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Preparation of fluoropolymer structures for orthogonal processing of diverse material by Micro-Contact Printing

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ABSTRACT

Micro-Contact Printing (μCP), one of the soft lithography techniques, has been widely used to fabricate patterns of various materials on inorganic or organic substrates because of its low process temperature and pressure. In this paper, using a poly(dimethylsiloxane) (PDMS) mold, poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate) polymer (PFDMA) films is patterned and deposited on various substrates such as silicon wafer, silicon oxide on silicon wafer, glass, poly(methylmethacrylate) (PMMA), and poly (vinyl pyrrolidone) (PVP). Because of the soft nature of PFDMA containing HFE-7500 as a casting solvent, the μCP can be done at room temperature without surface treatment or external pressure. The driving force of μCP of PFDMA is the very low adhesion force of 0.52 mN/m between PFDMA film and PDMS mold compared to those between PFDMA and the substrate materials. For surface energy estimation of PFDMA contact angle measurements are performed and the adhesion forces among various materials are calculated. It can be shown that the solubility of PFDMA in fluorine-containing solvents can settle down the solvent orthogonality problem. A complementary image can be formed by the subsequent embossing of the remaining PFDMA layers in the recess areas of the hard PDMS mold after the μCP processing. Lift-off deposition of Cr lines is demonstrated using the PFDMA polymer structure.

1. Introduction

Soft lithography has been studied extensively as an alternative to photolithography since the early 1990s [1]. Soft lithography can offer low process cost, easy implementation, applicability to various materials, and no limitation of substrate shape and material compared to photolithography. Therefore, this process is used widely in a range of applications, such as microelectronics [2], organic devices [3], and biomedical engineering [4]. Micro-Contact Printing (μCP), one of the soft lithography techniques, is a direct patterning method that can produce residue-free thin film patterns including polymers compared to those produced by the conventional imprint method. The key feature of μCP is that only a designed part of the deposited polymer films on an elastomer mold can be transferred directly to a substrate. Any elastomer can be used to cast a mold, even though most studies have focused on poly(dimethylsiloxane) (PDMS) because of its low cost and ease of fabrication [5]. PDMS has been patterned to be a mold by replication of master but there were other methods of patterning PDMS. Direct writing using MeV proton beam [6] and dry etching [7] have been reported. To achieve the successful transfer of patterned polymer film, the relative adhesion between the film and PDMS mold and film and substrate needs to be controlled carefully. There have been reports that the surfaces of PDMS or substrates have been treated using a range of methods, such as O_2 plasma [4,8,9] or chemical solution [2,8,10]. On the other hand, these surface treatment processes might cause a deterioration of the device properties in organic-based electronics. In addition, the solvent for removing the unwanted parts of transferred polymer films should be chosen carefully to avoid the orthogonality problems which may affect negatively the materials of the underlying organic layers [3,4,11]. This paper reports the μCP process of poly(1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate) (PFDMA) films that can skip any further surface treatment and avoid the solvent orthogonality problems. In addition, we show that PFDMA films can be transferred to a range of inorganic, or organic substrates to fabricate polymer structures for various applications.

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2. Experiment

Hard or soft poly(dimethylsiloxane) (PDMS) mold, the master of replica, was prepared by curing its prepolymer (Sylgard 184, Dow Corning) from the patterned SiO_2 layer on a Si wafer. The PDMS mold has line and spacing patterns with a spacing of 5 μm, a line width of 3 μm and a line height of 1 μm. 1*H*,1*H*,2*H*,2*H*-perfluorodecyl methacrylate (FDMA) and hydrofluoroethers solvent (HFE-7500, 3 M) were mixed at various weight percentage ratios ranging from 1 wt% to 17 wt%. This solution was spin-coated at 1000 rpm for 30 s on PDMS molds. PFDMA films were formed on the PDMS molds after dry at room temperature. The substrates used in this μCP study were inorganic substrates, such as silicon wafer, silicon oxide on silicon wafer and glass and organic substrates, such as poly(methylmethacrylate) (PMMA), and poly (vinyl pyrrolidone) (PVP). Micro-Contact Printing was done by placing the PDMS mold with PFDMA film on the substrates without any pressure at room temperature. After μCP the PFDMA layer still remained in the recess part of the PDMS mold, which was spacing area of the line and space patterns of the mold. We also tried to transfer this negative image of the PFDMA pattern to Si wafer by the standard embossing method. The PDMS mold could be cleaned completely with another hydrofluoroethers solvent (HFE-7300, 3 M) and reused repeatedly.

The surface morphology of the transferred PFDMA films with positive and negative patterns was examined by field emission scanning electron microscopy (FESEM, Hitachi S-4300). The thermal properties of PFDMA were analyzed by differential scanning calorimetry (DSC, Jade DSC, Perkin Elmer) at a heating rate of 10 °C/min. Its hydrophobic nature was confirmed by the contact angle measurement using the sessile drop method (DSA-100, Kruss) with 100 μl droplets of water and ethylene glycol.

3. Results and discussion

The process temperature in μCP is related to the glass transition temperature (T_g) of the transferred materials [12], and is typically between 50 °C and 140 °C. Sometimes, pressure as 294 Kpa was applied to ensure a close contact of the transferred layer with substrates [13]. PFDMA films can be transferred at room temperature without any pressure. Processing at room temperature is quite desirable because any inorganic or thermally fragile organic substrates can be used. Fig. 1 shows the thermal properties of completely dried FDMA by DSC. FDMA exhibited a marked heat

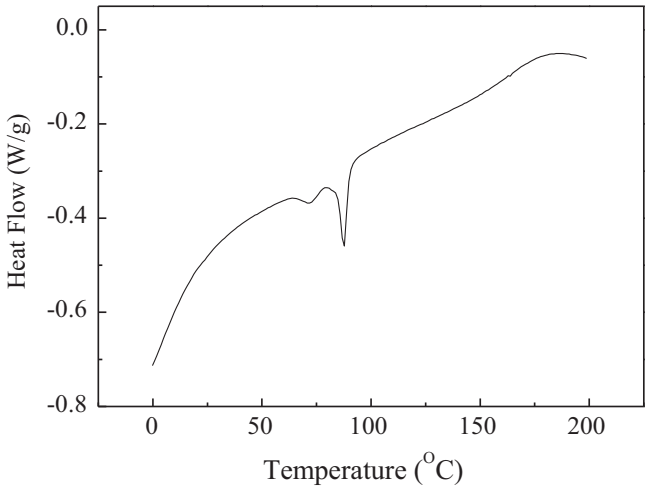

Fig. 1. Differential scanning calorimetry spectrum of 1*H*, 1*H*, 2*H*, 2*H*-perfluorodecyl methacrylate (FDMA).

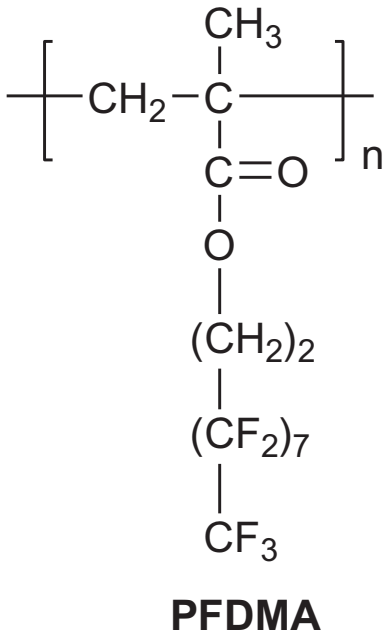

Fig. 2. Chemical structure of PFDMA.

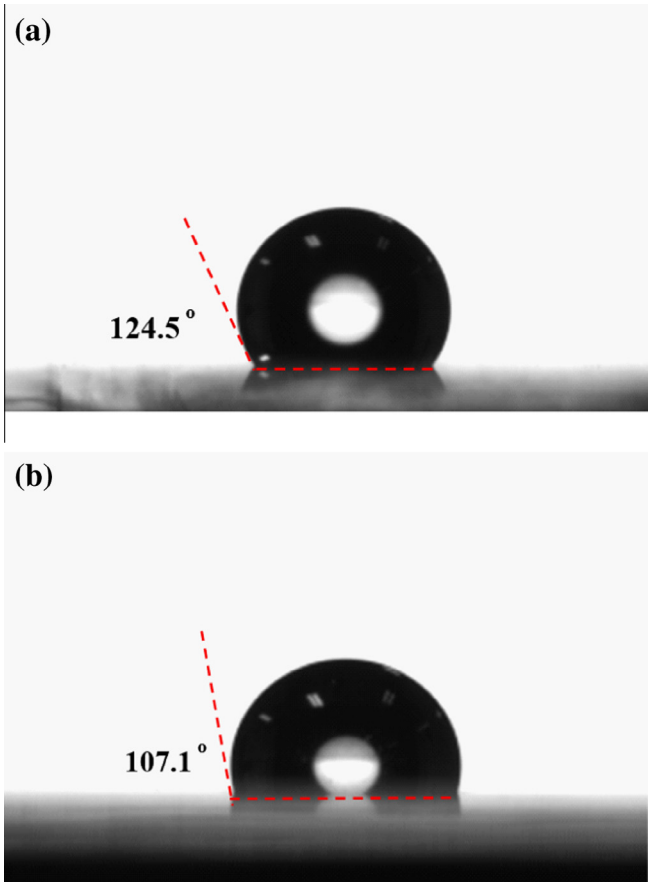

Fig. 3. Contact angles of PFDMA layer using (a) water (b) ethylene glycol.

absorption at 60–80 °C which might be a liquid crystalline phase transition and its melting behavior. However, because a considerable amount of fluorosolvent, HFE-7500, is present in the PFDMA films during the solution casting of PFDMA at room temperature,