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# A technique for transferring metal nano patterns from a plastic replica mold by using a metal oxide release layer

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ABSTRACT

Techniques for nano-scale metal patterning on plastic substrates are strongly desired for fabricating various novel devices such as printed electronics (PE), as well as plasmon photonics and optical devices. There are great hopes that PE devices on plastic substrates could replace conventional integrated circuits on silicon, because plastic substrates offer good transparency, flexibility, lightness and low cost. In order to simultaneously achieve high-resolution and high-throughput metal patterning on a plastic substrate, nano transfer printing (nTP) is a promising technique. However, conventional nTP processes require a poly(dimethylsiloxane) (PDMS) stamp. PDMS is a high-viscosity material before curing and thermosetting elastomer, so it is difficult to obtain PDMS stamps quickly by using injection molding or roll-to-roll nanoimprinting. To resolve these issues, we have developed a three-dimensional metal-pattern nanoimprinting technique that uses a metal oxide release layer. In this study, we examined a technique for transferring a metal onto poly(ethylene terephthalate) (PET) substrate using a cycloolefin polymer (COP) replica mold with a metal oxide release layer. We showed that the metal oxide release layer allows the nTP process to be implemented with a COP replica mold.



## 1. Introduction

There is growing demand for a fine metal-patterning technique for fabricating next-generation devices. In particular, there are great hopes that printed electronics (PE) devices [1–3] on plastic substrates will replace conventional integrated circuits on silicon, because plastic substrates offer good transparency, flexibility, lightness and low cost. Therefore, nano-scale metal-patterning techniques on plastic substrates are strongly desired. Nano transfer printing (nTP) [4] is a promising process for obtaining a fine metal pattern on a plastic substrate. Generally, the nTP process requires a poly(dimethylsiloxane) (PDMS) stamp, which has very low surface energy [5–7]. However, the too-low surface energy of PDMS causes some issues. For example, when a gold layer is deposited onto a PDMS stamp directly, the roughness of the gold layer surface is poor and micro cracks develop because of the stress resulting from the mismatch between PDMS and bulk gold on a small scale [8]. Therefore, oxygen plasma treatment [8] or a metal (titanium or chromium) adhesion layer [9] is needed to fabricate a smooth gold layer, which makes it difficult to carry out the nTP process continuously using a PDMS stamp and a step-and-repeat process, for instance. Furthermore, PDMS is a high-viscosity material before curing and thermosetting elastomer, so it is difficult to produce many PDMS stamps quickly by using injection molding or roll-to-roll nanoimprinting. On the other hand, we have developed a three-dimensional metal-pattern nanoimprinting technique that uses a metal oxide release layer [10,11]. Using our technique, it is possible to carry out the nTP process using various mold materials, such as spin on glass (SOG), glassy carbon (GC) and typical electron beam resist [12].

In this study, a plastic replica mold with metal oxide release layer was examined as an nTP process mold. Although there have been previous reports on the nTP technique using a plastic replica mold with self-assembled monolayer (SAM) treatment [13], SAM is expensive and hence not suitable for coating a large area or large volume of replica molds. In contrast, the metal oxide release layer used in our technique can be used to coat molds with a large area at low cost. We used cycloolefin polymer (COP) as a plastic replica mold in this study, because it has a sufficiently high glass-transition temperature to transfer a metal layer onto poly(ethylene terephthalate) (PET) substrate. Moreover, the transmittance of COP in the ultraviolet (UV) region is very high compared to conventional plastics, therefore it is easy to perform the nTP process using UV curable resin [12]. We showed that the metal oxide release layer allows the nTP process to be implemented with a COP replica mold. We believe that our technique is suitable for not only COP replica molds but also other plastic replica molds.

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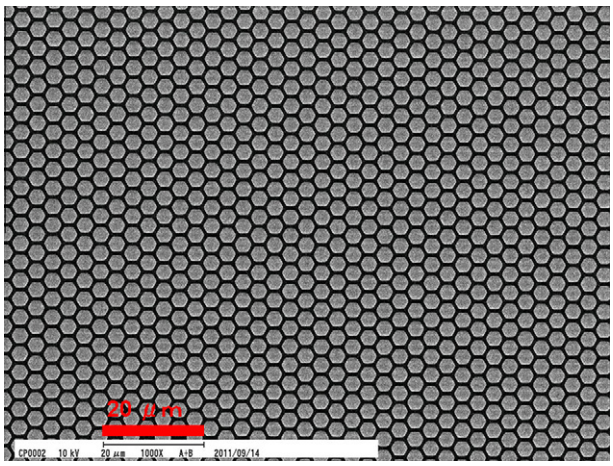


**Fig. 1.** SEM image of a fabricated COP replica mold with positive tone honeycomb pattern.

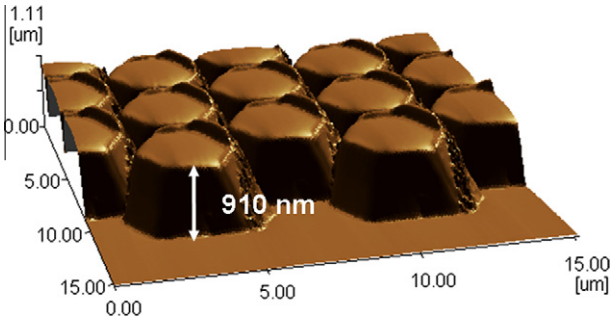


**Fig. 2.** AFM image of the positive tone COP replica mold.

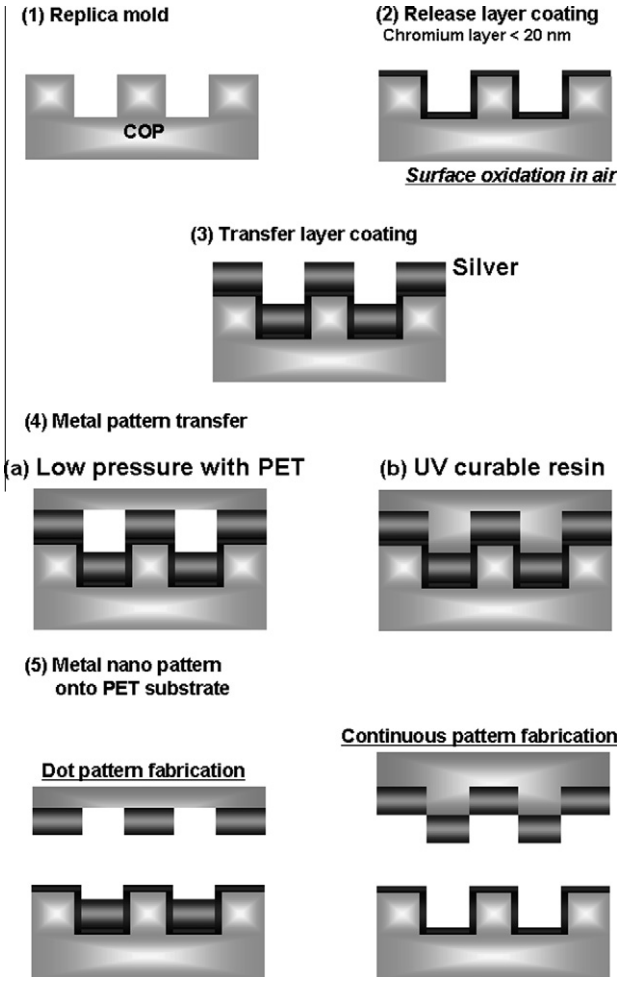


**Fig. 3.** Schematic diagram of transfer process using metal oxide release layer.

## 2. Experimental apparatus and procedure

First, COP replica molds were fabricated by a nano-scale honeycomb structure on silicon substrate using thermal nanoimprinting. In this study, ZEONOR® film (ZEONOR, ZEON Corporation) was used as the COP substrate. COP has good properties of dimensional stability at high temperature, low moisture absorption and high transmittance in the UV region, and is thus suitable for the plastic replica mold in the nTP process. Fig. 1 shows a scanning electron microscopy (SEM) image of a fabricated COP replica mold which has a nano-scale honeycomb structure. The dark area in Fig. 1 is a concave area and was defined as a positive tone pattern. In addition, we also prepared a COP replica mold with the reversed pattern as a negative tone pattern. Fig. 2 shows an AFM image of the positive tone COP replica mold. The height of the pattern was about 910 nm.

Fig. 3 schematically shows our metal pattern transfer process. After the preparation of COP replica molds, the surface of the COP replica mold was coated with a chromium layer of up to 20 nm thickness using a resistively heated vacuum evaporation system (VPC-260F, ULVAC KIKO Inc.). The pressure at deposition was $2.0 \times 10^{-3}$ Pa. The vacuum-evaporation system was then ventilated in air at room temperature to oxidize the chromium layer surface to form chromium oxide ($Cr_2O_3$) [10]. This oxidization is the most important part of our technique. Next, a silver layer of approximately 110 nm was deposited onto the $Cr_2O_3$ release layer using the same equipment. The metal materials were of high purity (greater than 99.9%, Nilaco Corporation). During metal deposition, the COP replica mold was not heated up to the high glass-transition temperature, and so there was no difference in the patterns of the COP replica mold before and after the deposition processes.

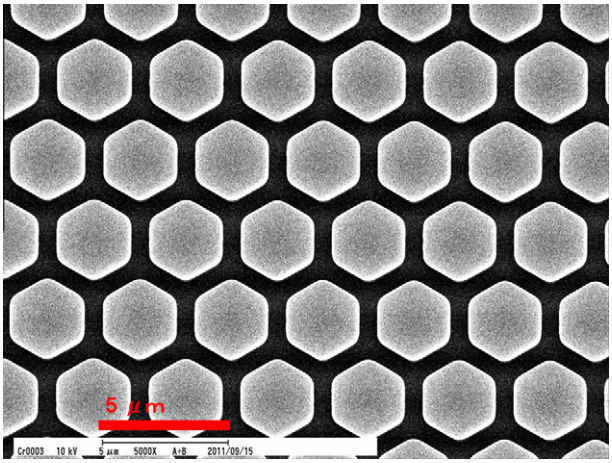


**Fig. 4.** SEM image of a COP replica mold with positive tone pattern after the $Cr_2O_3$ release layer coating.

Subsequently, two nTP processes were examined using the samples. One process was as follows: on a hot plate heated to 90 °C, a 1-mm-thick PET substrate was placed on the COP replica