Fine Pattern Transfer of Functional Organic Polymers by Nanoimprint

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Nano structures on organic solar material are expected to improve power generation efficiency instead of bulk hetero junctions. In this study, we fabricated high aspect ratio nano structures using poly-3-hexylthiophene (P3HT) by a novel nano-imprint process. Fine structures 70-nm wide and 550-nm high were successful obtained. However, the pattern defects in the de-molding process were increased by basing on the increment of the pattern’s aspect ratio. We also investigated the relation between aspect ratio and defect yield.

**Keywords:** nanoimprint, casting, organic functional material, photovoltage, P3HT

1. Introduction

Functional polymers are a promising material for advanced devices and technologies. For example, a photo polymer is indispensable for manufacturing advanced electronic devices. On the other hand, organic semiconductor materials are expected for mobile photovoltaic devices or flexible electronics.

For example, the nano-fabrication of poly-3-hexylthiophene (P3HT), a common functional material for organic solar cell materials, has been reported by a thermal nano-imprint process [1-7]. Using a nano-imprint process, fabrication of 50nm structures have been reported and demonstrated increment of power generation efficiency in organic photovoltaic cells.

To fabricate advanced devices using functional polymer materials, micro and nano-processing are indispensable to improve performances or to create new functions.

However, using organic solvents and a selective etching process is indispensable for conventional micro and nano-lithography process technologies, which are rarely applied for organic semiconductor materials.

To solve the problem, a thermal nano-imprint process is promising for functional materials because they are directly deformed in micro and nano size without any organic solvents.

However, the higher pressure sometimes causes mold defects or breaking. To avoid those problems, a nano-casting method was investigated to fabricate high aspect ratio nanostructures.

In this paper, we demonstrate nanofabrication for high aspect ratio structures of P3HT by novel nano-imprint.

2. Experiments and Results

The nano-casting process [8,9] is shown in Figure 1. Functional materials are dissolved in a solvent, and the solution is dropped onto the mold and spincoated to planarize the surface. The solution is filled into a fine mold pattern. Then, the mold is baked to evaporate the solvent and to solidify the functional material. Finally, the functional material is glued to the substrate and the mold is released. As a result, the fine pattern is transferred to the solidified functional material on the substrate. The proposed method is very easy and cost effective because a spin coating of the solvent is essential in inert and room temperature ambient. Also, the solvent evaporation is easy without explore to air.

In this case, P3HT is dissolved in a trichloroethylene, whose concentration is 3% wt. This solution was dropped onto a silicon mold and spincoated at 1300-rpms. Then the mold was baked at 120 °C for 30 minutes in a vacuum to evaporate the solvent. The solidified P3HT was released from the mold and transferred to the silicon substrate by using carbon tape.
In the nano-casting method, releasing the solidified functional material from the mold is essential. To avoid sticking between them, the mold surface is coated with a molecular film of fluoropolymer using a silane coupling agent. On the other hand, surface coating with high surface energy materials complicates filling the solution into the cavity of the mold pattern. To avoid this, the mold’s surface energy is optimized to successfully fill and to de-mold. To control the surface energy, an UV ozone treatment was done to damage the fluorine coating layer. The mold surface condition of the fluorine coating on the surface was evaluated by the contact angle of the liquid droplet both in the solvent and in the water. The contact angle for the solvent was measured just after the solution was dropped on the mold surface.

Figure 2 shows the the mold after coating it with the P3HT solution where the contact angles of the water droplet are 110° and 40°. In this examination, there are no patterns on the molds. If the contact angle is high, the mold repels the P3HT solution. It can’t be coated on the mold and doesn’t fill into the mold pattern. If the contact angle is small, even if the solution easily fills the mold pattern, demolding probably fails because the organic material sticks to the mold.

Next we examined the coating and demolding properties for various contact angles on the mold surface. Table 1 shows the results. The contact angle for the water droplets around 40° is good for both the resist filling and the mold releasing.

Table 1. Coating and de-molding properties for various surface conditions

<table>
<thead>
<tr>
<th>Contact angle for Water droplet</th>
<th>Contact angle for Trichloro-Ethylene droplet</th>
<th>Coating</th>
<th>Demolding</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>60</td>
<td>×</td>
<td>-</td>
</tr>
<tr>
<td>80</td>
<td>55</td>
<td>×</td>
<td>-</td>
</tr>
<tr>
<td>40</td>
<td>50</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>&lt;10</td>
<td>45</td>
<td>○</td>
<td>×</td>
</tr>
</tbody>
</table>

Next, we examined the pattern transfers with high aspect ratio structures from 45- to 200-nm line width.

Figure 3 shows the result for 200-nm lines whose pattern height is 800 nm(aspect ratio:4.0). Fine patterns were successfully transferred without defects. Figure 4 shows the results with a line width of 150nm and a height of 800nm (aspect ratio:5.3).
Several patterns were missing while the de-molding.

In accordance with increment in the aspect ratio, the tensile stress in the pattern increased, due to the friction force between the polymer and the mold, which caused the patterns braking when the critical value was exceeded.

To quantify the defect yield, the numbers of missing lines are counted by observing SEM. In this sample, 16 of 66 lines are missing, so the defect yield is 24%.

Figure 5 shows the results of a mold with a 100-nm wide and 700-nm high line (aspect ratio: 7.0). With increasing aspect ratio, defect yield increased drastically. In this case, 112 in 160 lines are missing, so the defect yield raised up to 70%.

We tried to fabricate a fine and high aspect ratio pattern as shown in Fig 6. The pattern with a 70-nm wide and 550-nm high (aspect ratio : 8) is narrowly fabricated.

On the other hand, a fine and low aspect ratio pattern fabrication is approached for a 45-nm wide and 40-nm high (aspect ratio : 0.9) as shown in Fig 7. The fine patterns were easily fabricated without defects, because of the low aspect ratio.
3. Discussion

As demonstrated above, the fine patterns of P3HT were successfully fabricated by a novel nano-imprint method without damages to fine molds, however defects for patterns increased as the increment of the pattern’s aspect ratio. This is due to the breaking down of the pattern by the stretching stress caused by the friction force on the side walls of the pattern. The friction force is in proportion to the aspect ratio of the pattern. On the other hand, the braking down occured when the applied stress exceeds the breaking stress.

If the breaking down phenomena occurs in accordance with a probability theory, the probability density function is expressed by Gaussian function as follows:

\[ p(x) = \frac{1}{\sqrt{2\pi}\sigma} \exp\left(-\frac{(x-\mu)^2}{2\sigma^2}\right) \]  

where \( \mu \) is the expectation value and \( \sigma \) is the variance of the matter.

In this study, \( x \) relates to the tensil stress, which is equivalent to aspect ratio of pattern, and \( \mu \) is braking down stress (equivalent to critical aspect ratio for breaking down) and \( \sigma \) is process conditions, which depends on material, de-molding process, etc.

The defect yield is related to a cumulative distribution function using error function as:

\[ \text{yield} = \frac{1}{2} \left(1 + \text{erf} \left(\frac{x-\mu}{\sqrt{2\pi}\sigma}\right)\right) \]  

\[ \text{erf} \left( x \right) = \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-t^2} dt \]

Figure 8 shows the relations between defect yield and aspect ratio of the pattern. Dots show experimental results and dashed line is fitted result of the cumulative distribution function as describe in equation 2. The extracted parameters are \( \mu = 6.3 \) and \( \sigma = 0.88 \). The defect yield is fairy expressed by the aspect ratio using probability function. We believe this inspection is useful for device and process design. For example, if you allow 5% in defect yield, fine pattern with aspect ratio of 3.5 is promising, which is enough for production of nano optics devices or photovoltaic solar devices having robust systems.
4. Conclusions

Fine pattern transfer with high aspect ratio structure was demonstrated for P3HT using nano-casting method. The 45nm line pattern having aspect ratio of 0.9 was successfully transferred without defects. However the pattern of 70nm line width having aspect ratio of 8.5 was narrowly transferred. Based on a probability theory, the defect yield is well expressed by the aspect ratio of the pattern, which related to the friction force at the side wall of the mold.

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References