



Metal microelectrode nanostructuring using nanosphere lithography and photolithography with optimization of the fabrication process

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ARTICLE INFO

Article history:

Received 21 May 2012

Received in revised form 15 April 2013

Accepted 19 April 2013

Available online 3 May 2013

Keywords:

Surface patterning

Nanosphere lithography

Nanofabrication

Nanostructured microelectrodes

Bimetallic microelectrodes

ABSTRACT

Nanostructured metal microelectrodes were fabricated using a combination of nanosphere lithography, conventional photolithography and physical vapour deposition techniques. Specifically, Pt and Ag microelectrodes, patterned by hexagonal nanotriangular Ag arrays were prepared, introducing Ag and bimetallic Ag on Pt microelectrode nanostructured systems. Enhancement of surface hydrophilicity was achieved via electric discharge on the electrode surface or via physicochemical interactions (dipping the substrates into NaOH solution). Following removal of the nanospheres, uniform hexagonal arrays of metal nanostructures were revealed and characterized by scanning electron and atomic force microscopy analysis. Parameters relevant to the self-assembly of the colloid arrays and the fabrication methodology employed is discussed with respect to process optimization.

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1. Introduction

Developments in nanotechnology, driven by size dependent properties and interactions in the nanoscale regime are leading towards smaller devices with functional highly ordered nanostructured arrays. However, nanofabrication techniques such as photolithography have limited resolution due to diffractive effects, whereas methods such as electron beam lithography are serial and of high cost. Nanosphere lithography (NSL) or colloidal lithography is an alternative, simple, low cost and versatile fabrication tool which can produce well ordered periodic particle array (PPA) surfaces on the nanometre scale. The NSL process, involves the self-assembly of a closed packed monolayer or multilayer structure which may be used as a mask template for deposition of the desired material in the interstices between particles. When the process is used for depositing metals, the subsequent removal of the nanosphere monolayer post thin film deposition usually reveals a 2D array of triangular shaped nanostructures in a hexagonal pattern (Fischer pattern [1]).

One of the main drawbacks of NSL is its limitation to certain substrates such as glass and Si where it is vastly applied, while applications on indium tin oxide [2], mica [3] and ultraflat Au [4] surfaces

are also reported. Recently, an effort of nanostructuring graphene has been presented [5] while a study which utilizes a Cr interlayer between a metal substrate and the nanosphere array has been published illustrating the aforementioned difficulty in the applicability of the method on metal substrates [6].

Applications of nanosphere lithography benefit from size-dependent optical [7,8], magnetic [9], catalytic [10], thermodynamic [11] and electrochemical properties [12] of nanostructured arrays and in particular, the use of transparent conducting oxides can be beneficial in terms of both their optical and electrochemical properties [13,14]. These applications may vary from controlled plasmonic nanostructures for surface enhanced Raman scattering studies [15] and nonlinear optical materials [16,17] to photonic band gap structures [18], hydrophobic [19], amphiphobic and amphiphilic functionalization of surfaces [20,21] antireflective arrays and solar cells [22], data storage media [23], biosensors [24,25] and recently metamaterials' fabrication [26].

In terms of electrochemical properties, the ability of the method to reliably control the size and morphology of the surface on which it is applied can provide numerous advances in the field of electrochemical sensors, by drastically influencing the electrode surface area. Desirable surface patterning may lead to various improvements including an increased surface area to volume ratio, decreased impedance, sensitivity enhancement, thermal stability, catalytic effects, increased diffusion rates, increased selectivity, lowering of the oxidation potential, signal amplification and faster reaction-response times. Additionally, the presence of metal nanoparticles can provide electrochemical reversibility for redox reactions that could not be obtained on the bulk metal electrode. Such nanostructured metal electrode systems prepared using

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the NSL technique are not widely reported in the literature as yet with some publications on transparent (ITO) conducting surfaces appearing recently [27]. Direct applications may be applied to neural recording electrodes [28], solar and fuel cells [29,30], Li-ion battery systems [31,32], and electrochemical biosensors [33,34]. Nanopatterning can also enable selective cell adhesion on electrode surfaces [35] or alter surface physical properties such as wettability [36] during hydrodynamic flow in micro- and nanofluidic channels.

In this research, the fabrication and nanostructuring of metallic and bimetallic thin film disc shaped microelectrodes using an improvisation of the method of nanosphere lithography and cleanroom techniques are presented. These nanostructured microelectrodes can serve as promising functional systems in the field of electrochemical sensing.

2. Materials and methods

The microelectrodes were fabricated on standard Si (100) wafer substrates using Cr/Pt and Cr/Ag as substrate materials. Organic residues and native silicon dioxide were removed from the surfaces with RCA-1 process and HF dip. The wafers were thermally oxidized in order to grow a SiO₂ layer of thickness ~1750 Å. Microelectrode discs with diameters of 200 μm and 300 μm were patterned with positive photolithography using a Quintel Mask Aligner Model Q4000. Subsequently a Cr layer deposition of approximate thickness 25 nm which acted as an intermediate layer for the growth of Pt and Ag thin film active layers, took place in the Kurt J. Lesker PVD 75 vacuum system. Depositions of Pt and Ag electrode systems were performed by DC sputtering and thermal evaporation respectively. The base pressure of the system was 1.3×10^{-5} – 1.7×10^{-5} Pa. Sputtering was performed under flowing Ar gas atmosphere of 0.4 Pa at room temperature whereas the thickness of Ag and Pt thin film layers ranged from 120 nm to 200 nm as measured using a quartz resonator microbalance.

Three alternative procedures depicted schematically in Fig. 1, were followed for the patterning of microelectrodes with NSL process in order to estimate the best methodology for efficient nanopatterning. In the first (Fig. 1a), the lift-off process of the photoresist layer took place following the nanosphere layer formation and metal deposition, whereas in the second the microelectrodes were fully prepared and passivated with an insulating protective layer of SU8-5 over the substrates prior to their coating with the colloidal particle solution (Fig. 1b). In a third case, the nanostructuring of the electrodes was attempted prior to the passivation process but after removal of the first photoresist layer (lift-off process) (Fig. 1c). The substrates were cleaned with acetone, isopropanol, ethanol and distilled water and sonicated where possible.

The Ag and Pt- microelectrodes were immersed in saturated NaOH solution for time periods ranging between 60 and 120 s, washed with deionized water and dried under nitrogen flow. Alternatively, a frequency generator was used over the substrate for a time period of approx. 3 s at a 5 cm distance from the substrate surface. Immediately after each process, aqueous polystyrene (PS) colloidal bead suspensions were drop coated and spread over the electrode area and left until the solvent was completely evaporated. Pure ethanol, 20 vol.% to 40 vol.%, was added to the solution of beads in order to increase the particle's mobility during the evaporation process. The final concentrations of the PS suspensions were selected to be 0.71 wt.% for the 1020 nm, 0.47 wt.% for the 456 nm and 0.31 wt.% for 200 nm diameter beads whereas each electrode was covered with a small drop of 1.5–2.0 μl.

The whole procedure took place in a controlled environment (cleanroom facilities) where the samples were placed in a tilted sealed chamber and left to evaporate at 12 °C. Post formation of the colloidal mask, thermal evaporation of Ag was performed where the microelectrodes were rotated at a constant velocity of 20 rpm, resulting in a layer of thickness in the range of some tens of nanometres and up to

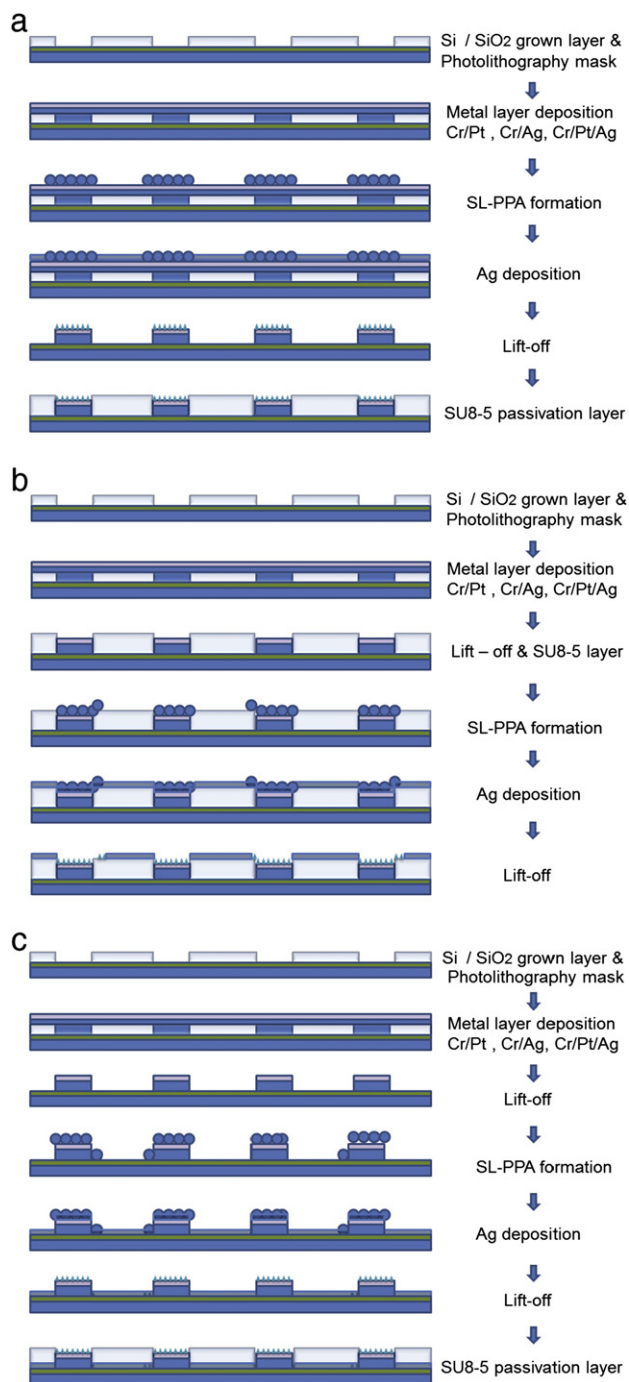


Fig. 1. a, b, c. Top to bottom description of the fabrication processes utilized for the nanostructured microelectrode systems.

250 nm. The coated electrodes were sonicated in acetone or isopropanol to remove the colloidal mask.

Deposition targets, pellets or granules of Cr, Ag, and Pt (99.99%) were purchased from Testbourne (UK) whereas the Polystyrene beads were purchased from Polysciences GmbH (Germany). Photoreactive polymers were bought from Chestech (UK) and all chemicals used were purchased from Sigma Aldrich (Ireland). Scanning electron microscopy (SEM) characterization was performed on the Jeol system JSM-6390 LV at acceleration voltage ranging between 10 kV and 30 kV and Atomic Force Microscopy (AFM) measurements were taken on an Agilent 5500 AFM in Acoustic AC mode using standard NCH cantilevers from NanoSensors. Contact angle (CA) measurements were

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