji castle pattern than that shown Fig. 9(a) to demonstrate nanoimprint graphoepitaxy on a P6CAM film. Figure 9(b) shows the POM images of the imprinted P6CAM pattern. The yellow arrow indicates the direction of the main stripe lines of the Himeji castle pattern. The brightness of the pattern depended on the direction of the polarizer and analyzer (orange arrows). These results show that unique molecularly oriented nano/microstructures are easily fabricated by nanoimprint graphoepitaxy.

4. Conclusion
Nanoimprint graphoepitaxy is a useful technique for the formation of molecularly oriented nano/microstructures. Furthermore, nanoimprint graphoepitaxy has the potential to generate new characteristics that arise from the combination of the molecular orientation patterns and nano/microstructure properties. We will continue to explore the mechanism of molecular orientation and the interesting characteristics of molecularly oriented nano/microstructures fabricated by nanoimprint graphoepitaxy.

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