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Nanoprint lithography of gold nanopatterns on polyethylene terephthalate

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ABSTRACT

Nano-order metal pattern printing on plastic substrates was established by using hard stamp nanoprint lithography (NPL). A spin-on-glass (SOG) material, which is almost the same as quartz in composition, was used as the material for the hard stamp. The SOG acted as a positive-tone electron beam (EB) resist. Nanopatterns were fabricated by using electron beam lithography (EBL), and a developed pattern of SOG was used as the hard stamp. Further, two types of release coating methods were utilized. One method used a conventional silan coupling agent and the other, a chromium layer. After comparing the results of the methods, we found that the chromium layer formed a smooth surface and therefore used this layer as the release layer. In addition, chromium was changed to Cr_2O_3 because of the exposure to atmospheric air. Gold was used as the transfer metal and was deposited on the hard stamp covered with the chromium release layer. This stamp was then placed in contact with a PET substrate at 80 °C for 30 min. A gap width of less than 30 nm of gold was transferred onto the PET substrate. This process is very simple, and yet, it makes it possible to obtain a very high resolution metal pattern transfer by using hard stamp NPL.

1. Introduction

Recently, the demand for flexible and transparent electronic devices has increased because they are used in the fabrication of wearable devices and bendable thin-film displays. These flexible and transparent electronic devices are mostly made of plastic, and thus, methods for fine patterning of metal material on plastic are required. However, conventional semiconductor processes such as lithography and dry etching are not suitable for the fabrication of these plastic devices because plastic gets damaged upon the application of heat and the use of developer compounds. Inkjet printing is a popular and promising process; however, it is difficult to obtain a resolution of less than 1 μm by using this process because of the limitation in the minimum size of the ink jet droplets [1,2]. In contrast, nanotransfer printing (nTP) [3–6] is a promising process for the metal patterning of plastic devices. The process of nanotransfer printing is almost the same as that of microcontact printing or nanoprint lithography (NPL) [7,8] except for the fact that in nanotransfer printing, a titanium layer is used as the adhesion layer. First, a polydimethylsiloxane (PDMS) stamp is fabricated by using a casting method. Next, gold and titanium are deposited by using the physical vapor deposition (PVD) technique. This stamp is then placed in contact with polyethylene terephthalate (PET) while heat is applied to stick the metal materials on the plastic. PDMS has a good release property; thus, after cooling and removing the stamp, we could transfer gold and titanium onto the PET substrate. By using this process, Hur et al. have obtained 300-nm dot patterns on PET [4]. However, PDMS is a soft material; hence, it deforms easily and results in the failure of a sub-100-nm resolution transfer. In order to improve the poor resolution, we have developed a hard stamp nanoprint lithography technique using spin-on-glass (SOG). The hardness of SOG aids the fine metal pattern transfer on PET without the need for high pressure, because PET is a soft substrate and fits well and contacts to the hard substrate. Moreover, the PDMS stamp is typically fabricated by silicon molds. In order to fabricate the silicon mold, there are many troublesome processes such a metal lift-off and dry etching. In our process, SOG is used for a positive-type electron beam resist and the obtained SOG pattern is directly available for the nanoimprint mold without the risk of etching [9,10]. This process has enabled the transfer of gold gap patterns with a resolution of less than 30 nm onto the PET surface.

2. Experimental apparatus and procedure

The process of direct printing of metal nanopatterns on PET by using hard stamp NPL comprises the fabrication of a hard stamp, a release coating method, and a transfer process.

The fabrication process of the hard stamp is shown in Fig. 1. Accuglass 512B (made by Honeywell Co.), which is an SOG material, was used for the fabrication of the positive-tone EB resist

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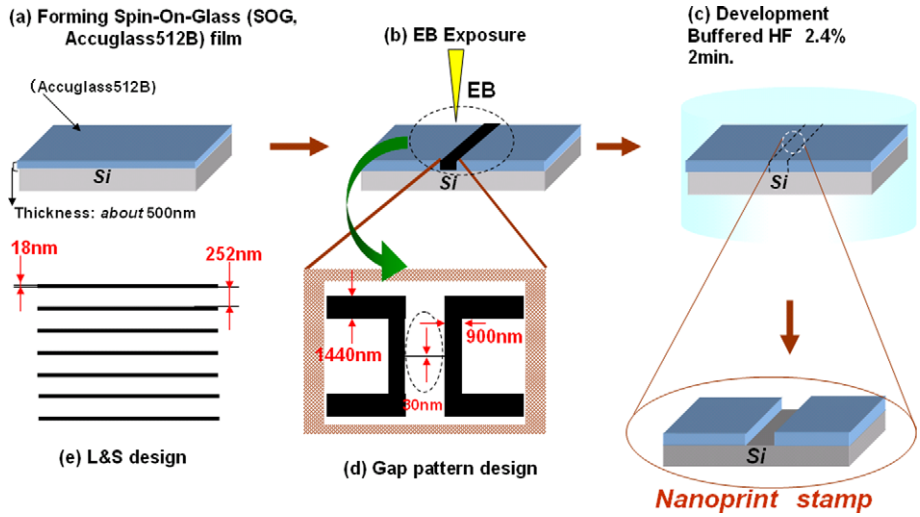

Fig. 1. Fabrication process of hard stamp. (a) Forming the SOG layer on silicon substrate. (b) EBL of SOG layer. The acceleration voltage was 30 kV and electron beam current was 20 pA. (c) Developing with buffered hydrofluoric acid, after which SOG resist layer was used as hard stamp. (d) EBL design gap pattern. (e) EBL design L&S pattern.

and hard stamp [9,10]. Accuglass 512B was spin-coated (pre: 300 rpm (3 s), main: 3000 rpm (10 s)) on silicon substrates. After spin-coating, Accuglass 512B (thickness: around 500 nm) was pre-baked at 425 °C (1 h). Next, a gap pattern was delineated by using electron beam lithography (EBL). The EBL machine was a scanning electron microscope (SEM; ERA-8800FE, Elionix Co.) with a drawing system. The acceleration voltage during the EBL was 30 kV and the electron beam current, 20 pA. The designed width of the gap pattern was 30 nm, and the designed line and space (L&S) patterns had a line width of 18 nm and a space distance of 252 nm. The delineated properties of this gap pattern were examined by changing the electron beam dose. Next, the exposed SOG layer was developed by using 2.4% buffered hydrofluoric acid (BHF; HF:NH_4F = 1:1) for 2 min. After developing this patterned SOG layer, we used it as the NPL stamp.

The developed SOG stamp surface had a poor release property; thus, release coating was necessary. Two types of release coating methods are shown in Fig. 2. One involved the use of a thin layer of Cr as the release layer. A Cr layer having a thickness of around 20–30 nm was deposited on a fabricated hard stamp by using a resistively heated vacuum evaporation system (VPC-260F, ULVAC KIKO Inc.). After coating the stamp with Cr, we ventilated the vacuum evaporation system and replaced the metal source with gold. Then, gold was deposited on the Cr layer at around 60–70 nm. The gold layer was used as the transfer metal layer on the PET substrate. The second release coating method uses a conventional release agent as the release layer [11,12]. HD1101-Z, a type of silane coupling agent made by HARVES Co, was spin-coated (pre: 300 rpm (3 s), main: 3000 rpm (10 s)) on the stamp and cured for 3 min at 80 °C. After that, a gold layer (thickness: approximately 60–70 nm) was deposited on this release agent layer by using the vacuum evaporation technique. An atomic force microscope (AFM: SPM-9600, SHIMADZU Co.) was used for evaluating the surface roughness of the gold layer of both methods.

The transfer process of gold on the PET substrate is shown in Fig. 3. The PET substrate (Sumitomo Bakelite Co Ltd.) with a thick-

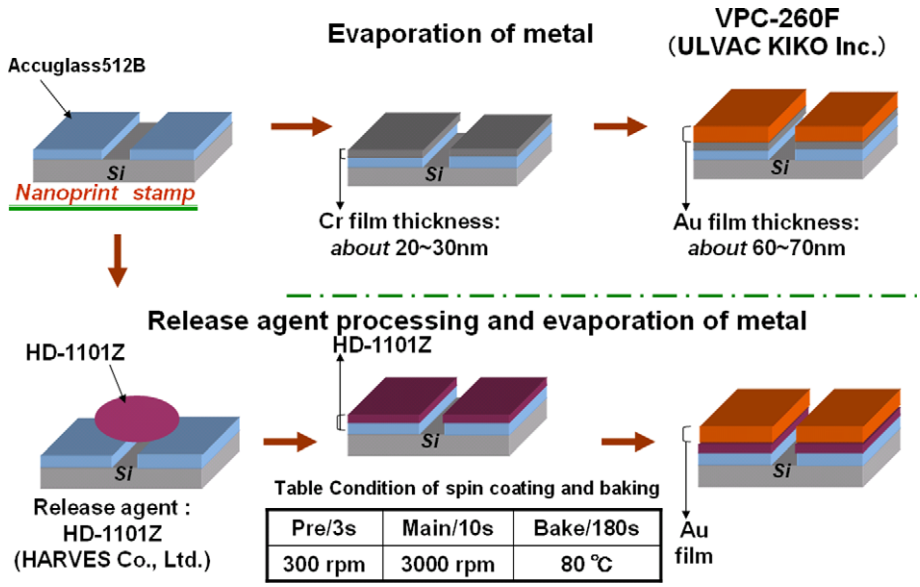

Fig. 2. Two types of release layer formation processes. The upper one uses a chromium layer as the release layer. The lower one uses a conventional release agent as the release layer. In both processes, the top layer formed is gold, and this layer is used for transfer onto PET.