Nanofabrication via direct transfer of BOE treated PDMS stamp patterns onto SiO$_2$ surfaces

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Abstract. Various PDMS patterns with a few microns to sub-micron size and thickness of 20~30 nanometers were successfully transferred on the substrate via simple printing process of a buffered oxide etchant-treated PDMS stamp on the SiO$_2$ substrate. The patterned PDMS layer acted as sacrificial layer for metal-film patterning and as chemical passivation layer for the selective adsorption of V$_2$O$_5$ nanowires. In particular, the electrical measurement of the patterned V$_2$O$_5$ nanowire network showed the semiconducting non-ohmic behavior in the channel.

1. Introduction

Soft lithography replacing conventional lithography technique has been studied in the field of micro and nano fabrication owing to its simplicity and applicability to the large-area patterning [1]. Among the various soft lithography techniques, micro-contact printing technique using a PDMS stamp has been used in patterning of molecules, nanomaterials [2, 3] and biomaterials [4], according to the shape of the PDMS stamp. Recently, decal transfer lithography (DTL) [5] and Light stamping lithography (LSL) [6], the methods that PDMS itself was transferred on the substrate along the shape of the stamp without using inks, were developed. PDMS surface modified by ultraviolet-ozone or ultraviolet light made chemical bonding between the PDMS and the Si surfaces. When the PDMS stamp was peeled off from the substrate, the contacted PDMS was left on the substrate. As a result, thin PDMS patterns were transferred on the substrate. Such transferred PDMS worked successfully as physical and chemical passivation layers over reactive ion etching [5] and atomic layer deposition processes [6].

In thin work, we will introduce a much simpler method than the previously reported techniques for transferring of PDMS pattern, where only the printing of buffered oxide etchant (BOE)-treated PDMS stamp was involved. PDMS patterns on the SiO$_2$ Substrate with various shapes and sizes could be obtained without any complicated and expensive equipments such as UV-ozone generator. The patterned PDMS layer could be utilized as physical and chemical passivation layers for patterning of metal thin film and V$_2$O$_5$ nanowires. The electrical property of the patterned nanowire channel showed a semiconducting non-ohmic behavior.

2. Experimental section
3-Aminopropyltriethoxysilane (APS) (Aldrich), tetrabutylammonium fluoride (TBAF) (Alfa Aesar), Poly (dimethylsiloxane) (Dow corning Sylgard 184) and Buffered Oxide Etchant (BOE 30:1 JT baker) were purchased and used without further purification. Replica molding was used to make PDMS stamps, from master pattern fabricated by photo lithography. 300 nm thick SiO₂ layer was thermally grown on p-type Si(100) substrate by wet oxidation. V₂O₅ nanowire sols were prepared following the previously reported recipe [7]. Nanowires grown for 6 months were used in this experiment. Optical microscope images were captured by Olympus BX41M, and all the AFM images were obtained with XE-100 (PSAI) and analyzed by XEI 1.5 software (PSIA). An electrical property of V₂O₅ nanowire channel was characterized by HP 4140B.

3. Result and Discussion

Figure 1 shows the schematics of patterning of PDMS layers using the BOE-treated PDMS stamp (A), subsequent metal deposition (B) and the selective adsorption of V₂O₅ nanowires (C) using the transferred PDMS as passivating layers.

First, we immersed the patterned stamp in a Petri-dish containing BOE solution for 5 minutes and pulled it out vertically and slowly to prevent forming of BOE drop on the stamp. The residual BOE solution on side wall of the stamp should be removed by paper towel. Otherwise, the residual solution would flow to the substrate and etch it. The BOE-treated stamp was put on the substrate for 3-5 min and then pulled off. However, the stamp on the substrate was not easily detached due to strong adhesion between the PDMS surface and the substrate. Therefore, the residues of PDMS stamp remained afterwards, resulting in the selective transfer of the pattern like the peeling off in DTL and LSL processes. The region printed by the stamp was not wet by water and showed hydrophobicity of the intrinsic PDMS.
AFM images of Figures 2(a)-(d) show that PDMS patterns were successfully transferred, regardless of the shape and the sizes of the stamp patterns. The index ‘a/b’ on the top-right corners of the AFM images represents the (separation)/(line width) for line patterns and the (separation)/(side length) for square pattern. Figs. 2(e) and (f) show the line profiles in Figs. 2(a) and (c), respectively. We could fabricate the various PDMS patterns with widths of a few μm to 600 nm and thickness of about 20 nm.

The PDMS layer could be used as sacrificial layer in fabricating microstructures of metal films, such as photoresist in photo-photography. Figure 3 shows the optical microscope (a, b) and AFM (c) images taken from the metal structures made following the step shown in Fig. 1(B). The Cr(a) and Ti/Au(b, c) was deposited on the patterned substrate by using e-beam evaporation under the pressure of $2 \times 10^{-6}$ torr and then the sacrificial PDMS layers were removed by immersing it in 1 M TBAF/THF. The metal structures were made according to the shape of the original PDMS pattern. The thickness of metal structure is about 20 nm and it could not exceed that of the patterned PDMS layer on the substrate. However, such problem can be overcome by combining with the conventional lithography technique such as RIE process.

We also manufactured PDMS/NH2 chemically functionalized patterns by printing a BOE treated PDMS stamp on an APS treated substrate. Figure 4 (a) shows V$_2$O$_5$ nanowires selectively adsorbed on amine-functionalized regions obtained in the process of Fig. 1(C).
It is known that V$_2$O$_5$ nanowires are adsorbed on NH$_2$-functionalized surfaces in the solution of acidic condition. This result is similar to the selective adsorption behavior on the 11-amino-undecanethiol region of amino-undecanethiol / octadecanethiol functionalized surface [8] and shows that a patterned PDMS layer on the substrate can serve as a chemical passivation layer such as alkanethiol or alkyltrichlorosilane monolayer used in V$_2$O$_5$ nanowire adsorption processes. To characterize electrical transport through the V$_2$O$_5$ network channel, the electrode structure of Fig. 4(b) was fabricated by using metal mask. Two Ti/Au electrodes were deposited by e-beam evaporation process. The channel length and the width of this structure are 49 μm and 1 mm, respectively.

Fig. 4(c) shows a representative current-voltage characteristic curve with a significant hysteresis. The larger current was observed for the case of the increasing direction than the decreasing direction. The application of the voltage bias can induce the alignment of the dipole molecules such as waters (H$_2$O) [9], resulting in the barrier lowering of the contact barriers [10]. Because the inversion of the aligned dipole layer requires the energy, the hysterical I-V curve can be possible. But the further systematic studies are more required.

4. Conclusion

In this paper, we proposed a very simple and selective pattern transfer technique using BOE-treated PDMS stamp. Various PDMS patterns with a few microns to sub-micron sizes were successfully transferred on the substrate via printing the BOE-treated PDMS stamp on the SiO$_2$ substrate. The patterned PDMS layer acted as sacrificial layer for the metal patterning and as a chemical passivation layer for the selective adsorption of V$_2$O$_5$. In particular, the electrical measurement of the V$_2$O$_5$ nanowire channel shows that the nanowires in network were electrically connected between the two electrodes with a semiconducting non-ohmic behavior. This fabrication method using BOE-treated PDMS stamp printing can be applied to the fabrication of the sensor device using a V$_2$O$_5$ nanowire.

5. Acknowledgments

This work was supported by the Ministry of Science and Technology (Grant No. M10503000187-05M0300-18710), Basic Research Program of the Korean Science and Engineering Foundation (Grant No. R01-2005-000-10648-0 (2005)) and Korea Research Foundation (Grant No. KRF-2004-005-C00068).

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