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기능성 나노 입자를 100 nm 이하의 패턴크기로  
프린팅하기 위한 재사용가능 스탬프

**Reusable Stamps for Printing  
Sub-100 nm Patterns of  
Functional Nanoparticles**

2012년 8월

서울대학교 대학원

화학생물공학부

성 승 현

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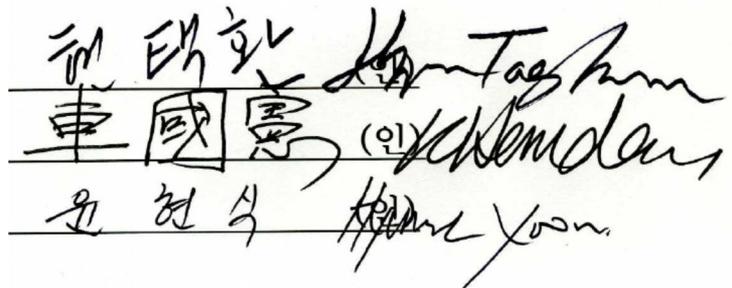
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The image shows three handwritten signatures on a white background. The first signature is in Korean characters '권태환' and English 'Kwon Taehwan'. The second signature is in Korean characters '차국현' and English 'Cha Guhyun', with '(인)' written next to it. The third signature is in Korean characters '윤현식' and English 'Yoon Hyunshik'.

## **Abstract**

# **Reusable Stamps for Printing Sub-100 nm Patterns of Functional Nanoparticles**

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Printed electronics recently seem to be ubiquitous in devices including photovoltaics, thin film transistor (TFT) backplanes, radio frequency identifications (RFID), and touch panel displays. Although printed electronics are close to commercialization, there exist still some restrictions or limitations on realizing high resolution patterns, such as sub-100 nm features, which are likely to replace the existing miniaturized semiconductor fabrication or nanoscale-controlled bulk hetero junction solar cell devices.

Pattern features in printing are highly dependent on stamp design. In order to realize high resolution patterns with a stamp, the stamp required some rigidity to overcome the lateral collapse of neighboring patterns, which is a serious problem for soft polydimethylsiloxane (PDMS) based stamps. Stamps should also have low

surface energy to transfer ink materials to a target substrate. After preparing a proper stamp with a complicated process, the feature must be coated with ink materials onto protruding parts of the stamps. Following spin-coating of functional materials like inorganic nanoparticles (NP), the NPs in the protruding parts of the stamp are transferred to a target substrate. And then, the designed stamps should be reusable for another transfer of NPs. However, the NPs in the recessed parts of the stamps are hard to remove, because especially some inorganic and metal NPs are not soluble in a general solvent.

In this study, we present a recyclable process of stamps for high resolution patterning of NPs. The process, which is applicable not only to organic stamps but also to inorganic stamps such as silicon wafer stamp, allows the same stamp to be reclaimed and reused the same stamp repeatedly for NP patterning. The NP patterning demonstrated here was in the sub-100 nm range (60 nm wide lines), which has never been reached before. The same technique makes possible sub-100 nm patterning without much difficulty with a proper choice of stamp material. The ability to transfer many different NPs with one single recycled stamp, as demonstrated here for the realization of an RGB display, must be valuable in fabricating various devices such as light emitting diodes, solar cells, thin film transistors, and displays.

**Keywords:** Printed electronics, Stamp, Polymer, Quantum dots, Nanoparticles.

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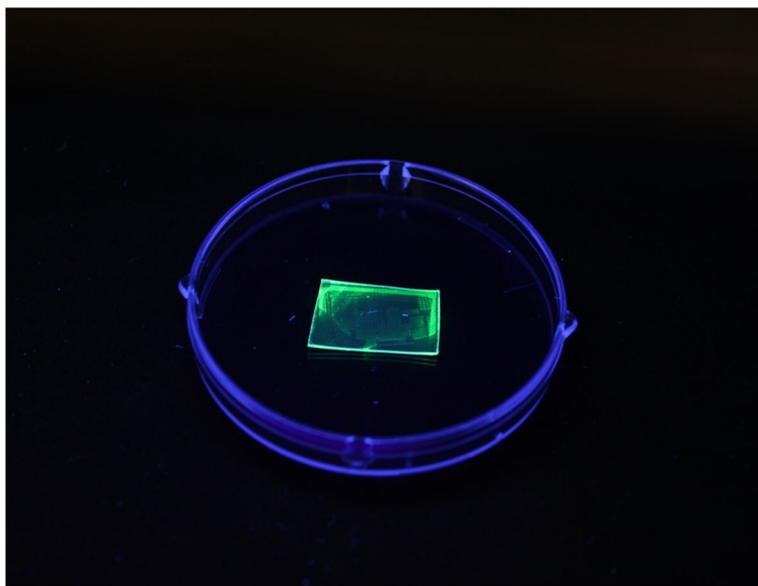
# Chapter 1. Introduction

Printed electronics are ubiquitous in many devices such as photovoltaics, thin-film transistor (TFT) backplanes, radio frequency identifications (RFID), and touch-panel displays.<sup>[1-3]</sup> The printing process has the advantage of reducing the fabrication cost, compared with conventional silicon-based processing, because the existing, expensive, patterning technologies are potentially expected to be replaced by the roll-to-roll process. It also has the benefit of employing various functional materials such as metal nanoparticles (NPs) and semiconductor nanocrystals, which are proven to be essential to photonic, electronic, and sensing devices.<sup>[4-8]</sup> Although printed electronics are close to commercialization, there still exist some restrictions or limitations on realizing high-resolution patterns, such as sub-100 nm features, which are likely to replace the existing miniaturized semiconductor fabrication or nanoscaled heterojunction solar cell devices.

To date, there have been several reports on the unconventional printing methods such as contact or transfer printing of functional materials.<sup>[9-16]</sup> It has been noted that the most important aspect for the printing technique is the stamp design because pattern resolution is significantly dependent upon the choice of stamp materials. In order to realize high-resolution patterns with a stamp, the stamp required some rigidity to overcome the lateral collapse of neighboring patterns, which is a serious problem for soft polydimethylsiloxane (PDMS) based stamps.<sup>[17]</sup> Stamps should also have low surface energy to transfer ink materials to a target substrate. Furthermore, the stamp materials should not be swollen by the solvent for functional materials. In order to satisfy those requirements, there have been many complicated attempts,<sup>[17-29]</sup> such as fabrication of rigi-flex stamps followed

by anti-adhesion surface treatments, or synthesis of stamp materials with special designs. After preparing a proper stamp with a complicated process, the feature must be uniformly coated with functional ink materials onto protruding parts of the stamps. In the case of sub-100 nm patterning of NPs, we would spin-coat the NPs onto the stamp because of the need for control of the film consistency. Following spin-coating, the NPs in the protruding parts of the stamp are transferred to a target substrate, then the designed stamps should be reusable for the next round of NPs transfer. However, the NPs trapped in the recessed parts of the stamps are hard to remove, especially because some inorganic and metal NPs are not soluble in typical organic solvents, as shown in **Figure 1** of the Supporting Information. Etching with strong acids is one possibility to remove the NPs; however, the stamps could be deformed or denaturalized due to these harsh processing conditions.

In this study, we present an effective process for reusable stamps in high pattern resolution of functional NPs. A patterned stamp is cleaned by removing NPs in the recessed region of the patterns with a UV-curable adhesive before moving on to the next cycle of printing with the stamp. The process, which is applicable not only to organic stamps, but also to inorganic stamps such as silicon stamps which have expensive processing costs, allows the same stamp to be reused repeatedly for the NP patterning. We demonstrate high-resolution patterning by rigid stamps with a low surface energy, the repeated use of the reusable stamp for defining sub-100 nm scale features, and the formation of an RGB (red, green, blue) pattern by transferring quantum dots (QDs) for three colors with these stamps. This color patterning has been performed using just one color per stamp, and then by using one stamp for multiple colors.



**Figure 1.** A fluorescence image of a used stamp after cleaning with toluene with sonication.

## Chapter 2. Experimental Section

### 2.1 PFPE Stamp Fabrication

We prepared PFPE stamps by blending PFPE precursor (5101x, Solvay Solexis Inc.) with 4 wt % photoinitiator (Darocur 1173, Ciba). The PFPE resin utilized is in solid state at room temperature (m.p :  $\sim 35$  °C). Thus, the material is heated up to around 60 °C and is blended with photoinitiator as well. By using this UV-crosslinkable PFPE material, we fabricated the silicon master by conventional photolithography and dry etching process. After drop-casting the precursor onto the master, we placed a PET film as a backplane on top of the PFPE precursor, following UV exposure ( $\sim 2$  mW/cm<sup>2</sup>, 365 nm) to crosslink the PFPE stamp for nano-particles transfer procedure. After detaching the stamp from the master at a rate of  $\sim 20$  mm/s), the stamp was fully cured under UV light ( $\sim 15$  mW/cm<sup>2</sup>, 365 nm, 30 min).

### 2.2 QD Synthesis

The QD utilized in this study is synthesized by the process as discussed in the previous works.<sup>[33, 34]</sup> The green and red QDs in this study have a core/shell structure ( $\text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$ ) with composition gradients, which relieve the lattice mismatch between the CdSe core and the ZnS shells. The emission wavelengths of the QDs are produced by changing the relative amounts of Cd, Zn, Se, and S. With a higher concentration of Cd, the core is larger and the peak shift results from the change in the core size of the QDs. The blue QDs were synthesized by introducing

S precursors into the mixed solution of Cd-Oleate ( $\text{Cd}(\text{OA})_2$ ) and Zn-Oleate ( $\text{Zn}(\text{OA})_2$ ). The emission wavelength of  $\text{Cd}_{1-x}\text{Zn}_x\text{S}/\text{ZnS}$  core/shell nano structures was finely tuned from violet (415 nm) to blue (461 nm) by adjusting the amount of S precursors in the first injection (S in 1-octadecene) and thus changing actual Cd content ratio in the alloyed  $\text{Cd}_{1-x}\text{Zn}_x\text{S}$ .

### 2.3 Transfer Printing with Cleaning Process

We spin-coated QDs suspended in toluene on the prepared PFPE stamp (3000 rpm, 30 sec). After evaporating solvents at room temperature, the QDs on the protruding parts of the stamp were transferred to PEDOT:PSS (Coating thickness :  $\sim 50$  nm) layer on silicon master. In transferring process, appropriate pressure and heat ( $\sim 400$  kPa,  $100$  °C for 10 min) make easier the particles transferred on desired position. After transferring QDs, we detached the residual QDs in the recessed area of the used PFPE stamp with a conventional UV-curable adhesive (NOA-73, Norland) by curing at  $\sim 2$  mW/cm<sup>2</sup> of UV for 5 min and peeling off. In this process, the used PFPE stamp is reused for NP transfer processes. As shown in **Figure 6**, we can transfer various nanoparticles onto a substrate in multi-step process such as RGB multicolor pattern with only a single reused stamp.

### 2.4 Measurements

The patterns generated were examined by scanning electron microscopy (SEM, XL30FEG) and atomic force microscopy (AFM, NS3A). The average height of the protruding parts on the substrate was obtained by the image analyzing

software (Gwyddion). We measured the height in 5 different areas and used their average values and standard deviations.

## Chapter 3. Results and Discussion

### 3.1 PFPE Replica Stamp

**Figure 2(a)** is the SEM image of PFPE stamp with 400 nm wide protruding lines (1  $\mu\text{m}$  high) separated by 200 nm wide space between lines. As shown in **Figure 2(b)**, the QDs on the protruding parts of the PFPE stamp are transferred onto a PEDOT:PSS layer. **Figure 2(c)** shows the magnified image of **Figure 2(b)**. It is noted that if the pattern is formed by pressure, the pattern shape should be a negative of the stamp. In order to demonstrate patterning of sub-100 nm features with NPs, we additionally used a master with a line width of 60 nm. The replicated PFPE stamp has lines 60 nm wide without lateral collapse as shown in **Figure 2(d)**. The QDs on the protruding parts of the PFPE stamp are transferred successfully (**Figure 2(e)**). **Figure 2(f)** shows the magnified image of **Figure 2(e)**.

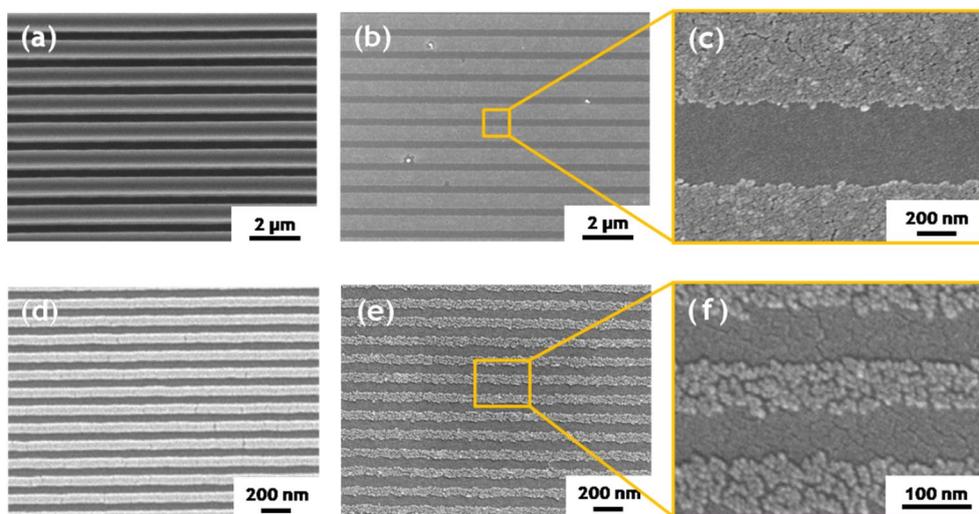
When the size of the feature of the stamp such as 60 nm lines in **Figure 2** is relatively small, the lines can collapse laterally or cling to one another unless the stamp material has a relatively high Young's modulus. The critical aspect ratio preventing lateral collapse has been shown to be determined by <sup>[29]</sup>

$$\frac{h}{w} \left( \frac{8\gamma}{3E^* w} \right)^{1/4} \leq \sqrt{d/w} \quad (1)$$

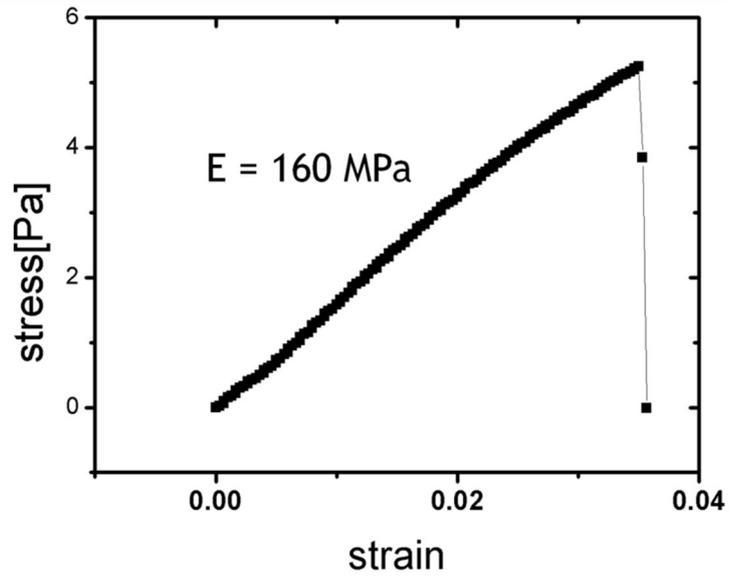
where  $E^* \equiv E/(1-\nu^2) \approx 4E/3$  ( $\nu$  is the Poisson's ratio of the material.),  $h$  is the height of the feature,  $w$  is the width,  $E$  is Young's modulus of material,  $d$  is the distance between the lines, and  $\gamma$  is the surface energy of the stamp material.<sup>[30]</sup> If the distance  $d$  is equal to the line width  $w$ , the equation can be rearranged to give

$$E \geq 2\gamma \frac{h/w}{w} \quad (2)$$

From the equation, the modulus for no lateral collapse can be calculated. The required modulus for 60 nm lines with an aspect ratio of 5 and a surface energy of 20 mN/m is 3.3 MPa. The PFPE replica stamp utilized in this study has a relatively high modulus (~160 MPa as shown in **Figure 3**) and a low surface energy (17.7 mN/m by the Owen–Wendt method).<sup>[31]</sup> Therefore, the stamp has the sufficient mechanical integrity to resist lateral collapse. When a silicon master is used as a stamp to transfer QDs, the feature size could be much smaller because of high modulus of inorganic master. It is noted that the theoretical approximation does not exactly define the resolution for sub-nanometer length scale features because there exist many other factors that can influence the pattern transfer fidelity such as feature size, aspect ratio, pattern density, sidewall profile, and processing conditions.<sup>[32]</sup>



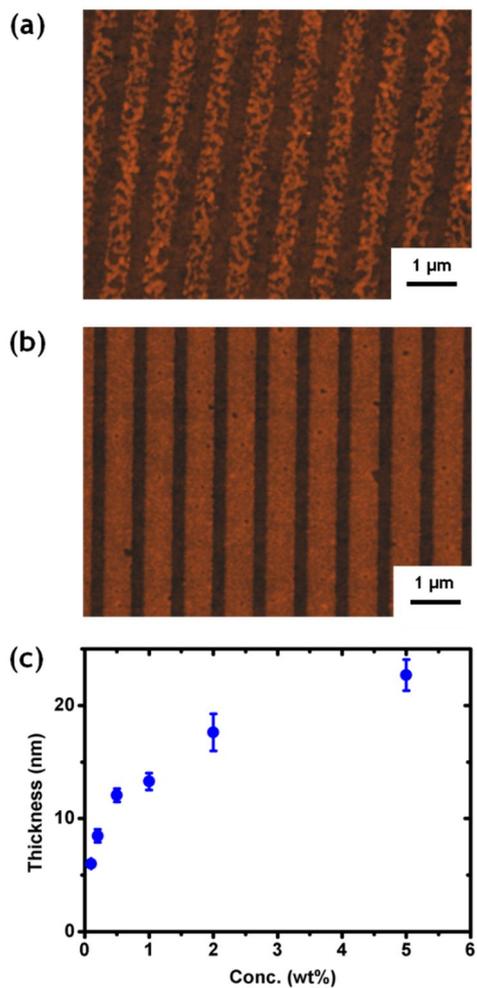
**Figure 2.** SEM images of PFPE stamps and QD arrays transferred on substrates. (a) A SEM image of a PFPE stamp with 400 nm wide lines separated by 200 nm space. (b) A SEM image of a QD array transferred on a PEDOT:PSS-coated substrate. Only QDs placed on the protruded area of the PFPE stamp are transferred. (c) An amplified image of (b). (d) A SEM image of a PFPE stamp with 60 nm wide lines separated by 60 nm space. (e) A SEM image after the QD transfer with the PFPE stamp shown in (d). (f) An enlarged SEM image of (e).



**Figure 3.** Stress-strain curve of a PFPE stamp used in the present study. Young's modulus is the ratio of stress to strain. Young's modulus is measured by a micro tensile tester.

### 3.2 Ability to Control Thickness of NPs

The ability to control thickness of NPs on the PFPE stamp by varying the concentration of  $\text{Cd}_{1-x}\text{Zn}_x\text{Se}_{1-y}\text{S}_y$  QDs in toluene, is shown in **Figure 4**. When the concentration is 0.1 wt %, the printed patterns exhibited some porosity due to partial coverage by NPs, as shown in the atomic force microscopic (AFM) image of **Figure 4(a)**. However, as shown in **Figure 4(b)** for 1 wt % QD solution, QD coverage is more than monolayer in all area of the substrate. **Figure 4(c)** displays the average thickness of deposited QD on the substrate as a function of concentration of QD solution. The thickness in this graph represents the average value of the deposited QD layer. In the case of 2 wt % QD solution, for instance, the thickness of the QD layer is about  $\sim 18$  nm.



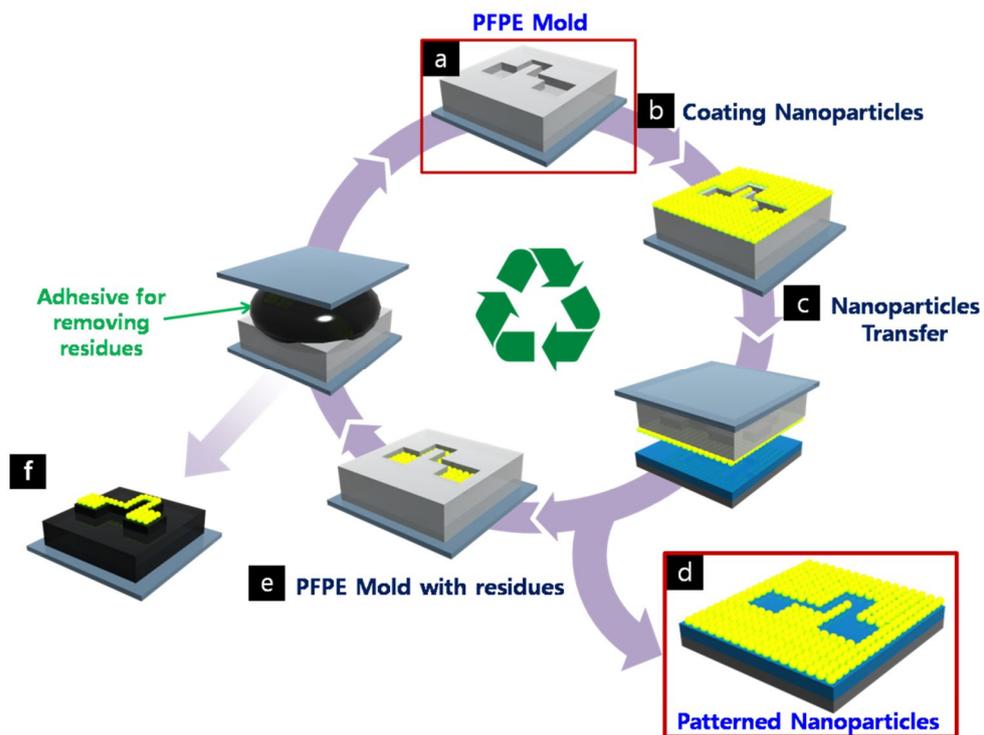
**Figure 4.** AFM images showing NP arrays on PEDOT:PSS-coated substrates when the concentration of QD in toluene is : (a) 0.1 wt % and (b) 1 wt %. The bright areas are the QD transferred areas. When QD concentration is 0.1 wt %, empty spots are clearly shown in the line shape patterns. (c) Coated layer thickness as a function of QD solution concentration.

### 3.3 Cleaning Process for Reusable Stamps

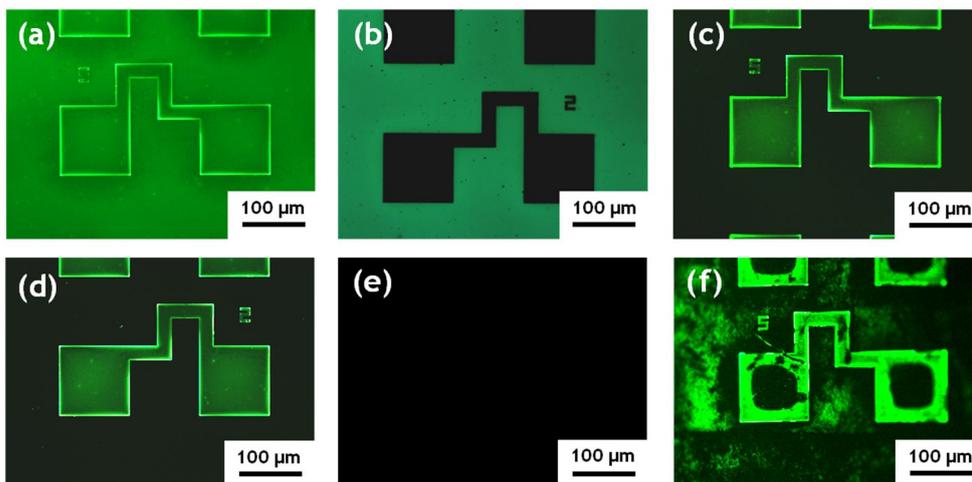
**Scheme 1** shows a schematic illustration of the cleaning process for reusable stamps. Shown in **Scheme 1(a)** is the PFPE stamp replicated from a silicon master. The stamp spin-coated with NPs is depicted in **Scheme 1(b)**. To transfer the particles (**Scheme 1(c)**), the PFPE stamp coated with QDs was placed on a PEDOT:PSS coated substrate, and then pressed against the substrate at  $\sim 400$  kPa and  $100\text{ }^{\circ}\text{C}$ . There was no pattern formed on the substrate under the same conditions when the bare stamp without NPs was used, which indicates that no imprinting is involved in the transfer process. **Scheme 1(d)** shows the substrate after the transfer. As illustrated in **Scheme 1(e)**, the NPs in the recessed part of the stamp still remain in the stamp. These NPs are difficult to remove and become increasingly cumbersome as the feature size shrinks. For repeated high resolution patterning of nanoparticles, however, these have to be removed. A commercialized UV-curable resin (Norland Optical Adhesive (NOA)) was used to remove the NPs from the PFPE stamp as shown in **Scheme 1(f)**. Through these steps, transferred NP arrays on a substrate were fabricated by repeated transfers with a reused PFPE stamp.

Given in **Figure 5** are the fluorescence microscopy images obtained during the cleaning process illustrated in **Scheme 1**. **Figure 5(a)** shows the PFPE stamp that was spin-coated with QDs suspended in toluene. **Figure 5(b)** is the image of PEDOT:PSS coated substrate after QD transfer. The used PFPE stamp after the QD transfer (**Figure 5(c)**) shows the mirror image of the QDs detached from the used stamp by UV-curable adhesive (**Figure 5(d)**). After the removal, the used stamp surface is devoid of QD as shown in the fluorescence microscopy image of **Figure**

**5(e). Figure 5(f)** shows the failure of removing QDs in recessed area of used stamp even after several sonication steps in toluene.



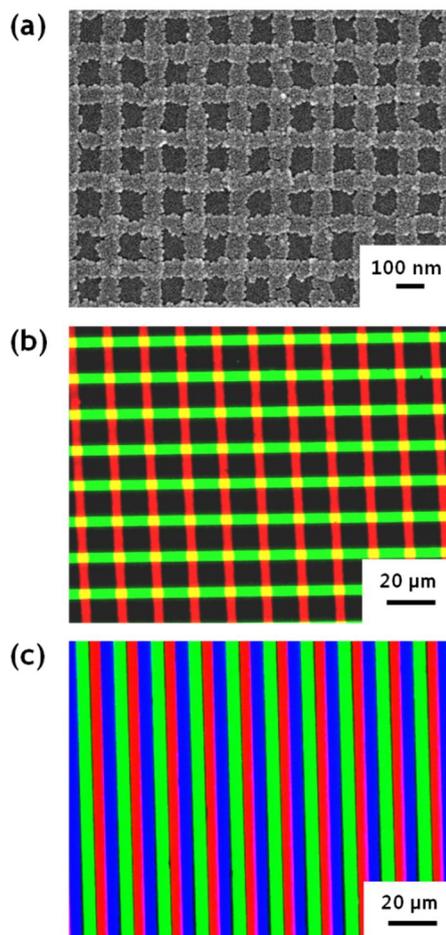
**Scheme 1.** A schematic illustration of the cleaning process for reusable stamps. (a) A PFPE stamp with desired feature size and patterns. (b) Spin-coating of NPs in top of the stamp; (c) NP transfer process with proper pressure and heat; (d) Transferred NP patterns on a substrate; (e) A PFPE stamp with residues in the recessed area of the stamp; (f) Removal of NPs in the recessed area of the stamp with a commercialized UV-curable resin.



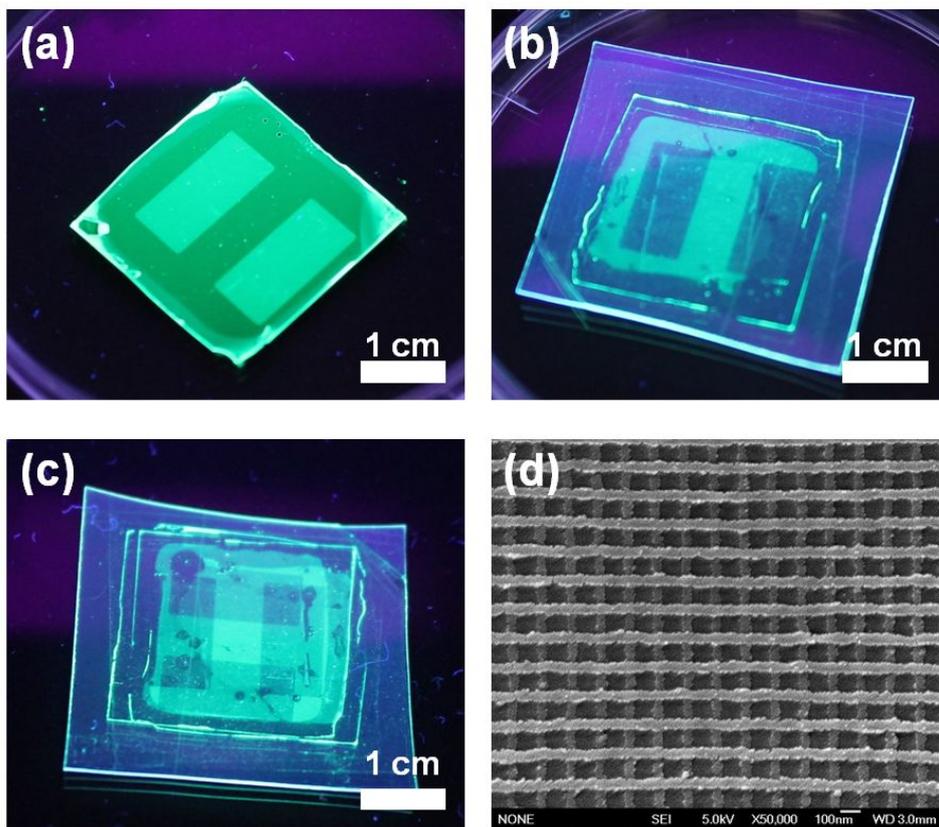
**Figure 5.** Fluorescence microscopy images obtained during the cleaning process for a reusable stamp. (a) A fluorescence microscopic image after coating QDs on a prepared PFPE stamp; (b) An image of a QD-transferred PEDOT:PSS-coated substrate. The green area is the QD transferred area; (c) An image of the PFPE stamp after QD transfer to the substrate. The green area represents the QDs left in the recessed region of the stamp after QD transfer; (d) An image of a UV-cured adhesive film containing QDs after removing them from the stamped PFPE; (e) An used stamp surface without residual QDs; (f) An image of a PFPE stamp obtained simply after sonication. Note that a large amount of QDs still remain on the stamp even after ultrasonication.

### 3.4 Transfer NPs with a Single Reused Stamp

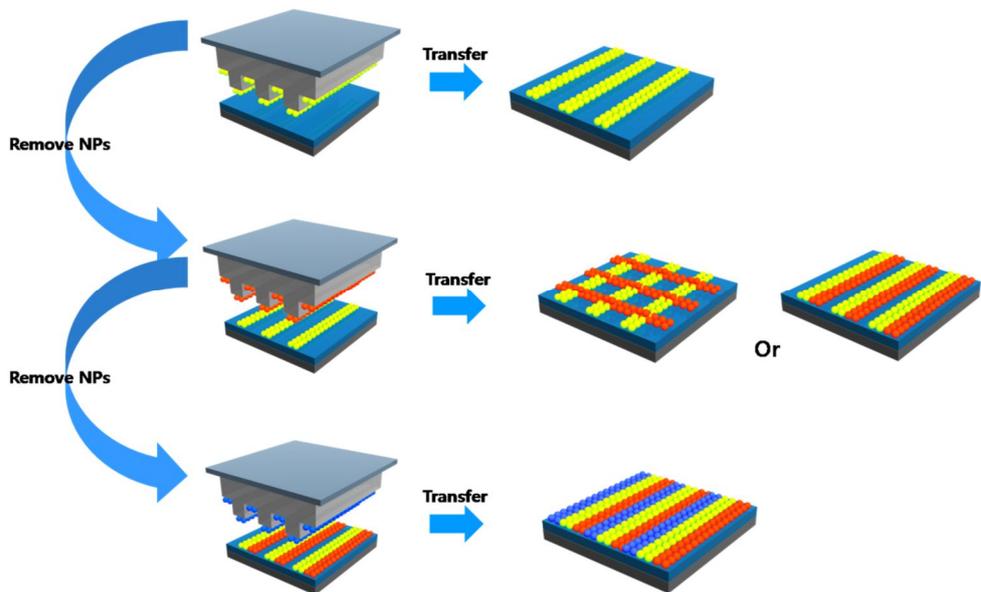
An important aspect of the present study is that it is possible to transfer more than one kind of particle with a single reused stamp as shown in **Figure 6**. For the nano-scale orthogonal pattern in **Figure 6(a)**, QDs are transferred on a line pattern (60 nm wide lines with 60 nm spacing) onto a substrate. After this first transfer of QDs, we cleaned up the stamp with the detaching method and used the same stamp again to transfer the line pattern in the direction perpendicular to the original lines. The same demonstrations with a silicon master are shown in **Figure 7**. Red (R) and green (G) lines were formed by first transferring red-emitting QDs onto a substrate and then green-emitting QDs with one single reused stamp in **Figure 6(b)**, as revealed by fluorescence microscopy. The same procedure as in **Figure 6(a)** was followed. Furthermore, it is possible to construct an RGB (B: blue) display by transferring red, green, and blue QDs onto a substrate. First, red color QD was deposited onto the substrate by the transfer process, and the used PFPE stamp was cleaned up by the detaching process. Subsequently, green and blue QDs were patterned by sequential transfer printings with manual alignment as shown in **Scheme 2**. The display of RGB lines constructed with one single reused stamp is shown in **Figure 6(c)**.



**Figure 6.** (a) A SEM image of criss-crossing stripes (60 nm width with 60 nm spacing) of QDs obtained by transferring QDs twice onto a PEDOT:PSS-coated substrate with a single reused stamp. (b) A fluorescence microscopic image of orthogonally transferred QD arrays with red and green emissions on PEDOT:PSS-coated substrate. (c) A fluorescence microscopic image of directionally transferred RGB QD arrays on a PEDOT:PSS-coated substrate.



**Figure 7.** (a) A fluorescence image of a silicon master after coating of QDs. (b) A QD-transferred PEDOT:PSS-coated substrate (PET). (c) A twice QD-transferred PEDOT:PSS-coated substrate in perpendicular direction. (d) A SEM image of criss-crossing stripes (60 nm width with 60 nm spacing) of QDs obtained by transferring QDs twice onto a PEDOT:PSS-coated substrate with a single silicon stamp.



**Scheme 2.** A schematic showing the repetitive transfers of different NPs by a single stamp.

## **Chapter 4. Conclusion**

In summary, we have presented a cleaning process of used stamps for repetitive high resolution patterning of NPs. The process, which is applicable not only to organic stamps but also to inorganic stamps such as silicon wafer stamp, allows the same stamp to be reclaimed and reused the same stamp repeatedly for NP patterning. The NP patterning demonstrated here was in the sub-100 nm range (60 nm wide lines), which has never been reached before. The same technique makes possible sub-100 nm patterning without much difficulty with a proper choice of stamp material. The ability to transfer many different NPs with one single reused stamp, as demonstrated here for the realization of an RGB display, must be valuable in fabricating various devices such as light emitting diodes, solar cells, thin film transistors, and displays.

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## 국문초록

최근 프린트드 일렉트로닉스는 photovoltaics(PV), 박막형 트랜지스터 (TFT)의 뒷판, radio frequency identifications (RFID), 터치 패널 디스플레이 등의 분야에 널리 이용되고 있다. 이러한 프린트드 일렉트로닉스는 현재 거의 상업화 단계에 이르러 있지만, 여전히 반도체 칩의 소형화나 나노 크기의 태양전지 개발에 이용되는 100 nm 크기 이하의 미세 패턴을 구현하는데 있어서 문제점이 많다.

프린팅 공정에 있어서 패턴 크기는 스탬프에 따라 달라지는데, 미세 패턴을 구현하기 위해서는 기존의 PDMS 가 가지고 있는 패턴 간 붕괴현상을 극복하는 것이 중요하다. 또한 사용하는 스탬프는 원하는 물질을 원하는 위치에 전사하기 위해 낮은 표면 에너지를 가지고 있어야 한다. 일반적인 프린팅 공정은 제작된 스탬프에 원하는 물질을 코팅하고, 패턴의 돌출된 부분에 코팅된 물질이 원하는 위치에 전사되도록 적절한 조건을 가해 공정을 수행한다. 그러나 여기서 사용한 스탬프를 다시 사용하기 위해서는 별도의 클리닝 공정이 요구되는데, 특히 돌출되지 않은 부분의 잔류물질을 제거하는 것이 문제가 되고 있다. 또한 무기물이나 금속 나노 입자의 경우 용매에 쉽게 녹지 않기 때문에 이를 제거하는데 어려움이 많다.

본 연구에서는 기능성 나노 입자의 미세 패턴을 구현하고자 재사용이 가능한 스탬프를 이용한 공정을 소개하고자 한다. 이 공정은 유기물 스탬프 뿐 아니라 실리콘 웨이퍼와 같은 무기물 스탬프에도 쉽게 적용이 가능하며, 같은 스탬프를 여러 번 반복적으로 사용하여 여러 나노 입자를 전사시킬 수

있는 장점이 있다. 본 연구에서 수행한 나노 입자의 패터닝은 이전에는 찾아볼 수 없었던 100 nm 이하의 패턴 (60 nm 패턴) 을 구현해냈다. 이 공정을 이용하면, 적절한 스탬프를 찾아야 하는 어려움이 없을 뿐 아니라, RGB 패턴처럼 하나의 스탬프를 이용하여 여러가지 나노 입자를 원하는 위치에 전사시키는 것이 가능하다. 이는 현재 각광을 받고 있는 LED, 태양전지, 박막형 트랜지스터 및 디스플레이 분야에서 유용하게 쓰일 수 있다.

**주 요 어 :** 프린티드 일렉트로닉스, 스탬프 고분자, 양자점, 나노 입자.

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