A MULTISCALE TRANSFER PRINTING WITH A HIERARCHICAL STAMP FOR SIMPLE GENERATION OF METALLIC NANOPATTERNS

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ABSTRACT

A multiscale metallic pattern having in nanoscience exhibits unique and unusual optical properties in plasmonics. Conventional fabrication methods for multiscale metallic pattern involved many steps and restricted in shapes. Here we present a simple yet robust method for fabricating multiscale metal patterns through a transfer printing techniques by simply employing a polymeric hierarchical mold having low surface energy as a stamp. Multiscale metal patterns are easily transferred on a Norland Optical Adhesive (NOA) surface having relatively higher surface energy than that of PFPE hierarchical stamp without surface treatment.

KEYWORDS

Multiscale transfer printing, hierarchical stamp, metallic nanostructure

INTRODUCTION

Metal patterning is one of essential steps in the fabrication of plasmonic nanostructure [1]. Traditionally, photolithography has been used to define an array of metallic features aided by suitable dry or wet etching step. An alternative process is lift-off (after photolithography) or transfer printing utilizing the difference of work of adhesion [2, 3], which is especially useful for low-cost, wet chemical-free processes for organic devices. For transfer printing, researchers have employed an inert stamp material such as polydimethylsiloxane (PDMS) or polyurethane acrylate (PUA) to transfer a group of metal dots or lines to a target substrate. However, several problems have been found, restricting the widespread use of the methods. First, the pattern resolution is typically limited to > 100 nm due to low mechanical properties of stamp materials. A rounding or roof collapse of the stamp results in non-uniform distribution of the contact, thereby deteriorating the overall pattern quality. Second, multiscale metal patterns are difficult to fabricate with a simple transfer printing step. For example, if a designed pattern consists of a group of 100-nm dots separated by 1-10 μm spacing, a single scale polymeric stamp hardly produces the pattern in one-step printing since the space part of the stamp would touch the substrate while enforcing the stamp in contact. Therefore, a relatively complicated process involving a series of photolithography and selective etching has been developed in order to achieve a metal pattern with multiple length scales. It is noted that such a dual-scale metal pattern is receiving much interest as an essential component of plasmonic metamaterials or devices.

Here, we present a one-step, multiscale transfer printing (MTP) method to fabricate well-defined dual-scale metal patterns. A key idea is to utilize an inert polymer stamp with dual-scale structures in the form of nanoscale pillars or lines integrated with microstructural bases. The microstructure allows for a sufficient structural height so as to ensure a robust, conformal contact with the substrate. Such a hierarchically organized architecture is similar to the gecko's toe pad, which is known to enhance the structural compliance and thus induce conformal contact via contact splitting.

EXPERIMENT AND RESULTS

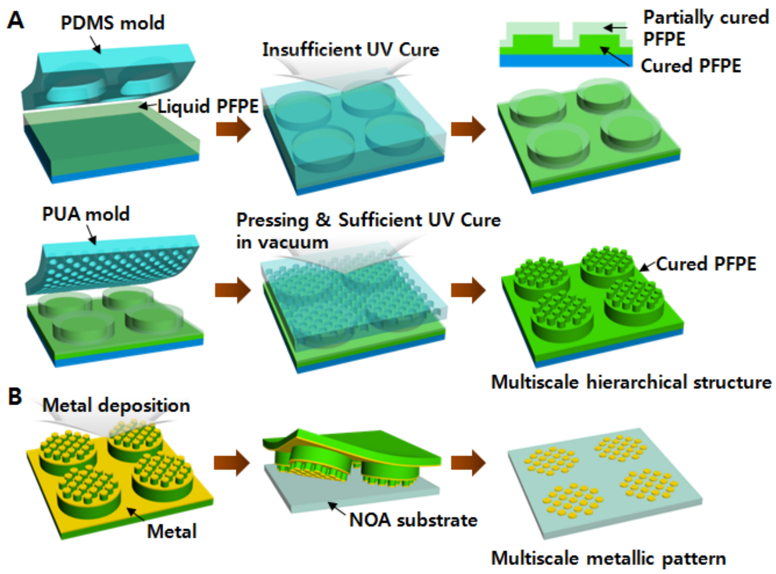

Figure 1. Fabrication of multiscale metallic patterns using a hierarchical stamp

Figure 1 depicts the fabrication process of multiscale metal pattern using a UV-curable perfluoropolyether (PFPE) resin. In the first molding step with PDMS stamp, the PFPE resin is not completely cured due to oxygen inhibition effect, resulting in a less-cured layer on top of the fully-cured base structure. Then, nanoscale structures are monolithically integrated in the second molding step by placing a nanopatterned PUA mold under a slight pressure in vacuum. It is known that the oxygen acts as a scavenger against the initiator or free radicals, so that the surface remains tacky and partially-cured after photopolymerization. The thickness of the partially-cured layer is determined by the competition between oxygen consumption rate and permeation rate of oxygen through the PDMS stamp, typically on the order of several micrometers. After preparing a hierarchical PFPE stamp, a thin metal layer (e.g., Au, Al, Pt, 20~60 nm) was deposited with a thermal evaporator and transferred to the acceptor substrate via the difference of work of adhesion (Figure 1b).

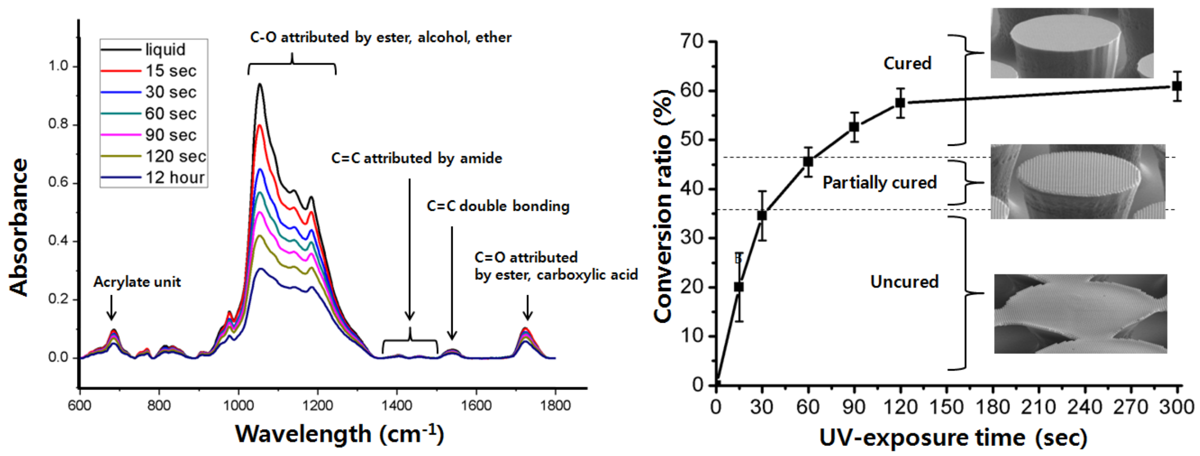

Figure 2. FT-IR spectra and conversion ratio of PFPE below the PDMS mold depends on the UV exposure time.

To monitor the structural evolution of the partially-cured layer, FT-IR analysis was performed with various UV exposure times up to 2 hr. Here, several peaks were identified as fingerprints of photopolymerization: C=O group located at 1720 cm-1, C=C double bonds at 1530 cm-1, and acrylate units at 690 cm-1. As shown in Figure 2, these peaks were all decreased with the increase of exposure time and unchanged approximately after 120 sec. By comparing the relative magnitude of these peaks, one can calculate the conversion ratio of each state, which can be used as a key index to determine the curing degree of the layer. when the conversion ratio of the partially cured PFPE was approximately 60%, there is no more deformable volume of resin in the outer surface of PFPE structure which means the upper structures on the predefined structure cannot be formatted in fully UV-curing process. The conversion ratio of the layer ranged between 35 and 45%, which gave rise to a well-defined hierarchical structure shown on the middle of right panel. When the conversion ratio was lower (too viscous) or higher (too rigid) than this range, the hierarchical structure was either collapsed (bottom of right panel) or not formed (top of right panel), respectively.

There are several notable advantages in using the PFPE as a stamp material. First, the PFPE has a relatively high diffusivity to oxygen, allowing for a fairly large process window in the partially-cured regime compared to other materials such as PDMS. Second, it has low surface energy; the metal layer can be easily transferred to the underlying substrate without additional surface modification. Third, it is mechanically stable enough to maintain sub-100-nm structures without any structural collapse. Figure 3 shows examples of the resulting hierarchical structures with various shapes and scales: 800 nm dots on 45 μm pillars (C), 550 nm lines on 30 μm pillars (D), and 10 μm pillars on discrete concentric circles of 200 μm width.

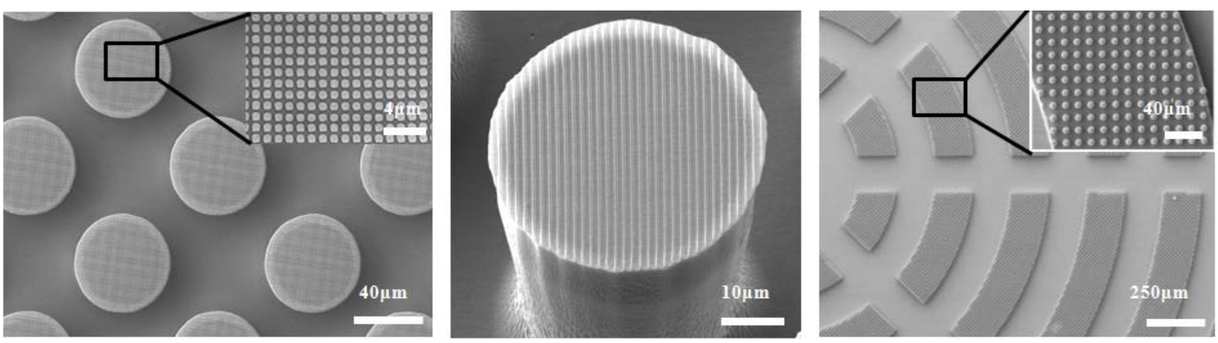

Figure 3. SEM images showing examples of hierarchical structures with various shapes and scales

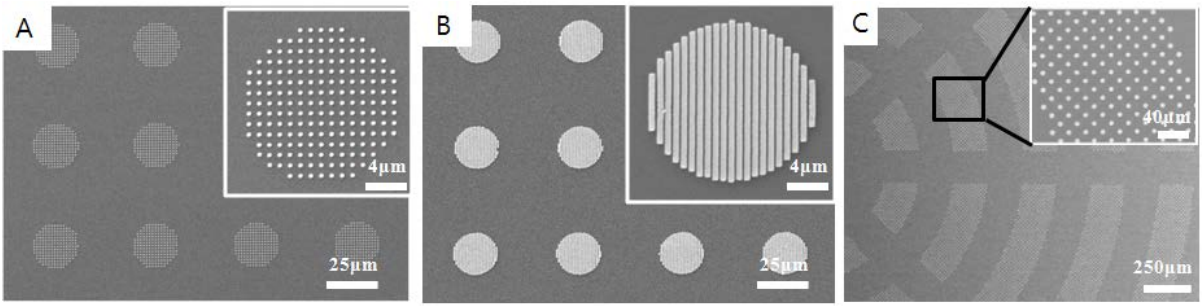

Figure 4. SEM images of various transferred metal patterns using hierarchical stamp

Next, we fabricated various metal patterns using the MTP process. In Figure 4, groups of nanoscale dots (300 nm diameter, Pt) and lines (400 nm width, Al) were formed in one-step transfer with a uniform distance of 20 μm between the adjacent groups. This result demonstrates the ability to use different nanopatterns even on the same microstructure base. Similarly, groups of the same nanoscale dots (Au) were formed in a discrete concentric pattern, which is exactly matched with the hierarchical stamp shown in Figure 3. Here, the thickness of metal layer was ~40 nm. Furthermore, a nanoscale stencil (hole diameter: 250 nm) was faithfully transferred to the substrate in the shape of 20 μm diameter circles with the thickness of 40 nm.

The operating principle of the MTP process lies in the difference of work of adhesion at the metal-stamp and metal-substrate interfaces. For example, the calculated works of adhesion were 54.02 and 99.01 mJ/m^2 for the Pt/PFPE and Pt/NOA, respectively, suggesting that the Pt layer could be readily transferred to the NOA-coated substrate without any surface modification. Although not shown, the metal layer could be transferred to other substrates such as polymethyl methacrylate (PMMA), silicon, and glass substrates with a modification of surface energy.

In the MTP process, multiscale metallic structures are simply transferred on the acceptor layer by hierarchical structure. This result demonstrates the ability to use different nanopatterns even on the same microstructure base as a hierarchical stamp. Metallic nanostructures with micro length scale gap can be easily generated from the hierarchical stamp simply by a single transfer printing step. The surface energy of the PFPE stamp is significantly low that is available to form the multiscale metallic structure without surface treatments on the acceptor layer.

CONCLUSION

we have presented a simple method for creating various PFPE stamps with hierarchical structures and its application to multiscale metal transfer printing. It turned out that a partially-cured layer was obtained with the conversion ratio in the range of 35 to 45%, and then a dual-scale structure with minimum resolution down to sub-150 nm (nanoscale feature) and sub-5 um (microstructure base) was formed via two-step molding process with high physical integrity and pattern fidelity. It is envisioned that the method presented here will broaden the scope of metallic nanostructures in plasmonic metamaterials as well as in microfluidic and optical devices where simple metal patterns are needed to be integrated. The current method would be useful in patterning multiscale metal arrays with potential applications to nano-optics, electric devices and sensors.

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