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Fabrication of metallic nanostructures by negative nanoimprint lithography

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Abstract
This paper describes a negative nanoimprint lithography (N-NIL) technique for fabricating metallic nanostructures via combining conventional nanoimprint lithography (NIL) with wet chemical etching. Various metallic nanostructures such as gold grating, gold/chromium alternate bimetallic grating and gold nanoelectrode arrays, which are negative replications of the stamp pattern, have been fabricated with N-NIL. This method has demonstrated its advantages on varying the feature size of obtained metallic nanostructures with a single stamp as well as on fabricating bimetallic nanostructures. In addition, it offers a unique path to fabricate micro–nano complex structures in a single imprint process, which compensates the limitation of conventional nanoimprint lithography and maintains the advantages of conventional nanoimprint lithography such as high throughput, low cost and sub-100 nm resolution.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Metallic nanostructures are of great research interest because of their potential applications in electronics [1], optics [2], sensors [3], DNA detection [4] and catalysis [5]. A wide range of nanofabrication techniques are available to generate such nanostructures, including electron beam lithography (EBL) [6], microcontact printing (μCP) [7], dip-pen nanolithography (DPN) [8], nanoimprint lithography (NIL) [9] and so on [10, 11]. A general procedure in a nanofabrication process is to use these techniques to generate a patterned resist layer on supporting substrate as a mask for the following metal deposition or wet chemical etching. Polymer patterns generated by EBL or NIL are used as deposition masks in the metal deposition process and metallic nanostructures are obtained after lift-off, while self-assembled monolayer (SAM) patterns on metal surface transferred by μCP or DPN are utilized as etching mask in the wet chemical etching process. Although these lithography techniques are well developed and have demonstrated their capability in producing sub-100 nm scale metallic features, further improvements are necessary to overcome their inherent shortcomings.

Nanoimprint lithography (NIL) is a high resolution, high throughput, and low cost parallel lithographic technique [8, 12]. In a NIL process, a patterned stamp is pressed onto a substrate spin-coated with a thin polymer layer at a temperature higher than the glass transition temperature (T_g) of the polymer. After cooling and stamp removal, the stamp pattern is replicated to the polymer layer. Such an imprinted pattern can

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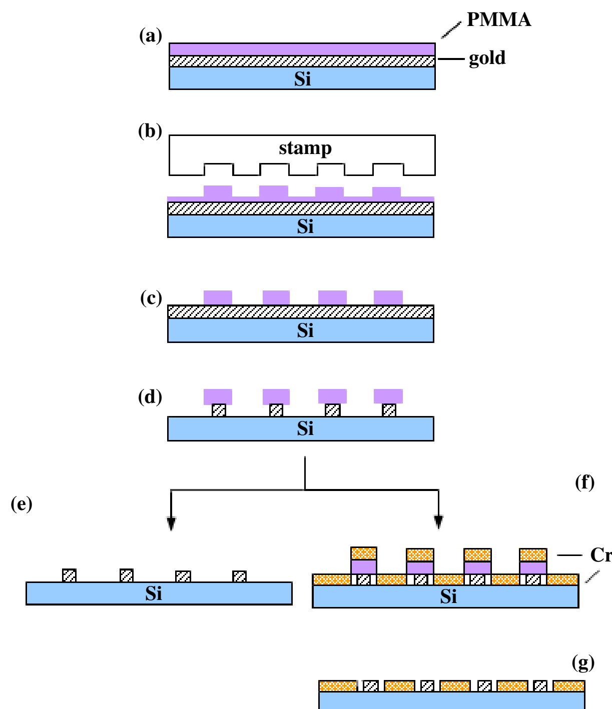

Scheme 1. Schematic illustration of the negative nanoimprint lithography (N-NIL) technique. (a) The silicon substrate is precoated with a metal film and a thin PMMA film is spin-coated on the metal; (b) after imprinting, the stamp pattern is replicated onto the PMMA film; (c) residual PMMA in the trenches is removed by reactive ion etching; (d) the exposed metal film is dissolved by wet etchant; (e) metallic nanostructures after lift-off of residual PMMA; (f) a second metal is deposited using a PMMA pattern as mask; (g) bimetallic nanostructures after removing PMMA.

be further transferred onto the substrate by reactive ion etching (RIE), and metallic nanostructures are obtained through metal deposition and lift-off processes. Such nanostructures are a faithful replication of the original stamp structures. Besides the difficulties in alignment, antisticking and so on, replication of micro–nano complex structures in a single imprint process is a great challenge to NIL technology though great efforts have been made up to now [13, 14]. This problem originates from the dynamic transport behaviour of fluidic polymer in the imprinting process.

Herein we present a negative nanoimprint lithography (N-NIL) technique for fabricating metallic nanostructures. The fabrication procedure in an N-NIL process is different from the conventional NIL technique: a metallic thin film is precoated onto the substrate surface, followed by spin-coating of PMMA resist, imprinting by stamp, RIE treatment and wet chemical etching of the metal film (scheme 1). The metallic structures thus fabricated are always negative replications of stamp protrusion structures, which is also different from the conventional NIL technique. The advantages of this new modified NIL technique are the following:

(1) the feature size of metallic nanostructures could be simply varied by changing chemical etching time with a single imprinting stamp;
(2) bimetallic nanostructures are easily available by depositing another metal after wet etching treatment of the first precoated metal; and
(3) the negative replicating capability provides a unique path to fabricate micro–nano complex structures in a single imprint process using a specially designed stamp.

To demonstrate the N-NIL technique, we fabricated typical gold nanostructures on silicon substrates, which have found various applications in nanosensors [15], nanoelectronic and optical devices [16, 2], controlled growth of ZnO nanowires [5], and DNA immobilization [17].

2. Experimental details

The N-NIL process consists of stamp fabrication, metal deposition, PMMA spin-coating, imprinting, O_2 RIE, wet chemical etching and PMMA removal. We kept all the experimental parameters at the optimized values except for wet etching time in the fabrication process.

Two stamps were fabricated on SiO_2/Si substrates by e-beam lithography, CHF_3 RIE and lift-off. One stamp with 170 nm linewidth, 370 nm spacing and 130 nm depth (figure 1(a)) was used to fabricate gold gratings with different feature sizes. The other stamp which was negative to nanoelectrode arrays with two contact pads was utilized to generate micro–nano complex structures. The stamps were treated for antisticking by vapour deposition of tridecafluoro-(1,1,2,2)-tetrahydro-octyltrichlorosilane (F13-TCS) before imprinting [18]. Gold films (20 nm) were prepared by thermal evaporation onto the clean silicon substrates after priming with 2 nm titanium. PMMA ($M_w = 5000$) resist was spun onto the gold surface at 4000 rpm for 40 s from a 4 wt% solution in anisole. The coated substrates were then baked at 170 °C for 30 min in a vacuum oven. The imprinting operation was carried out at 200 °C, 45 bar for 5 min with a 2.5 inch Nanoimprinter (Obducat AB, Malmö, Sweden). After imprinting, the O_2 RIE

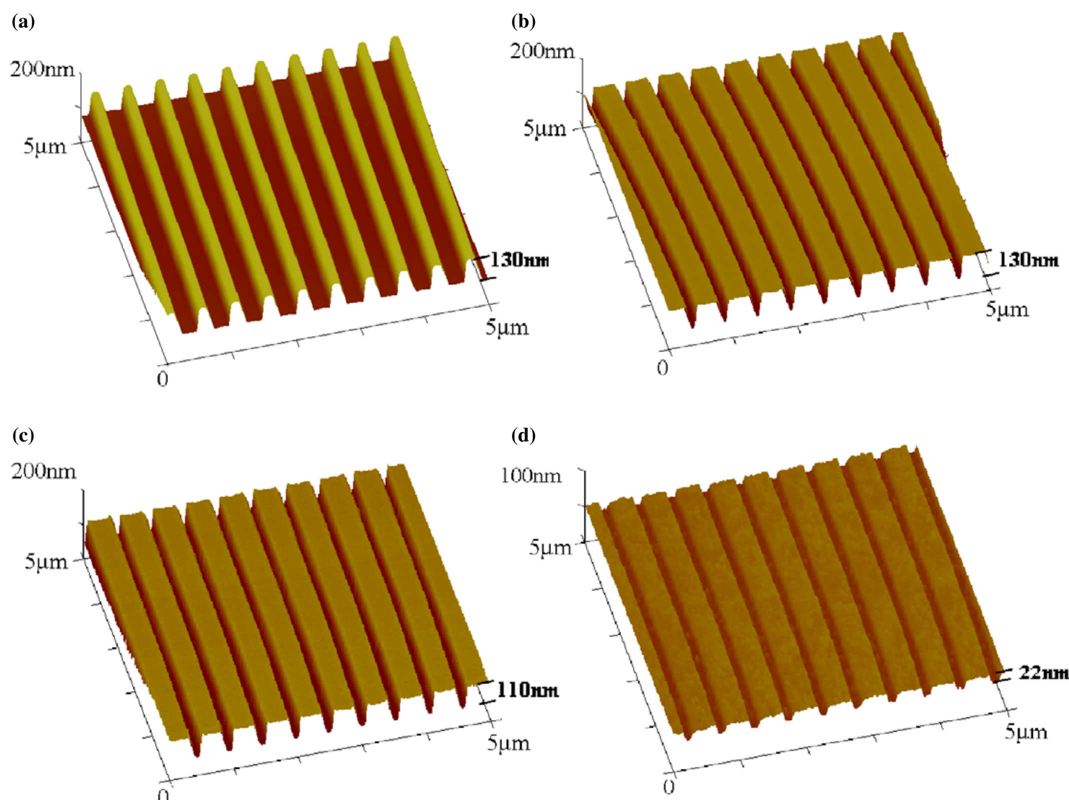

Figure 1. Tapping mode AFM images: (a) the SiO_2 stamp, in which the height of the protrusion is 130 nm, the linewidth is 170 nm and the spacing is 330 nm; (b) the PMMA pattern after imprinting, in which the depth, linewidth and spacing are 130, 370 and 130 nm, respectively; (c) after removal of residual PMMA in the trenches of (b) by RIE, where the depth, linewidth and spacing are 110, 370 and 130 nm, respectively; and (d) the gold grating obtained after 65 s wet etching in KI/I_2 solution and removal of PMMA, where the height of the pattern is 22 nm, the linewidth is 360 nm and the spacing is 140 nm.

was used to anisotropically remove the remaining thin PMMA layer in the trenches. Then a drop of wet etching solution composed of 0.0025 M I_2 and 0.015 M KI was added onto the substrate surface to remove the exposed gold. After etching for 40–100 s and removing PMMA in acetone at 50 °C for 30 min, gold gratings with different linewidths were fabricated.

AFM imaging was done with a NanoScope III Multimode AFM (Digital Instruments, Santa Barbara, USA) in tapping mode under ambient conditions. SEM images were taken with a LEO 1530VP scanning electron microscope (LEO Elektronenmikroskopie GmbH, Oberkochen, Germany).

3. Results and discussion

3.1. Fabrication of gold gratings with controlled dimension

To demonstrate the N-NIL technique, gold gratings were fabricated with the stamp pattern shown in figure 1(a). As shown in figures 1(b) and (c), the stamp pattern was completely transferred onto the PMMA layer after imprinting and O_2 RIE. About 110 nm thick PMMA was left after O_2 RIE treatment. Thus-formed PMMA pattern was used as the wet chemical etching mask to fabricate gold gratings through etching out the unprotected precoated gold film. The KI/I_2 etching solution has been used to selectively etch gold with thin photoresists as mask [19]. In this system, I_2 was the oxidizing agent to oxidize the metal and I^- was the complex-forming ligand to dissolve the oxidized metal from the surface. The etching solution used in the following experiments was composed of 0.0025 M I_2 and 0.015 M KI, which gave a suitable etching rate of about 40 nm min^{-1}. This etching solution did not react with PMMA, so the 110 nm thick PMMA film could well protect the underlying gold against wet etching. The etching process was isotropic, which made it possible to fabricate gold patterns with different linewidths simply by controlling the etching time.

To illustrate this controllable chemical etching, we carried out the etching treatment for 40, 65, 90 and 100 s, respectively. Figure 2 shows the SEM images of thus-obtained gold gratings after removal of PMMA. The widths of the gratings corresponding to 40, 65 and 90 s etching times were 400 nm (figure 2(a)), 350 nm (figures 2(b) and 1(d)) and 290 nm (figure 2(c)), respectively. After etching for 100 s, the edges of the gold gratings became highly roughened and even disconnected (data not shown). The extended etching could reduce the linewidth in a controllable way and at the same time led to an increased edge roughness. Obviously the etching reaction would proceed easily along the grain boundaries of the gold film, so the resulting line edges would somehow reflect the granular structures of the gold film. This suggests the possibility of improving the gold grating quality by optimizing the deposition parameters of the gold films and also suggests that the smallest linewidth we could obtain by the N-NIL technique is mainly determined by the grain size of the gold films.

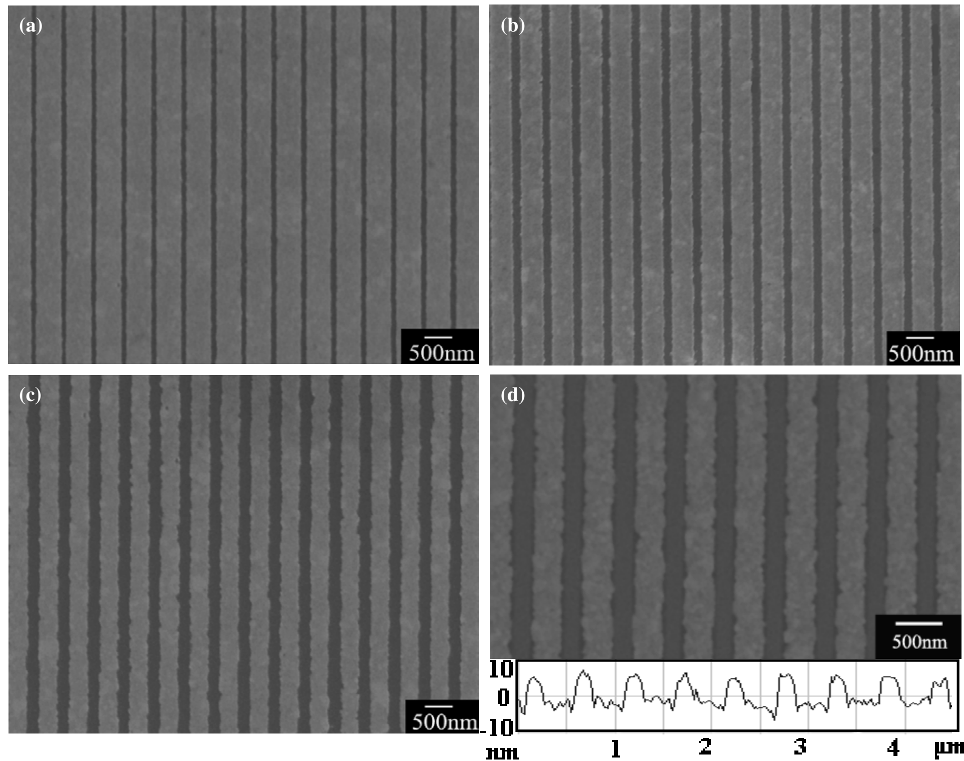

Figure 2. (a)–(c) SEM images of a gold grating fabricated from a 20 nm thick gold film by N-NIL using the same stamp but different etching times. (a) 40 s wet etching, linewidth 400 nm; (b) 65 s wet etching, linewidth 350 nm; (c) 90 s wet etching, linewidth 290 nm. (d) SEM image and AFM section profile of gold/chromium alternating bimetallic structures (etching time 90 s). The darker lines correspond to chromium and the bright ones to gold.

Obviously the obtained metallic grating structure was not the exact replication of the stamp. Instead, it was a negatively imprinted structure with an adjustable feature size, demonstrating its advantage over the conventional NIL technique.

3.2. Fabrication of bimetallic nanostructures

The N-NIL technique provides a simple way to fabricate bimetallic nanostructures. Figure 2(d) shows the SEM image and AFM section profile of the Au/Cr bimetallic nanostructures fabricated by N-NIL. The fabrication procedure is shown in scheme 1(d), (f), (g). After imprinting on 20 nm thick gold film, RIE and etching in KI/I_2 solution for 90 s, a 30 nm thick chromium layer was thermally evaporated onto the substrate, where the PMMA pattern served as the deposition mask. Gold and chromium alternating gratings were obtained after removing the PMMA in acetone under 1 h ultrasonication treatment. Gold lines with rough edges formed in a wet chemical etching process could be distinguished from chromium lines clearly in the SEM image. The widths of gold and chromium lines were about 300 and 230 nm, respectively, and the gold lines were about 8 nm lower than the chromium lines. Because undercutting could be easily realized by controlling the etching time under an isotropic etching process, spacing-tunable nanogaps could be obtained between the adjacent gold and chromium lines by adjusting the relative linewidth of PMMA mask and the underlying gold gratings. Such kinds of structures with nanogaps are of great importance for studies of molecular and nanoelectronics.

3.3. Fabrication of micro–nano complex structures

The conventional NIL technique has some intrinsic problems when patterning micro–nano complex structures. These problems originate from the replication principle of NIL. In the imprinting process, the protrusions on the stamp deform the resist and replace the polymer. Larger protrusions on the stamp must replace more polymer over longer distance and thus are more difficult to imprint. Heyderman *et al* investigated the flow behaviour of molten polymer in an imprinting process in detail and deduced the following equation from hydrodynamic theory [20]:

$$t_{\mathrm{f}} = \frac{\eta_0 S^2}{2p}\left(\frac{1}{h_{\mathrm{f}}^2} - \frac{1}{h_0^2}\right) \quad (1)$$

where t_{f} is the imprinting time, h_0 and h_{f} the initial and final heights of the polymer, respectively, η_0 the polymer viscosity, S the width of the protrusion structure on the stamp, and p the imprinting pressure. Apparently the width of protrusion in the stamp (S) determines the imprinting time t_{f} when other parameters are fixed. Therefore, a micrometre scale protrusion in the stamp cannot fully penetrate into the polymer layer in tens of minutes, which thus results in incomplete replication of the micrometre scale pattern in a time frame that is practical for NIL. Meanwhile, the nanometre scale structures next to the micrometre scale pattern are strongly affected [14]. Therefore, it is ideal to use a stamp with small protrusions in the imprinting process. The N-NIL technique is capable of generating large metallic patterns with a specially designed small protrusion stamp. The protrusion pattern on the stamp is removed from

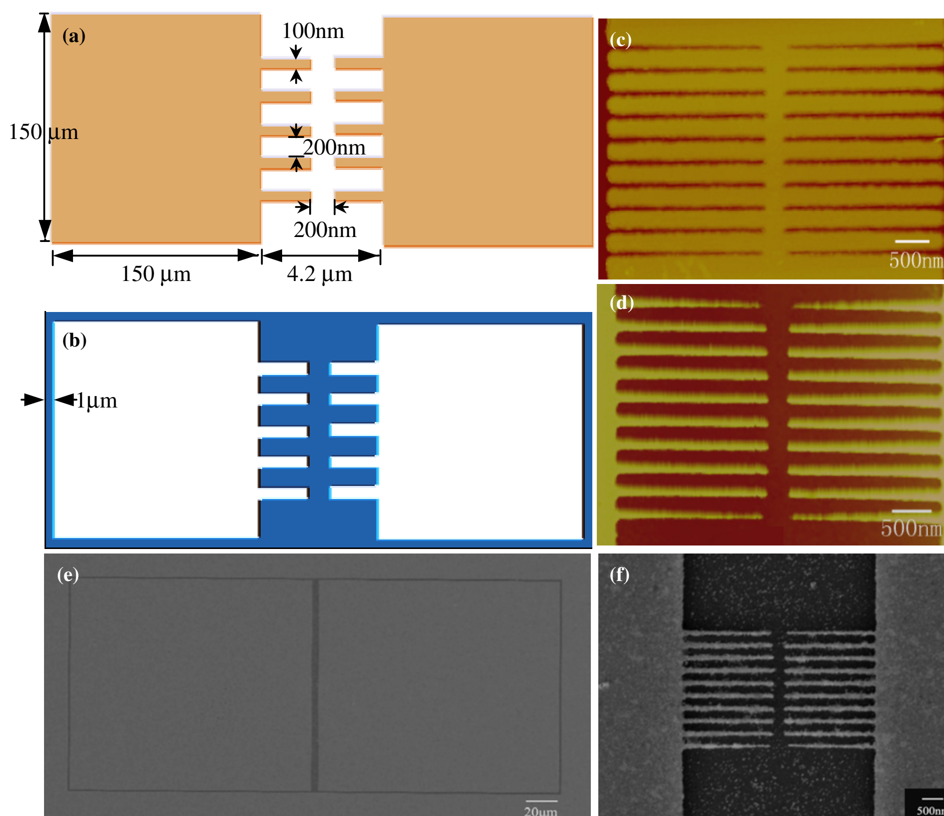

Figure 3. (a), (b) Schematic diagram of 100 nm width nanoelectrode arrays with two 150 μm × 150 μm contact pads and the stamp design for fabricating (a) using N-NIL in which the border of protrusion is 1 μm in width. (c), (d) Tapping mode AFM images of the central part of the SiO_2 stamp made by EBL and the imprinted PMMA pattern. (e), (f) SEM images of the micro–nano complex electrodes fabricated by N-NIL and the zoom-in of the central part. The darker area corresponds to silicon and the bright area to gold. The linewidth of the electrode is about 80 nm, the line spacing is about 200 nm and the electrode gap is 200 nm.

the metal film at the end of the N-NIL process, and a pattern negative to the stamp is left on the substrate surface. As a result, a large micro–nano metallic structure could be generated by using a stamp with a small protrusion which is negative to the desired pattern.

A typical micro–nano complex structure is illustrated in figure 3(a), in which the 100 nm width electrode arrays are connected with two 150 μm × 150 μm contact pads for wire bonding or probe contacting. Figure 3(b) shows the imprinting stamp designed for fabricating the micro–nano complex structures given in figure 3(a), which is a partial negative to the desired structure. The border of protrusion on this stamp is 1 μm wide, much smaller than that of figure 3(a) (150 μm). Therefore, a precise pattern replication is expected by imprinting. Figures 3(c) and (d) show the tapping mode AFM images of the central part of the actual stamp fabricated by EBL and of the imprinted PMMA pattern, respectively, where the latter clearly indicates the precise replication of the original structures. Figures 3(e) and (f) demonstrate the finally obtained micro–nano complex gold structures after RIE, 60 s wet etching in KI/I_2 solution, and PMMA removal in acetone. The obtained electrode arrays with two 150 μm × 150 μm contact pads were separated by a 1 μm wide gap from the neighbouring gold film. The electrode width was about 80 nm, the spacing between the adjacent electrodes was about 200 nm and the electrode gap was about 200 nm. These parameters could be easily adjusted by tuning the etching time. This preliminary result demonstrated the capability of N-NIL technique for fabricating various micro-nano complex metallic structures.

4. Conclusion

We have developed a negative nanoimprint lithography (N-NIL) technique for the purpose of fabricating various metallic nanostructures. Different from the conventional NIL, a PMMA pattern generated by imprinting and RIE is utilized as a mask for wet chemical etching of the precoated gold film. A KI/I_2 etching solution with proper concentration is utilized to realize a controllable etching of gold to obtain structures with desired dimensions with a single stamp. Bimetallic structures as well as micro–nano complex structures can be easily fabricated using the N-NIL technique, which thus compensates the limitation of the conventional NIL. This technique can be used for fabricating general metallic structures by choosing suitable etchants. Further studies are in progress for improving the quality of thus-fabricated structures and for investigating its limit to obtain high aspect ratio nanostructures. The N-NIL technique provides a convenient way to fabricate metallic and bimetallic gratings, nanoelectrode arrays with micro–nano complex structures etc, which may find wide applications in the studies of optics, electronics and biosensors.

Acknowledgments

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