Fabrication of high aspect ratio Si nanowires by metal-assisted chemical imprint

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Silicon nanowires (SiNWs) are great candidates for energy applications, due to their excellent thermoelectric properties[1] and great capacity for Li-ion storage[2]. Metal-assisted chemical (Mac) imprint, which combines MacEtch and nanoiprint, has been exploited recently as a promising technology which enables direct MacEtch of Si substrate using a hybrid imprinting mold having noble metal mask, which leads to inexpensive SiNWs fabrication[3,4]. However, only low aspect ratio structures have been obtained because of the mass-transport limitation by the confined structures of the mold[3,4]. In this work, we effectively solved this problem by employing the Pt-coated anodized aluminum oxide (AAO) membrane mold where the holes through the entire thickness drastically enhances the mass-transport. High aspect ratio (~1:50) SiNWs were achieved by MacImprint.

Pt coated AAO membrane mold was prepared by an electroless plating process. AAO membrane (10×10 mm size, 50 μm thick) has 200-300 nm diameter holes through the entire thickness. AAO membrane was first surfactant treated, followed by Pd catalyst deposition. Finally, Pt coating on AAO was achieved by electroless deposition, to achieve an average thickness of ~30nm. Figure 1 shows a schematic of MacImprint. It was performed in the etchant (49% HF : 30% H_2O_2 = 4:1) for 3 min on p-type Si (100) substrate with resistivity of 1-10 Ωcm. SiNWs were successfully fabricated.

Figure 2 shows the SEM images of AAO membrane before and after Pt coating and Figure 3 shows the SEM images of SiNWs bundles fabricated by MacImprint. Very high aspect ratio SiNWs arrays were obtained. The diameters of these SiNWs are in good agreement with the hole diameters of AAO membrane and the aspect ratios and the etching rate are estimated to be ~1:50 and ~3 μm/min respectively. They have been dramatically improved from the previous report ~5:1 and ~10 nm/min respectively[4]. This indicates that the process was no longer limited by the mass transport of etchants and by-products. Moreover, it has been shown that MacImprint can be performed not only on heavily-doped n-type Si substrate but also on p-type Si substrate. It can be concluded that the mass-transport is a more important factor in the MacImprint process than the semiconductor/metal junction model reported previously[3,4].

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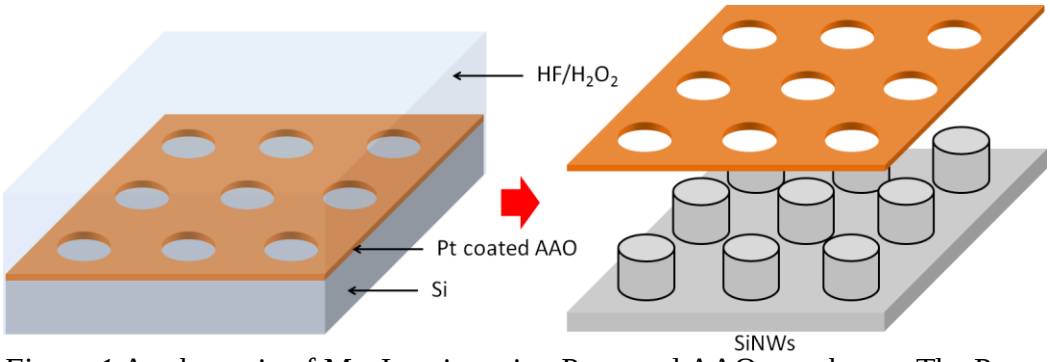

Figure 1 A schematic of MacImprint using Pt coated AAO membrane. The Pt coated AAO membrane was put on a Si substrate in the etchant of HF/H_2O_2 for 3 min. Finally, Si nanowires are fabricated corresponding to holes of the AAO membrane.

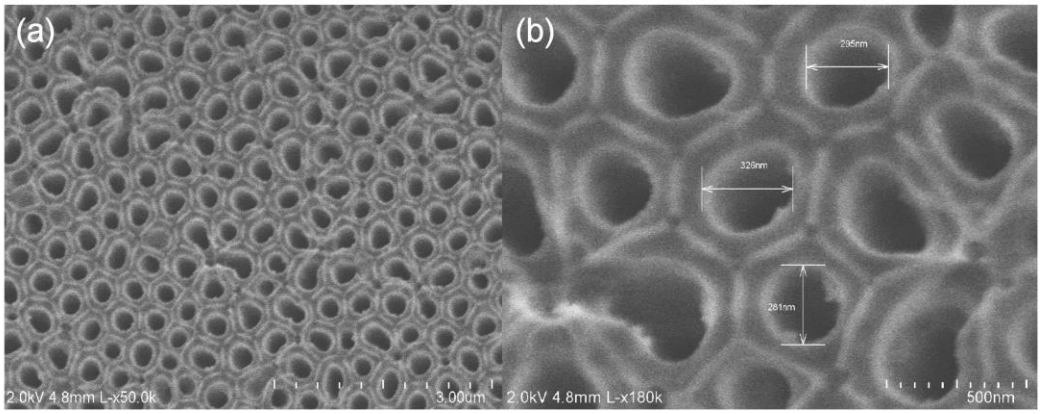

Figure 2 (a) SEM images of AAO membrane after Pt electroless plating and (b) close-up view. Hole diameters are 200-300 nm and hole spacing is ~500 nm.

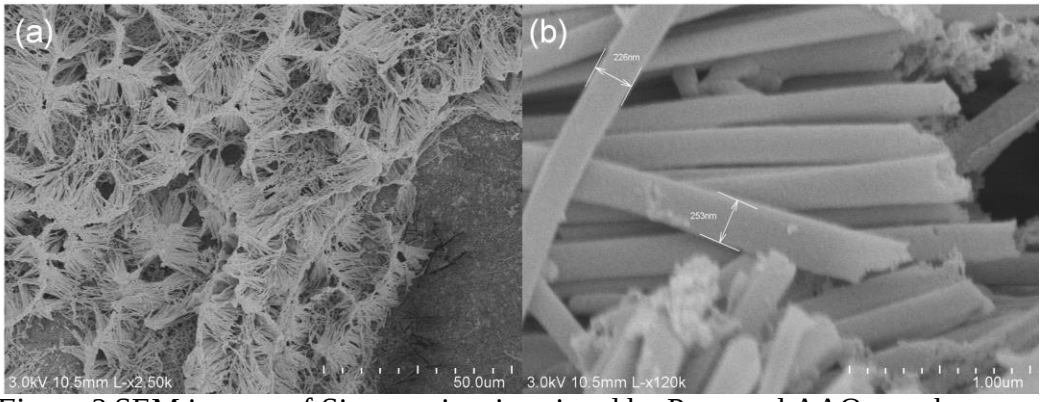

Figure 3 SEM images of Si nanowires imprinted by Pt coated AAO membrane. (a) Large area tangled Si nanowires due to their high aspect ratios. (b) Diameters of Si nanowires are in good agreement with hole diameters of AAO membrane.