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Stacking of nanoscale metal dot array using liquid transfer imprint lithography with roll press

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ABSTRACT

The stacking of metal nanodot patterns is useful for plasmonic devices and metamaterials. Metal nanodot patterns are conventionally fabricated using a combination of lithography and a metal lift-off process, which is time consuming and complex. On the other hand, there is demand for an expanding the patterning area of the metal nanodot. Therefore, the fabrication method with high throughput is required. For more efficient fabrication, we have developed a novel stacking technique that combines ultraviolet nanoimprint lithography (UV-NIL), contact printing, and liquid transfer imprint lithography (LTIL). UV-NIL was used to obtain a replica mold with a nanoscale hole pattern, and the metal layers were deposited onto the mold by using a vacuum evaporator. Contact printing removed a metal layer on the mold surface, leaving a metal nanodot array in the holes of the replica mold. This metal layer was transferred by UV-NIL, and LTIL with a roll press was employed to reduce the thickness of the UV-curable resin; the excess resin was split from the mold in the liquid phase. The replica mold with the metal dots and an intermediate layer was then transferred to a polyester film. In this study, this process was repeated to obtain five stacked layers. The stack consisting of gold nanodots displayed a red plasmonic color, whereas the stack of silver nanodots displayed a blue plasmonic color. Scanning electron microscopy was used to confirm the stacked structures through tilted angle and cross-sectional view images. The advantages of this process are that nanodot patterns can be fabricated using a mold-based process and that the thickness of the stacking layer can be controlled by LTIL. This process can therefore be used for high-throughput fabrication of stacking metal devices such as plasmonic memory.

1. Introduction

There is a growing demand for a nanoscale metal dot stacking technique to fabricate next-generation devices including plasmonic devices, metamaterials, and memory devices. For example, hole-patterned aluminum on a transparent substrate acts as a color filter, a stacked silver checkerboard nanostructure embedded in transparent resin acts as a metamaterial with a negative reflection index, and a stacked 30-nm gold rod array embedded in transparent resin acts as a plasmonic memory device [1–3]. Stacking these metal structures in transparent resin and insulators is usually achieved with lithographic patterning, metal deposition, and a lift-off process: the desired pattern of resin is first fabricated on the substrate, the metal layer is then deposited by thermal evaporation or sputter coating, and the resin is removed by chemical dissolution. Resin patterning is typically performed using electron beam lithography (EBL) or nanoimprint lithography (NIL) [4], but for further efficient fabrication, NIL can also be used to transfer both the metal patterns and the intermediate resin layer. However, it is difficult to control the thickness of the intermediate resin layer with this technique. Furthermore, the residual layer that arises in NIL must be controlled for metal stacking purposes. Liquid transfer imprint lithography (LTIL) is one candidate for solving these problems because excess resin is split from the mold in the liquid phase [5–8]. In this study, we examined a stacking process by using NIL and LTIL for the fabrication of metal stacking devices. In the case of our process, NIL is used to transfer the nanoscale metal pattern structures, and LTIL is used to control the thickness of the intermediate resin layer. As a result, we have succeeded in the stacking of five layers of metal nanodot arrays with the thin intermediate resin layers by using replica molds.

2. Experimental method

Master molds were silicon molds of a pattern of pillars with a diameter of 230 nm, pitch of 460 nm, and height of 230 nm. The patterned area of the master mold was 1 cm^2. In this study, a

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replica mold was fabricated using parallel-plate UV-NIL with a UV-curable resin (PAK-01-CL; Toyo Gosei Co., Ltd.) on a polyester film (Cosmoshine A4300; Toyobo Co., Ltd.). The UV-NIL pressure was 0.5 MPa, the exposure time was 5 s, and the UV dose was 400 mJ/cm^2. As a result, replica molds with a hole pattern were obtained.

Figs. 1 and 2 show the schematic view of our process using NIL and LTIL for stacking the layers with metal nanodot patterns. Fig. 1 explains the method for preparing the metal nanodot arrays and Fig. 2 explains the stacking process via LTIL. First, the replica mold (Fig. 1(1)) was coated with a 30-nm-thick layer of Cr (Fig. 1(2)) using a resistively heated vacuum evaporation system (VPC-260F; Ulvac Kiko Inc.). Deposition was carried out when the pressure reached 2.0×10^{-3} Pa. The vacuum evaporation system was then ventilated with air at room temperature to oxidize the surface of the Cr layer, forming a coating of Cr_2O_3 [9–11]. Our previous study found that Cr_2O_3 acts as a release layer. After that, we deposited a layer of gold or silver about 100 nm thick (Fig. 1(3)) using the same evaporation system. This metal layer thickness is shallower than the depth of the hole pattern on the replica mold. The pressure for gold or silver deposition was also 2.0×10^{-3} Pa. Fig. 3 shows an SEM image of the replica mold after the formation of the Cr_2O_3 release layer. The replica mold was not damaged by heating during the deposition process. Following the deposition process, the metal layer on the mold surface is to be removed to obtain the isolated metal nanodot arrays. In this study, the contact printing method was used for this purpose, as shown in Fig 1(4 and 5). At this time, a 1-mm-thick polyethylene terephthalate (PET) substrate was placed in contact with the replica mold (Fig. 1(4)) for 5 min on a hotplate heated to 90 °C. As the replica mold consisted of a soft material, this helped to ensure good contact between the mold and the PET substrate without a high external pressure. After cooling the sample, the PET substrate was released from the replica mold (Fig. 1(5)).The metal nanodot structures then remained in the bottom of the mold cavities, similarly to the microcontact and nanoprinting processes. Next, we transferred the metal nanodot array in the bottom of the replica mold by using a combination of NIL and LTIL processes, as shown in Fig. 2(a). First, a UV-curable resin (PAK-01-CL) was poured onto the replica mold. Then, the poured resin was pressed by roller together with a polyester film (Fig. 2(a)(1)) to obtain a thin intermediate layer and to fill the mold cavities with the resin. The optimum parameters for thinning the intermediate layer were found to be a moving speed of 0.785 m/min and a pressure of 2.5 MPa (Fig. 2(a)(2)). After applying pressure to the whole area using the roller, the polyester film substrate was demolded, resulting in a coating of thin UV-curable resin on the replica mold (Fig. 2(a)(3)). These processes (Fig. 2(a)(1–3)) are the LTIL for obtaining a proper intermediate layer thickness. Second, another polyester film substrate was placed on the replica mold, and the UV-NIL process (Fig. 2(a)(4)) was carried out at 0.5 MPa for 5 min at a UV dose of 400 mJ/cm^2. After curing the resin, the remaining metal nanodot pattern was transferred from the bottom of the hole pattern to the UV-curable resin layer while holding the inverted shape of the replica mold (Fig. 2(a)(5)). Note that the Cr_2O_3 release layer was not transferred to the UV-curable resin layer. We previously prepared five replica molds with the isolated metal nanodot pattern in one deposition process, shown in Fig. 2(a)(1), and repeated only the steps shown in Fig. 2(b)(1 and 2) by using one polyester film. Consequently, a metal nanodot stacking arrangement with five layers was obtained (Fig. 2(b)(3)). At this time, the thickness of the intermediate layer was controlled to be thicker than the depth of nanodot pattern. Therefore, the unevenness of the mold surface was flattened by the UV curable resin. In this study, we fabricated the samples with gold or silver nanodot arrays. The obtained patterns were observed using a scanning electron microscope (SEM; ERA-8800FE; Elionix Co.), and the relative reflectance of the metal nanodot stacked arrays were measured using a spectral photometer (SolidSpec-3700; Shimadzu Co.).

3. Results and discussion

We first examined the properties of the Cr_2O_3 release layer. Fig. 4 show SEM micrographs of the gold and silver patterns transferred onto the polyester film substrate (1st layer), which confirm that the Cr_2O_3 layer acted as a release layer. The gold and silver nanodots had heights of 116 and 121 nm, respectively. Another four layers were fabricated similarly, and Fig. 5 shows the tilted-angle and top view of the 5th layers of the gold and silver nanodots transferred onto the polyester film substrate. This result shows that it is possible to the stacking process at least five times via our process. In addition, we observed 10,000 of the dots in the 1st, 3rd and 5th layers using a new sample. In this case, we ignored defects due to dust. As a result, the transfer success rate for metal nanodots was over 97% whether using gold or silver material, regardless of, and the position of the stacking layer.

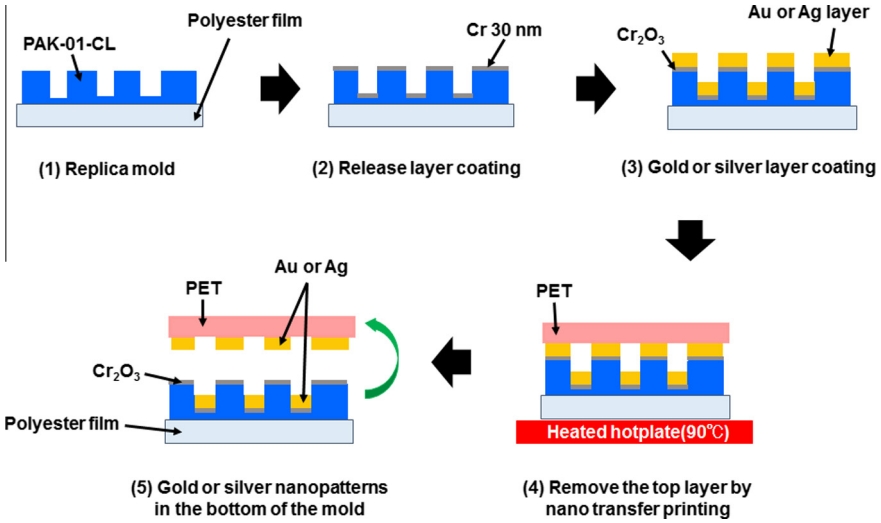

Fig. 1. Schematic illustration of the preparation method for the isolated metal nanodot pattern via nanoprinting process.