Nano-scale height manipulation in sputter-deposited photolithographic patterns

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A sequential combination of thermal oxide growth, photolithography, buffered hydrogen fluoride (BHF) etch, sputter deposition and lift-off process were used to produce square-shaped nano-islands of gold and silica grid patterns on a doped silicon support. This nanofabricated surface was characterized by profilometry, optical microscopy, atomic force microscopy (AFM) and cyclic voltammetry (CV). The height difference between gold and silica was tailored to be ~ 35 nm. This kind of chip can be used as bio-sensors for detecting various metalloproteins grafted on gold islands, as well as caged analyte molecules inside the protein, from their corresponding electrochemical read-out.

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1. Introduction

Well-defined precise patterns of surface-immobilized proteins with patch sizes in the micrometer range can be produced by a number of established techniques and have attracted wide interest for applications such as biosensor chips [1-3], tissue engineering scaffolds [4,5], cell-based sensor concepts [6-8], microarray technologies for genomics and proteomics, medical diagnostics, molecular electronics [9-11] as well as control of cellular adhesion, growth and functionality [12, 13] and bacterial detection [14]. Biologically designed patterns in the sub-micrometer or nanometer range are more difficult to produce.

Several ways of micro/nano fabrication can be found in literature. The most commonly used serial methods are electron-beam writing [15], focused ion-beam [16,17] and scanning probe based lithography [18,19]. The main disadvantages of these delicate methods are high cost and long writing time, and thus lack of scalabilty (although techniques like dip-pen nanolithography or DPN, a method to deposit molecules having chemical affinity with substrate by using dip-coated AFM tips, can be improved by using multiple inkers [20]). The most widely accepted parallel techniques include microcontact printing or μCP (a method where elastomeric polydimethyl siloxane (PDMS) stamp is used to transfer molecules of the "ink" to the surface by contact – polyolefin plastomer or POP stamps showing better performance [21], a techniques originally proposed to fabricate self-assembled monolayers or SAMs of alkanethiolates onto gold [22] but soon applied to protein patterning on surfaces [23-26]), "controlled" colloidal lithography [27], X-ray interference lithography [28] and nanoimprint lithography (NIL) [29-31]. Direct printing of proteins using elastomeric stamps as used in μCP (''top-down" approach) in combination with a background passivation against non-specific protein-binding ("bottom-up" approach) is a very popular technique for creation of protein patterns [25, 32, 33]. However, submicron structures of arbitrary geometries are difficult to achieve reproducibly [34]. Moreover the final transfer of the protein patterns to the substrate is delicate and often causes stamp sagging for submicron features, in addition to deformation of protein native structure [35]. Although NIL is capable of producing nano-scale resolution that may rival with DPN or e-beam patterning, but the method requires specialized processes like reactive ion etching (RIE).

A whole new world of planar devices has been opened up nowadays, with the advancement in fabrication methods fueled by semiconductor and microelectronics industry. This paper reports the process of nanofabrication on doped silicon wafer using lithographic techniques, to make a device which can be used by protein chemists for electrochemical measurements. This fabrication is particularly advantageous due to experimental simplicity, low-cost, scalability and generalized application.

The aim of this nanofabrication was to obtain square gold islands separated by silica regions all on silicon wafer and to establish electrical connection from a specific gold island thru the backside of the wafer. This kind of device is specifically targeted for scientists working with thiolated metalloproteins with redox metal centers. A bunch of papers can be found on de-novo design of helical bundle proteins and subsequent intra-molecular electron transfer [36-38], effect of distance and driving force on electron transfer rates thru redox proteins [39] and pathways models of protein electron-transfer [40]. The idea is to place different protein solutions in different gold islands for anchorage, protein molecules being spatially confined by PEG molecules adsorbed on silica regions and to measure the current due to electron-transfer thru these different proteins. This kind of electrochemical read-out may also be helpful in detecting small analyte molecules present inside the metalloprotein cavities, a realistic

example being detection of glucose level in human body and hence can be used as bio-sensors.

2. Materials and methods

The process for obtaining gold-silica patterned surface can be outlined as shown in the schematic diagram (Fig. 1). p-doped Silicon wafers (<100>, 381-483 microns thick, 0.025-0.1 ohm-cm resistivity, 4 inch diameter, Nova Electronic Materials Inc.) were wet oxidized to grow a ~650 A thick oxide layer in a high temperature furnace at 950 ^{o}C for 5.5 hrs. Adhesion Promoter HMDS-X20 (0.5 ml) and Positive Photoresist (Microposit SC 1827, Shipley Co. Marlborough, MA) (1ml) were subsequently spin-coated at ~3000 RPM for 60 sec each, using a Spin Coater (Model WS-200-4NPP, Laurell Technologies Corporation) and soft-baked in an oven at 93 ^{o}C for 5 min.

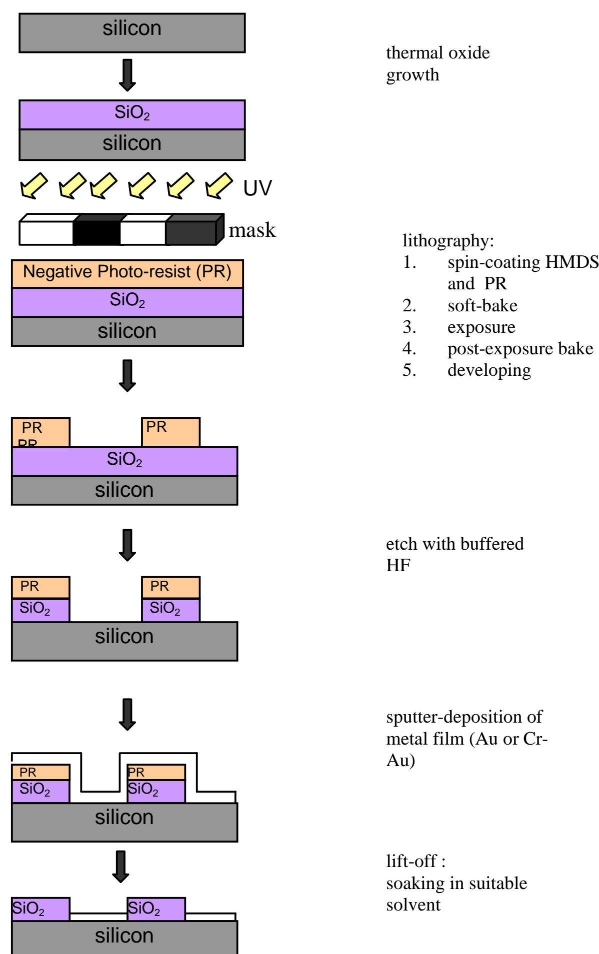

Fig 1. Schematic diagram of the entire process for obtaining gold-silica nanopatterned surface

A home-made lithographic apparatus was used to expose the wafer to mercury lamp (i-line, 365 nm) for 15 sec with TEM grids acting as photo-mask [41]. *No post-exposure bake* was necessary (unlike negative photo-resist). The wafer was developed in MF 319 solution (Shipley Co.) for 2.5 min to complete the lithography. This patterned surface was etched with 10:1 BOE (Buffered Oxide Etchent from Transene Company Inc. containing 40% ammonium fluoride, 5% hydrogen fluoride and 55% water) for 13 min, rinsed with millipore water and dried. A chromium (Cr) thin film was sputter deposited on the wafer (3 min) as an adhesion layer followed by a gold (Au) film (17 min) using Technics Hummer II sputter coater operated at 65 mTorr in Argon, 2 m Amp current and 10 kV power. A lift-off was performed thereafter by immersing the wafer in acetone for 5 hrs, *no sonication* (for silica-silicon sample) and for 27 hrs, fresh solvent after initial 9 hrs, *only 1 min sonication* (for silica-Cr and silica-Cr/Au bilayer samples). Finally the wafer was rinsed with millipore water and dried.

Characterization methods involved use of Dektak 3030 Surface Profilometer VEECO, Optical Microscope Olympus SZX12, Nanosurf easyScan 2 Atomic Force Microscope (AFM) and HP 4275A multi-frequency LCR meter with HP-VEE software for Cyclic Voltammetry (CV) measurement.

3. Results and discussion

A positive photo-resist, SC 1827 (propylene glycol monoethyl ether acetate 67 wt%, novolac resin and photoactive compound 33 wt%) was used for this work, where the exposed parts of resist becomes soluble after development (unlike negative resists where the exposed portion gets cross-linked forming high MW compounds); producing gold islands separated by silica grid-pattern. Positive resists are costly but are known to produce better resolution; although polyhydroxystyrene based negative resists (used by the author before) are known to be resolution-wise good enough (devoid of swelling problem) [42].

The thickness of silica layer was measured after thermal growth by ellipsometry, which agreed with the theoretical growth rate curve [43]. From the surface profile after BHF etch (not shown), where the silica patterns still have the PR on the top of it, the mean height difference was found to be 35,466 $\mathring{A}$. Lift-off process means basically stripping off the resist, hence the hypothesis was that it can be performed right after BHF etch and Cr (only) deposition to find out the height difference between silica-silicon and silica-Cr respectively. Fig 2 (a) shows the surface profile of silica-silicon pattern with a mean height difference of 65.5 nm, which supports the ellipsometric results obtained earlier (64.6 nm). Both silica and silicon has a silvery appearance which is reflected in the corresponding optical microscope image (not shown). Fig 2 (b) shows the surface profile of silica-Cr pattern with a mean height difference of 59.3 nm, making the thickness of Cr layer as [65.5-59.3] = 6.2 nm. Fig 2 (c) and Fig 3 represents the surface profile and optical microscope image of the silica-Cr/Au pattern respectively. The mean height difference was found to be 34.3 nm, making the Au

thickness as [(65.5–34.3)–6.2] = 25.0 nm. Based on these results, the metal deposition rates were found to be 2.1 nm /min for Cr and 1.5 nm /min for Au, which is quite consistent with the calibration curves obtained by the author before.

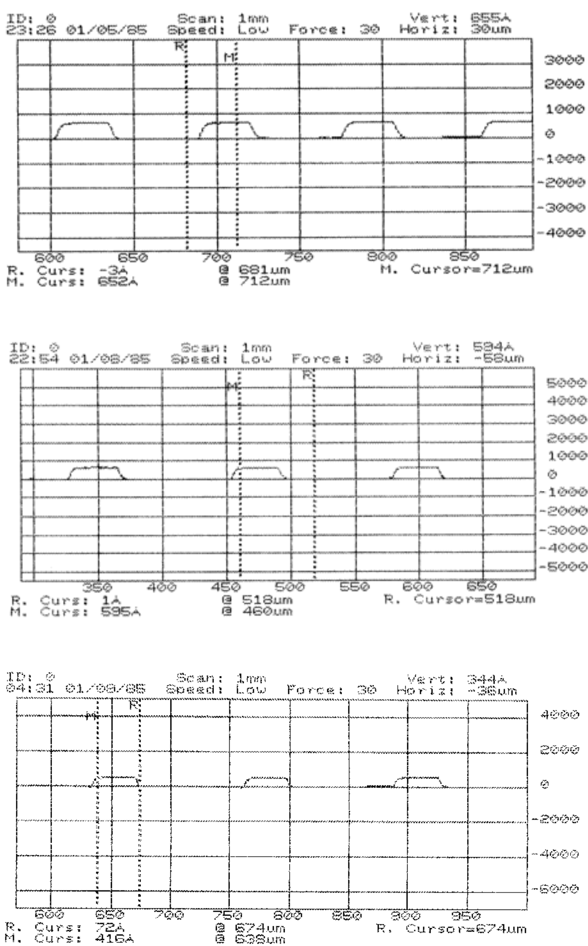

Fig 2. Surface profiles after lift-off with acetone leading to patterns of (a) silica-silicon (b) silica-Cr (c) silica-Cr/Au bilayer.

A height difference of ~35 nm was required for this particular project, assuming the grafted protein and PEG molecules to be in upright configuration; although this height difference can be tailored according to the protein molecules under investigation just by varying the times of metal deposition.

For protein grafting the gold surface needs to be atomically flat or ultraflat, which was verified by surface roughness measurement with AFM (Fig 4). The gold regions were found to have an average roughness of 3.57 nm and a root-mean-square roughness of 4.17 nm over a 1 μm^2 area.

Fig 3. Optical microscope image after lift-off with acetone for the fabricated end-product (pattern of silica-Cr/Au bilayer).

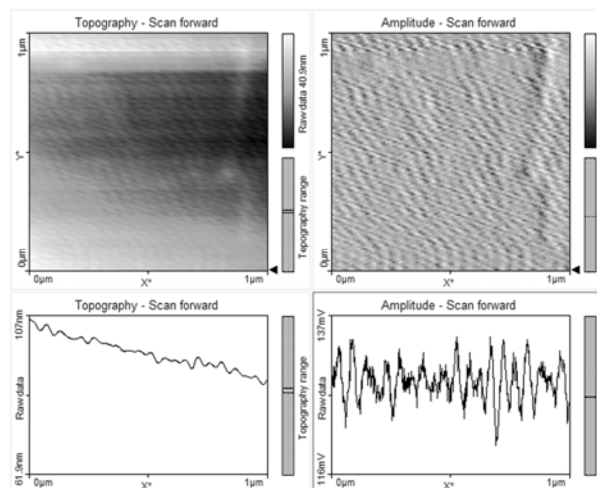

Fig 4. AFM image showing the flatness of a gold island

A suitable nano-dispensing technique is required to place necessary volume of protein solutions on those tiny little gold islands, although the hypothesis of electrochemical study was checked by preparing a larger gold island and performing CV measurements with simple electrolytic solution. For this a doped silicon wafer was taken, Cr and Au was sputter-deposited successively (for 3 min and 17 min respectively) and then only a portion on the backside of the wafer was scratched with a diamond-pen (to remove oxide). After that, the backside was sputter-deposited again with Cr and Au successively (5 min and 20 min respectively) just to make that side conducting. Then 200 μl of freshly prepared NaCl solution was taken on the top-side of the wafer (which can be imagined just as an enlarged gold island) and CV measurements were performed (not shown) with and without the NaCl solution, to check the electrical conductance.

4. Conclusion

The preparation of this nanofabricated chip with gold islands and silica grid-patterns and its subsequent characterization by profilometer, optical microscope, AFM and cyclic voltammetry confirms its application potential as a biosensor.

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