Templated Fabrication of Nanowire and Nanoring Arrays

Combinatorial Polymer Libraries
Templated Self-Assembly of Block Copolymers
TiO$_2$(B) Nanowires as Battery Anode Materials
Templated Fabrication of Nanowire and Nanoring Arrays Based on Interference Lithography and Electrochemical Deposition**

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Lithographically defined arrays of metallic or semiconductor nanorings with feature sizes in the sub-100 nm range have attracted great attention recently, because of their unique magnetic,[1-15] optical,[16] or electrical properties. Several fabrication methods for ordered arrays of ring-shaped structures have been developed.[13-15,17-26] Conventional structuring techniques such as photo- and electron-beam lithography (EBL) are limited in spatial resolution and low throughput, respectively. Alternatively, low-cost template-based synthesis approaches for ring-shaped nanostructures have been developed very recently. For example, arrays of metallic nanorings have been fabricated via self-assembled polymeric nanospheres positioned on planar substrates. In this case, metallic thin films were first deposited onto the nanospheres. Subsequently, the metallic nanorings were obtained by ion-beam bombardment and removal of the nanospheres.[18-22]

However, the arrangement of the nanorings fabricated by these approaches is often random, or ordered in small areas only when self-ordering strategies have been applied for the nanosphere assembly. Membrane structures were also utilized for the fabrication of ring arrays such as porous anodic alumina oxide (AAO)[23,24] and nanochannel glass (NCG).[25] They are scalable and suitable for the fabrication of large, ordered arrays of circular nanorings. On the other hand, the template preparation on a large scale is not straightforward. In the last two years, much attention has been drawn towards elliptical magnetic rings[13-15] with an in-plane magnetic anisotropy for potential application in magnetic random access memory (MRAM) devices. These magnetic nano-objects have been intensively investigated by the C. A. Ross group at Massachusetts Institute of Technology and were generated by conventional EBL. Except for conventional lithography techniques, no efficient fabrication method has been reported so far on large-scale arrays of elliptical ring structures.

A very different fabrication approach for lateral nanowire arrays based on a bottom-up technique called electrochemical step edge decoration (ESED) has recently been reported by Penner and co-workers.[27-30] Highly oriented pyrolytic graphite (HOPG) was used as a template substrate for electrochemical deposition of hemicylindrical nanowires on the atomic step edges with diameters ranging from 10 nm to 1 μm. However, the step edges of HOPG are not perfectly aligned; therefore electrodeposition of perfectly ordered nanowire arrays is not feasible. Furthermore, deposition of nanoparticles occurs frequently on the graphite terraces.

Here we report a large-scale fabrication technique for ideally ordered lateral metallic nanowire or nanoring arrays over wafer-scale areas. Our approach is based on the generation of Si₃N₄ nanohole arrays or grating structures on silicon wafers by laser interference lithography (LIL) and the selective electrochemical deposition on the step edge of periodic Si₃N₄ patterns. The fabrication procedure is schematically illustrated in Figure 1.

LIL is employed as a promising, low-cost, and scalable tool for the generation of precise 2D periodic structures with sub-100 nm features. A single exposure by interference lithography gives a line pattern with a spatial period \( P = \frac{\lambda}{2 \sin \theta} \), where \( \theta \) is the half-angle between the two beams. We used a...
Lloyd’s mirror interferometer\cite{31–33} and a HeCd laser ($\lambda = 325$ nm) as a light source. The periodicity of the pattern could be adjusted from 170 nm to 2 $\mu$m. Circular or elliptical holes in the negative tone photoresist (PR) were generated by two consecutive exposures. Between the two exposures, the sample was rotated 90°, 60°, or by even smaller angles, in order to achieve periodic patterns with circular or elliptical holes on the resist layer with small or large aspect ratios, respectively.

For LIL exposure, an antireflection coating (ARC) and negative-tone PR were spin-coated and then baked on highly n-doped Si wafers (resistivity ca. 0.01–0.02 $\Omega$cm) with a Si$_3$N$_4$ layer (ca. 35 nm). The resist stack was simulated in order to avoid strong absorption at the interface of the ARC and the PR, which can significantly reduce the sharpness of the resist profile. The polymer structures generated by LIL served as etching masks for an anisotropic reactive-ion etching (RIE) through the Si$_3$N$_4$ layer and they were also over-etched into the Si substrate. At the end of the pattern-transfer process the remaining polymer resist was removed by O$_2$ plasma. Before the electrochemical deposition, the sample was treated with 5% HF solution for 90 s to remove partly the native oxide layer. Subsequently, the silicon substrate with the Si$_3$N$_4$ pattern was utilized as the working cathode for the electrochemical deposition of metals (e.g., Au, Ni). The insulating layer of Si$_3$N$_4$ on the mesa layer and the native oxide layer in the valleys ensured that the electrochemical deposition of metal occurred exclusively on the etched undercuts of the patterns and not everywhere on the top surface of the template. The current density was adjusted to the area and structure density of the templates.

The deposition of metals occurred successfully only along the edges of the RIE undercuts. On samples with line and circular or elliptical holes patterns, arrays of nanowires and nanorings with different aspect ratios were obtained, respectively. The width of the nanowires could be controlled by monitoring the amount of total integrated charges involved in the electrochemical reaction. In the present method, the feature size and the 2D arrangement of metallic rings could be controlled by varying the parameters employed in the LIL and/or the electrodeposition process. Typically, feature sizes ranging from 50 to 300 nm can be obtained by our approach.

Figure 2 shows representative scanning electron microscopy (SEM) images of gold nanoring arrays with different geometries; a) hexagonally arranged elliptical rings array with a 57 nm wire thickness, b) circular ring array with 103 nm wire thickness, c) top and d) cross-sectional views of elliptical ring array with an aspect ratio of 11:1 (long-axis/short-axis) and a wire thickness of 189 nm.

Figure 3 shows SEM images of gold nanowires with a wire thickness of 110 nm in a) top view and b) cross-sectional view.
It is worth noting here that in each groove, two nanowires were deposited on both edges. This enables us to fabricate nanowire arrays with half of the periodicity of an LIL-defined pattern, e.g., 90 nm instead of 180 nm periodicity.

The transmission electron microscopy (TEM) image presented in Figure 4a shows the topographic profile of the silicon substrate, the step edge, and a gold nanowire. It is apparent from the TEM image that the Si$_3$N$_4$ layer was opened and the mask pattern was successfully transferred into the underlying Si substrate by the RIE process. The undercut generated by RIE was estimated to be about 9 nm. Step edges were formed on a highly conductive Si substrate. As in the case of ESED, nucleation of metal occurs preferentially along the step edges at the initial stage of electrochemical deposition because the electrical field is focused on the edges. It is believed that the electrical charges tunnel across the ultrathin oxide barrier at the edge areas, reducing metal ions at the interface of the oxide and the electrolyte.

It is also believed that the inhomogeneity of the thickness of the native oxide layer plays an important role in the selective electrodeposition of metal along the step edges. In order to get an insight into the effect of oxide thickness on the electrodeposition process, a series of control experiments were performed by electrodepositing gold on patterned substrates that were etched by using 5 % HF for different periods of time prior to electrodeposition. For the substrate etched for 90 s, the metal deposition took place along the step edges (Fig. 5a) and a metallic ring structure was successfully formed. On the other hand, electrodeposition performed on the substrate etched for 120 s results in a high density of metallic dots on the Si valley surfaces (Fig. 5b). The schematic cross-section for the ideal case of edge-selective plating is presented in Figure 4b. We assume that the native oxide layer at the edge is thinner than that on the terrace. As a consequence, the passivating SiO$_2$ layer along the step edges is preferentially removed by a short HF treatment (< 90 s), compared to the relatively thick native oxide layer in the area of the valley. The thick insulating oxide layer existing in the valley could be completely removed by an extended HF treatment (> 120 s). Therefore, selective electroplating could not be achieved, and metal deposition could take place on the entire surface except for the area masked with Si$_3$N$_4$. As can be seen in the inset of Figure 5b, the density of metal deposition along the step edges is nevertheless higher than in the Si valleys. We can deduce that the topography of the step edges leads to a preferential nucleation during the electrodeposition process, although the oxide layer has been completely removed by the extended HF treatment.

We have found five major arguments for the selective metal deposition along the step edges of the hole or grating structures: 1) The resist pattern was transferred 5–10 nm deep into the silicon substrate by RIE. The topographic profile induces a preferential nucleation at the step edges. 2) The final oxygen RIE process generates an amorphous passivation layer in the valleys of the patterned Si substrate which can prevent the
direct electrodeposition on the bare silicon surfaces. 3) HF treatment on patterned substrates removes preferentially the native oxide layer on the step edges. 4) The strong focusing effect of the electric field at the step edges during electrodeposition results in selective reduction of metal ions at the step edges. 5) The electric-field-assisted fast diffusion of metal ions towards the step edges strongly guides the deposition of the metal nanowires and nanorings.

In terms of potential applications, the present approach is highly appealing for tuning of magnetic nanorings and fundamental studies of their magnetic properties, e.g., storage media or novel ring-shaped MRAM. Due to the existence of more than two stable magnetic states in the elliptical nanorings, potentially more than one bit of information can be stored within a single nano-object. Further potential applications might be gas-sensing devices based on arrays of semiconductor or metallic nanowires.

In summary, a novel fabrication method for large-scale and periodic arrays of nanorings and nanowires with well-defined feature sizes by a lithographically guided electrodeposition technique has been presented. The novel combination of LIL, RIE, and electrochemical deposition allowed the fabrication of metallic or semiconductor nanowire or nanoring arrays over a wafer-scale area and provided flexible control over shape, arrangement, and thickness of the wires and rings. In contrast to nanostructured arrays fabricated by, e.g., electron-beam lithography, our samples, with countless well-defined and identical nano-objects, can be easily studied with conventional bulk-characterization techniques.

**Experimental**

The LIL exposures were done on a stack of ARC (WIDE-88, i-line wet developable ARC, Brewer Science, USA) with a thickness of 70 nm and PR (TSMR-iN027, Tokyo Ohka Kogyo, Japan) with a thickness of 180 nm that were baked for 40 s at 110 °C and subsequently 60 s at 179 °C (ARC) and 90 s at 90 °C (PR) after spin-coating. The exposed resist was developed using NMD-W 2.38 % (Tokyo Ohka Kogyo, Japan). The RIE of a 35 nm Si3N4 layer was performed with a CHF3 plasma (30 sccm, 20 mTorr (1 Torr ≈ 133.3 Pa), −320 V) for 120 s and subsequently the remaining polymer resist was removed by O2 plasma (30 sccm, 10 mTorr, −285 V, 90 s) in a Si-220 system (Sentech GmbH, Berlin, Germany). The electrodeposition of gold was carried out by using a commercially available plating solution (Auruna 5000). A typical current density was about 0.9 mA cm−2. All SEM images were obtained with a JEOL JSM 6340 SEM. TEM investigations were carried out by using a commercially available plating solution (Sentech GmbH, Berlin, Germany). The electrodeposition of gold was carried out by using a commercially available plating solution (Auruna 5000). A typical current density was about 0.9 mA cm−2. All SEM images were obtained with a JEOL JSM 6340 SEM. TEM investigations were carried out with a Philips CM 20 STEM.

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