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Original Article

Time and pressure dependent deformation of microcontact printed channels fabricated using self-assembled monolayers of alkanethiol on gold

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ABSTRACT

In this work, the replication-based microcontact printing method has been presented to study the deformation effect of different printing times and printing pressures on the microcontact printed structures. Cost-effective microcontact printing channels of self-assembled monolayers of alkanethiol have been prepared on gold surface. The alkanethiol inking the polydimethylsiloxanes stamp effectively forms the self-assembled monolayers on the noble gold surface that protects the metal against etchant solution and thereby forms channel-like structures. To address the deformation issue, variations in the printing time in the range of 30 s–60 min and the printing pressure ranging from 840 to 4200 Pa have been studied. The estimation of differing the channel width and channel space with varying printing time and pressure shows the best resolution structures printed under minimal printing time at atmospheric pressure.

1. Introduction

The rapid miniaturization aspect of electronic components requires the development of patterning techniques to obtain large-capacity and high-speed device functionalities [1–6]. The general trend of these techniques has been towards the versatile, cost-effective and smaller devices in microscopic to nanoscale [7]. Even though the development of transistors addressed the miniaturization aspect by integrating the circuit components, designing circuit for complex functionality was still challenging since manual soldering for connectivity was unavoidable [7,8]. The integrated circuits developed afterward effectively overwhelmed these issues [9,10] embedding different components onto a single chip. In the fabrication of reliably miniaturized electronic devices, conventional photolithography is a prominent technique to initialize patterns of electronic circuits [10,11]. This technique utilizes photosensitive materials, masks, developers and etchants solution to generate a pattern on a substrate, which make the procedures costly [12,13] and time-consuming. Furthermore, the application of this technique is limited to materials sensitive to lights and etchants or some biological recipes that cannot be deposited on the photoresist materials [7].

Microcontact printing (μCP) is a non-photolithographic technique, which is used to transfer the patterned self-assembled monolayers (SAMs) onto a metal or silicon substrate addressing many of the issues limited by the conventional photolithography [7,14,15]. A soft elastomeric stamp made of polydimethylsiloxanes (PDMS) is 'inked' with self-assembled monolayers (SAMs) of functional molecules [16]. The molecules of SAMs from the PDMS stamp are then transferred onto the substrate as a same pattern on the stamp. Thus the patterned SAMs on the substrate can be used as resists for etching or as passivation layers to prevent deposition. Even though μCP was initially introduced to pattern

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gold [17,18], eventually it became popular for other applications on silver [19,20] and copper [21,22] substrates. Since SAMs of functional molecules serve as resist in wet etching to control both the electronic and ionic movement in between the electrolyte and the metal substrate, microcontact printed SAMs have been reported in various applications including the electrode and microarray patterning for the applications in biosensors [23–25], developing lipid bilayers on electrode surfaces [26–29], and also in the adsorption and nucleation phenomena [18,30,31]. The μCP technique has also been found to be utilized in antigen detection, patterning of conducting and semiconducting polymers of organic thin-film transistors, gradients to study cell migration, and protein [32–34].

In μCP, a printing stamp is a key element to transfer microscale pattern onto a metal surface. A number of stamps made of polyurethanes, PDMS, TPT, polyimides have already been reported that provide conformal contact with the surface of the substrate during the transferring of a pattern [35,36]. Among them, PDMS is the most commonly used one so far. Several properties that make PDMS incomparable are the tunable selective ratio of the monomer/cross-linker. It provides the estimated elastic moduli of the PDMS stamp for the specific applications [37]. Moreover, a number of PDMS stamps can be created from a single master without cleanroom environment. But due to the inherent physical properties of PDMS stamp along with its flexibility, the topographical features during the printing process may distort affecting the resolution of the patterned microstructures [38–40]. In this context, time and pressure dependent deformation effect on the polymeric stamp during conformal contact for printing bears a significant importance, which was rarely found. Kumar et al. reported the pattern transfer of alkanethiols onto Au surface by μCP in the early 1990s using a microstructured PDMS stamp [38]. Silanes, lipids, proteins, DNA, nanoparticles are also found to be printed by μCP technique [40] along with alkanethiols on Au. Thiols have been reliably found to form SAMs on the metal surfaces of Au, Ag, Cu, Pd, and Pt because of (i) strong sulfur–metal bond formation (as sulfur is the linking terminal of the alkanethiol molecules), and (ii) strong van der Waals interaction between the molecular backbones of thiol molecules [38]. Printing of alkanethiols on Au surface forms stable, densely packed and ordered crystalline patterned SAMs, which is used as etching masks, whereas Au in the non-contacted areas can be etched away to yield Au patterns on the underlying glass or polyethylene terephthalate (PET) substrates [38].

In this work, alkanethiol has been used as ink to prepare the cost-effective μCP. The total μCP has been executed in three key steps including (i) the fabrication of master structure onto a silicon substrate via standard optical lithography, (ii) the production of patterned PDMS stamp using the master and Sylgard material, and (iii) the transferring of patterned structure from PDMS stamp onto the Au surface on PET substrate inking the stamp with alkanethiol solution. PET is a cost-effective, excellent moisture barrier material in the form of flexible and semi rigid to rigid with good chemical resistance except to alkalis [41,42]. The coverage area on the Au surface by alkanethiol SAM during the conformal contact was protected during etching and the removal of the no-contact area provides the structures as patterned onto the printing stamp. To study the deformation effect on the microstructure initiated by μCP, printing time and applied pressure on the PDMS stamp during pattern transfer have been systematically varied. Finally, the deformation effect was estimated from the average width and space of the scanning electron microscopy (SEM) image of the prepared channel structures.

2. Principles, materials and methods

During contact printing, the conformal contact between the inked stamp and surface of the substrate is a major user concern for the high-resolution of the transferring patterns. This conformal contact is mainly influenced by the flexibility of the elastomeric stamp. The flexibility of the stamp can be tailored by the proper selection of elastomer materials, controllable applied pressure on the elastomeric stamp during printing, and a systematic variation of the printing time. A PDMS stamp is generally fabricated by replica molding technique as shown in Fig. 1. The major demerit of PDMS is that it may affect the printing resolution by the deformation caused by the gravity, adhesion and different forces exerted on the PDMS stamp during printing. Also, Fig. 2 shows the schematic view of regular and distorted microcontact printed patterns because of any of the issues affecting the regular flexibility of the PDMS stamp.

In preparation, a commercially collected Si substrate has been used as a substrate to prepare master for PDMS. A thin uniform layer of negative photoresist SU-8 obtained from Sigma Aldrich was spin coated on the properly cleaned Si substrate and baked at 90 °C for 4 min. Then the sample was exposed to UV source for 30 s, pre-baked at 95 °C for 2 min and chemically developed. After developing, the samples were rinsed with DI water, dried and post-baked at 95 °C for 5 min. A mixture of elastomer and curing agent (with 10:1 ratio) was prepared and kept inside the desiccator to get bubbles out. The solution, thus prepared, was then poured on the developed pattern on the Si substrate, cured inside an oven at 70 °C for 60 min and again cooled for more 60 min. Releasing of the developed pattern from the prepared mold after 60 min provides the PDMS stamp as shown in Fig. 1.

Fig. 2 corresponds to the schematic procedure for microcontact printing on Au using alkanethiol SAM as an ink including regular and distorted patterns of SAM [43]. Firstly, Au of 100 nm thickness was sputtered on the PET substrate. Afterward the PDMS stamp was inked with few drops of 5 mM alkanethiol solution and dried, the thiol inked PDMS stamp was then placed on the UV ozone cleaned Au layer [44]. Finally, etching of the unaffected area of the Au surface during stamping using gold etchant provides a patterned channel of microcontact printed SAM of alkanethiol on Au [45]. The study of the effects of printing time and printing pressure on the PMDS stamp to the resolution of the transferred pattern has been executed with some electrode patterns prepared by following the same procedures. And during printing, a systematic variation of printing time of 30 s, 1 min, 5 min, 10 min and 60 min at atmospheric pressure and custom made metal blocks to apply pressure on the printing stamp at a constant time of 30 s have been adopted. Finally, the microstructures of Au, thus prepared, were studied under scanning electron microscopy (SEM).

3. Results and discussion

3.1. Scanning electron microscopy (SEM) imaging

For SEM imaging, the patterned electrodes were washed using acetone and DI water several times and dried using N_2 gas to remove the contamination from the sample surface, and dried for 2 min on a hot plate. The patterns of the microcontact printed Au microstructures resulting from the etch examined using SEM (Hitachi S-4000) and SEM images were acquired on photographs to quantify the average electrode channel width and space of the structures.