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Fabrication of Periodic Metal Nanowires with Microscale Mold by Nanoimprint Lithography

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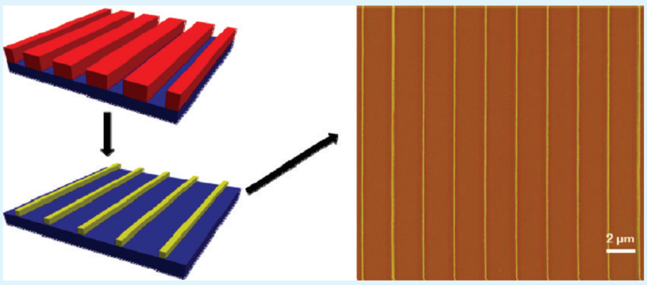
S Supporting Information

ABSTRACT: In this paper, a simple method is demonstrated for fabricating periodic metal nanowires based on the unconventional nanoimprint lithography (NIL) technique. Using this method, sub-100 nm metal nanowires with the rectangular cross-section are fabricated with microscale stamp. Furthermore, the metal nanowires with different widths and heights can be generated by adjusting the imprinting parameters with the same stamp. The metal nanowires prepared with this method can be used for chemical sensing, such as ammonia sensing, and it may have applications in optical signal processing.



KEYWORDS: nanoimprint lithography, P-SPEL, PMMA, metal nanowires, large-scale mold, gas sensor

INTRODUCTION

Metal nanowires have attracted a great deal of interest during the past decade because of their unique optical, electrical, magnetic properties[1−4] and potential applications in solar cells,[5] sensors,[6−8] and nanodevices. In this respect, a number of lithography processes have been used to achieve sub-100 nm metal nanowires, such as dip-pen nanolithography (DPN),[9] electron beam lithography (EBL),[10] focused ion beams (FIB) lithography,[11] and so on. Although these conventional methods have advantage in fabricating high resolution structures, which are limited by low-throughput and high-cost because of the serial "writing" processing and utilization of expensive instrumentation. To overcome the limits, some innovative lithography processes, e.g., lithographically patterned nanowire electro-deposition (LPNE),[12,13] modified microcontact method,[14−16] and capillary force lithography (CFL)[17] have been developed. The similarity of these innovative methods is that the metal nanowires are generated with microscale stamps. However, most of the methods cannot be used to fabricate periodic and uniform nanowires, which may limit the applications of the metal nanowires in optical devices. Compared with the above methods, nanoimprint lithography (NIL) as a mature technology,[18] which has the characteristic of precise control of experimental conditions, and the unique advantage in the fabrication of nanoscale patterns with large areas.

NIL has been used to produce Au metal lines down to 30 nm in width. But generally, the nanoimprint mold for nanoscale is patterned by EBL, which still needs high cost. Therefore, to fabricate nanoscale pattern with microscale mold is becoming increasingly important. In 2008, a new method called self-perfection by liquefaction (SPEL)[19] is brought out by Chou

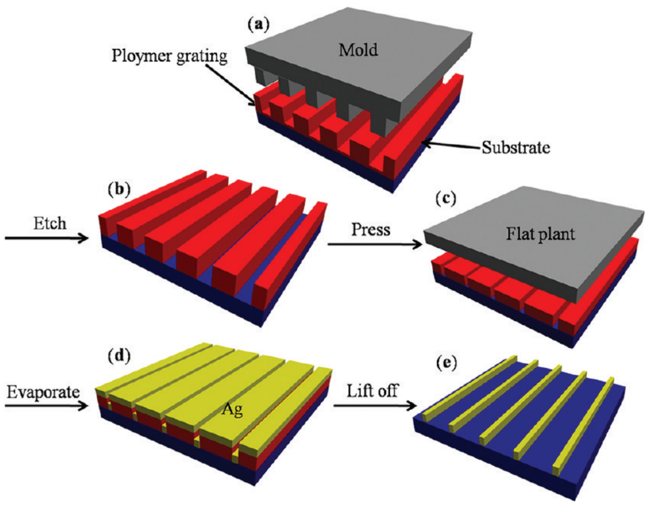


Figure 1. Schematic illustration of the fabrication process of the metal nanowires.

et al. to remove fabrication defects and improve nanostructures postfabrication, and then an amendatory approach called pressed SPEL (P-SPEL)[20] is developed to reduce the size of the structure by press the structure in the viscoelastic flow regime. By using this new method, some structures, including trench, line, and hole with sub-10 nm in width and diameter were fabricated on the

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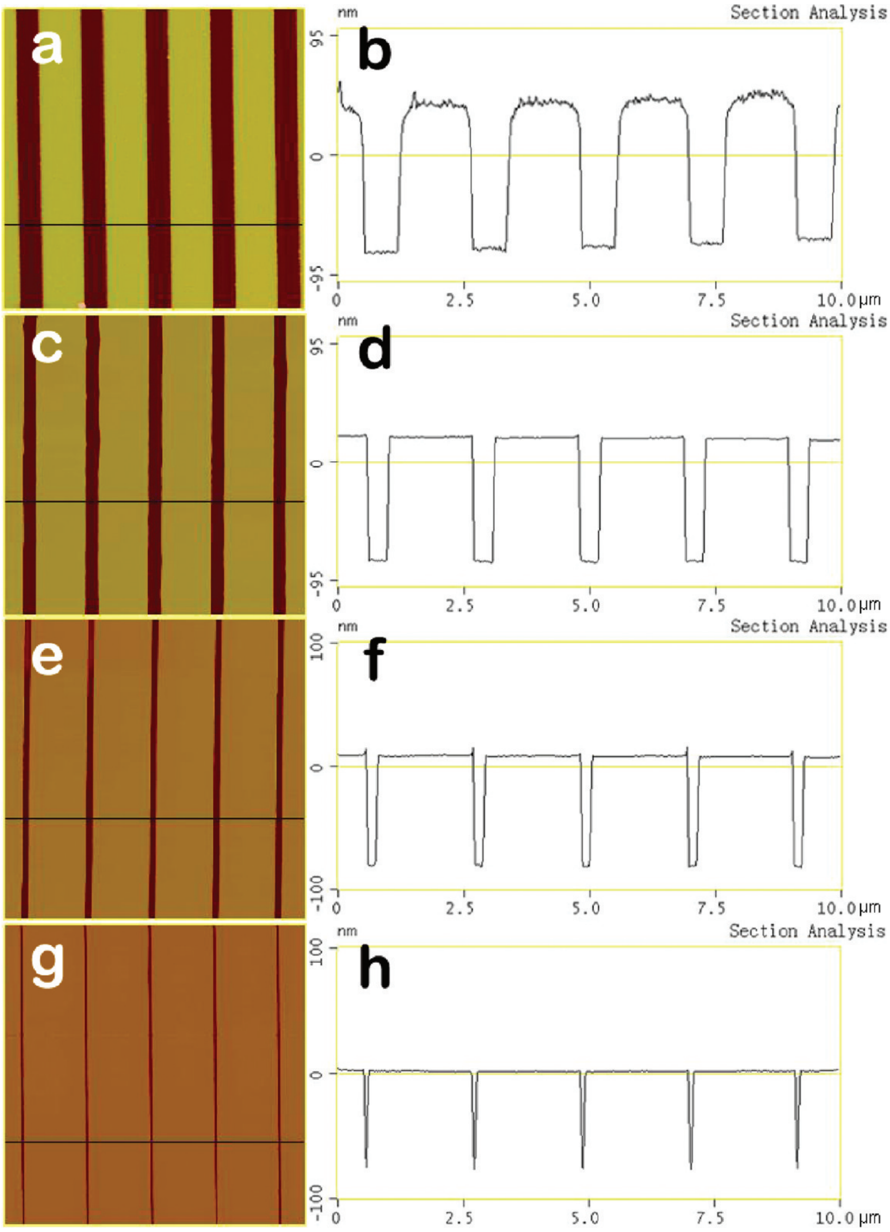

Figure 2. AFM images and the section analysis of the imprinted PMMA grooves of different widths. (a, b) PMMA grating after normal NIL process, with the width of 750 nm. After applying pressure with a flat silicon substrate, the width of PMMA grating changes to (c, d) 390, (e, f) 175, and (g, h) 80 nm, respectively. The unit of the section analysis is μm in width and nm in height.

homemade resist polymer. Furthermore, 20 nm Cr lines were produced with this method through 7 step fabrication process.[21] As for other metals with poor adhesion with the substrate, such as silver and gold, more steps will be needed to produce nanowires. Therefore, more efficient and simple method is still highly needed.

Here, we demonstrate a simple method for fabricating periodic metal (Au, Ag et al.) nanowires based on unconventional NIL. With this method, different sized metal nanowires can be obtained by adjusting the imprinting parameters using a single microscale stamp. In this work, the widths of Ag nanowires range from 800 nm to sub-100 nm are fabricated by using the stamp with period of 2.1 μm (0.8 μm line and 1.3 μm space). It leads to a cost-efficient method for the fabrication of high-resolution metal nanowires with large areas.

EXPERIMENTAL SECTION

Materials. Polymethylmethacrylate (PMMA, molecular weight M_w = 96 700) and (3-mercaptopropyl)-trimethoxysilane (95%) were purchased from Sigma-Aldrich. Ethanol, chloroform, acetone, and dimethylbenzene, used for cleaning the substances and the lift-off process, were purchased from Beijing Chemical works at the highest available purity and used without further purification. The silicon wafers with a 100 nm thermally oxidized SiO_2 layer were purchased from Si-mat Company. The silicon stamp is 180 nm in depth, and 2.1 μm in period, which is fabricated by photolithography and followed by an anisotropic etching.[22] The stamp and blank silicon for press were treated with an antiadhensive layer (tridecafluoro-1, 1, 2, 2,-tetrahydrooctyl-trichlorosilane) by vapor phase deposition, resulting in a very low surface energy.

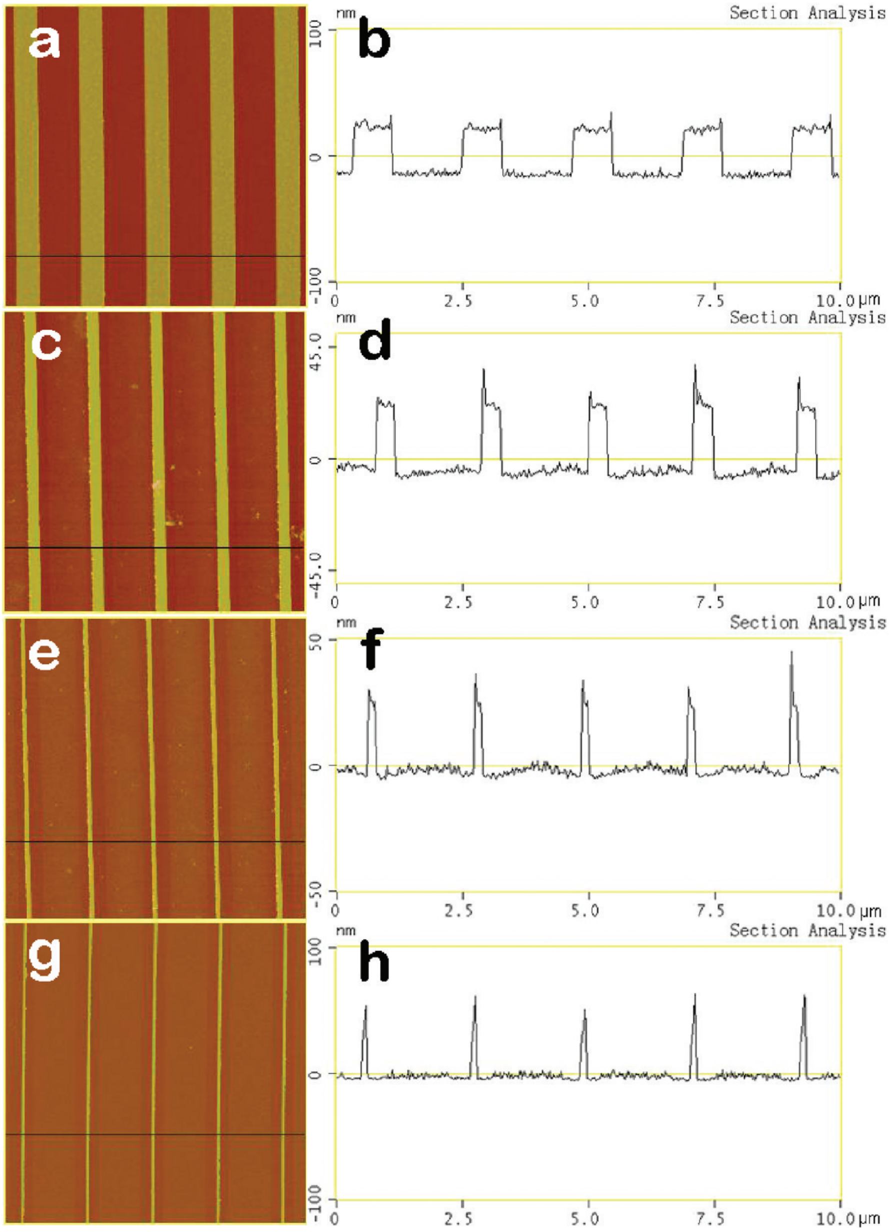

Figure 3. AFM images and the section analysis of the fabricated silver nanowires with the width of (a, b) 780 nm, (c, d) 390 nm, (e, f) 176 nm, and (g, h) 84 nm. The unit of the section analysis is μm in width and nm in height.

This treatment can prevent the resist polymer from sticking to the stamp during the imprinting process, facilitating the separation of the stamp and the imprinted patterns.[23,24]

Patterning. The silicon substrates were sonicated consecutively in a bath of acetone, chloroform, ethanol, and pure water for 5 min, respectively. Subsequently, these substrates were treated with oxygen plasma at 300 W for 3 min for thoroughly cleaning. A 150 nm PMMA layer was spin-coated onto the clean silicon substrate, followed by annealing at 120 °C for 10 min to remove residual solvent. The imprinting was carried out on a 2.5-in. Nanoimprinter (Obducat AB, Malmö, Sweden). Imprint process was performed at 175 °C, under 40 bar for 500 s. After peeling off the stamp from the substrate at 90 °C, the residual polymer was removed with the process of Reactive Ion Etching (RIE) by using a Plasmalab Oxford 80 Plus (ICP65) system (Oxford Instruments Co., UK) with a gaseous of oxygen for 1 min. The press process was performed at 115 °C (little higher above the glass transition temperature (T_g) of PMMA), under 40 bar for different times by using the same Nanoimprinter. The metal-depositing process was performed under a base pressure of 5×10^{-4} Pa on a commercial vacuum thermal evaporation system (Shenyang Keyou Institute of Vacuum Technology, China).

Characterization. Atomic force microscopy (AFM) measurements were taken on a Multimode Nanoscope IIIa instrument (Digital Instrument, Santa Barbara, CA), operated in the tapping mode with silicon cantilevers (resonance frequency in the range of 280−340 kHz). Scanning electron microscope (SEM) images were obtained using an environmental scanning electron microscope (ESEM, Model XL 30 ESEM FEG from Micro FEI Philips). The samples were sputtered with a thin layer of Pt (2 nm in thickness) prior to imaging. The current density−time

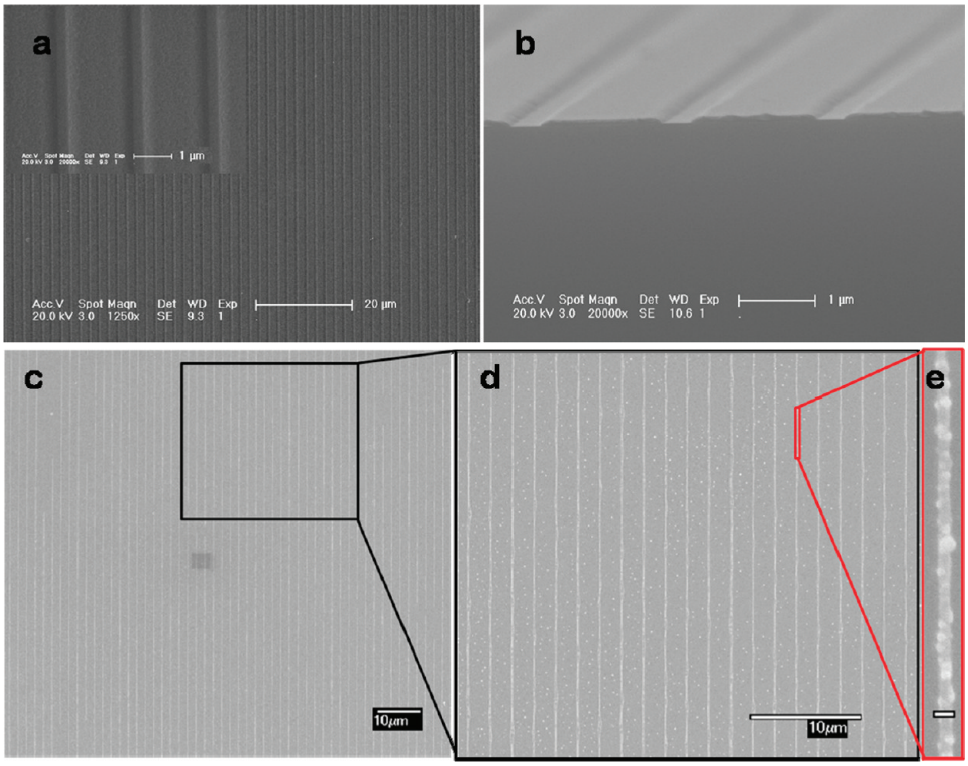

Figure 4. SEM images of (a) the pressed PMMA grating with large areas, and the inset shows the local detail of the structure; (b) the section of the pressed PMMA grating; (c) the fabricated silver nanowire gratings with large areas; (d) a part of c and show more detail; (e) a single silver nanowire with the width of about 70 nm. The scale bar of photo (e) is 100 nm.

(I—t) curve was recorded by an electrochemical workstation system (CHI600, made in China).

RESULTS AND DISCUSSION

The fabrication process is schematically shown in Figure 1. First of all, a layer of the thermoplastic resist polymer (PMMA) was spin-coated onto the substrate, and then patterned with NIL. After removing the residual resist polymer with the RIE process, the initial polymer grating for next unconventional nanoimprint was fabricated, just as shown in panels a and b in Figure 2, the groove width is about 750 nm. In next step, a piece of flat silicon substrate was put on the top of the PMMA grating and pressure was applied. As presented in Figure 2c—h, the groove widths decreased to 390, 175, and 80 nm, respectively with extending the press time, and the height of the grating accordingly decreased. It can be observed that the groove width was decreased to about 10% of the origin width (Figure 2g,h). What's more, through the section analysis shown in Figure 2b, d, f, and h, we can clearly find that after the press process, the surface roughness of the polymer grating is greatly improved. And at the same time, the side of the grating is close to the vertical with the substrate, which will be convenient for the next lift off process. When the groove was decreased to the required width by applying pressure, the sample was treated with oxygen plasma for 10 s to make the uncovered Si substrate hydrophilic, and then a monolayer of alkane thiol was assembled on the bared area of Si substrate via the vapor phase deposition. The assembled monolayer can enhance the adhesion of metal on the substrate, which makes the evaporated metal remain on the substrate after the process of the lift-off. Then, the 30 nm Ag layer was evaporated

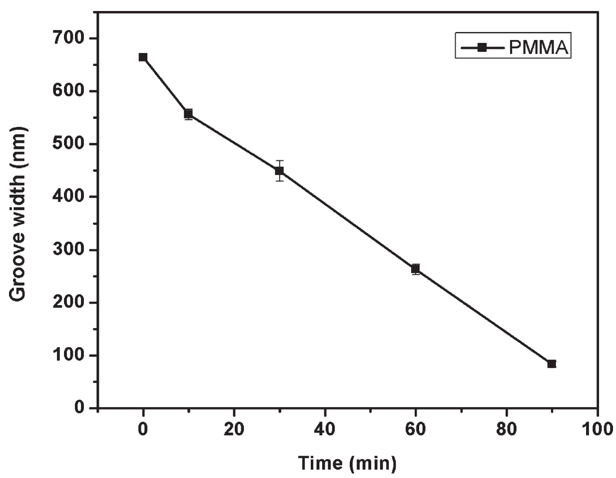

Figure 5. Correlation of the width of PMMA groove and the duration of applying pressure.

onto the surface of the sample. After getting rid of the residual resist polymer by keeping the sample in acetone for 1 min, we obtained the metal nanowires.

As shown in Figure 3, the widths of the Ag nanowires are 781, 390, 176, and 84 nm, and the section analysis of the Ag nanowires reveals that the cross-section of nanowires is rectangular. It should be noted that the nanowires are slightly wider than that of polymer grooves shown in Figure 2. This phenomenon might be caused by the edge roughness of the polymer gratings, which is introduced by the oxygen plasma etch process. Although the step of unconventional nanoimprint can improve the smoothness of the edge, some metal may still remain on the edge. The section analysis of the Ag nanowires also shows that there are some tips on the top of the wires, which can further confirm the explanation about the phenomenon. Figure 4b shows that the bottom of the PMMA structure is little wider than the top of it. In our approach, before the process of metal deposition, a 10 s oxygen plasma process was brought out to make the uncovered Si substrate hydrophilic, and this process will reduced the polymer height for about 10 nm, at the same time, this process may also make the groove little wider since the edge of the polymer grating bottom is not so high. In this case, the width of the Ag nanowires still can be controlled to 84 nm. By close inspection of AFM images e and g in Figure 3, we can observe a thin layer of PMMA between the Ag nanowires, the amplified AFM image and its section analysis displayed in Figure S1 reveals that the PMMA layer is about 3 nm high, which is due to the nature of the polymer and the process of NIL. The residual PMMA layer does not affect the character of the fabricated metal nanowires.

The large area (more than 100 μm × 100 μm) fabricated PMMA structure and Ag nanowires are shown in images a and c in Figure 4, which can be easily achieved with this method. The higher-magnified SEM images are shown in images d and e in Figure 4, which clearly indicates that the width of the fabricated Ag nanowires is about 70 nm. With current experimental parameters, the minimum width of the fabricated wires is 70 nm.

The correlation of the width of PMMA groove and the duration of applying pressure is plotted in Figure 5. Three different sites were measured on each sample with different press time to calculate the average groove width. It can be observed that the PMMA groove decreases linearly with increasing the duration of applying pressure. The ultimate limit size of the PMMA grating groove is 80 nm in our measurement. To control the groove width precisely, the temperature was set at 115 °C, which is little higher than the T_g of PMMA. The temperature allows for a very low fluidness, which is necessary for a steady expansibility. At this temperature, PMMA expands at the same speed from top to bottom under pressure. If increasing the temperature to 130 °C, the stability is poor because the fluidness is higher.

Silver mesowires can be used to test for ammonia.[25] The mechanism of the detection is based on the resistance change. The inelastic scattering of conduction electrons of chemisorbed molecules at the surface can result in the resistance increase. Many factors will affect the gas sensing performance of the metal nanowires, such as the wire width, interparticle boundaries and so on.[26,27] Because this paper mainly focus on the method of fabrication of metal nanowires with microscale mold, the gas sensing of the silver nanowires is provided to show the potential applications of this method. (For details of the test process, see Figure S2 in the Supporting Information) This fact indicates that Ag nanowires can be used for gas sensing. And further investigations will be conduct about the applications and the performance in the future.

CONCLUSIONS

In summary, we demonstrated a feasible method for the fabrication of periodic Ag nanowires with the scale of sub-100 nm by using the microscale mold. Furthermore, different sized wires with the defined width and height can be obtained by adjusting the press parameters with the same stamp. This method can be applied for other materials and structures. The result also implied that it is potentially possible to develop an ammonia sensor at room temperature based on Ag nanowires fabricated by this method.

ASSOCIATED CONTENT

S Supporting Information. The section analysis of the silver nanowire, and the details of the gas sensing measurement are provided. This material is available free of charge via the Internet at http://pubs.acs.org/.

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