

Synthesis of High Density, Size-Controlled Si Nanowire Arrays via Porous Anodic Alumina Mask

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Porous anodic alumina (PAA) masks are employed for the template synthesis of high density silicon nanowire (SiNW) arrays on a silicon substrate by the vapor–liquid–solid method. The uniform-sized ordered arrays of nanopores in the PAA mask anchored to Si(111) substrate are shown to enable the realization of vertically aligned epitaxial SiNWs with uniform diameter and spacing. The average diameter of the wires is 72 nm while the density is 60 wires/ μm^2 . The high packing density and tightly controlled dimensions of SiNWs obtained by this nonlithographic method allow their effective integration into nanodevices for mass production.

Introduction

Intense research efforts are currently focused on the synthesis of one-dimensional nanoscale materials and on the understanding of their novel electrical, optical, magnetic, and mechanical properties, derived from the reduced dimensionality and size. In particular, semiconductor nanowires are gaining significant attention as a result of their potential applications in electronic, optoelectronic, electromechanical, and sensing devices.^{1–4} Among the semiconductor nanomaterials investigated so far, remarkable achievements have been obtained in the fabrication of single crystalline silicon nanowires (SiNWs). Practical applications of SiNWs include their use as building blocks for next future nanoelectronic devices such as sensors and field effect transistors^{5,6} and for the fabrication of thermoelectric devices.⁷ More recently, the application of SiNWs for label-free, multiplexed electrical detection of cancer markers has been demonstrated.⁸ The well-established vapor–liquid–solid (VLS) growth method is commonly utilized for the growth of SiNWs.^{9–12} In the VLS process, gold is typically used as the “catalyst” for nanowire growth. The process starts with the diffusion of Si

into nanoscale islands of the catalyst to form a Au–Si eutectic liquid alloy followed by the supersaturation of the droplet and precipitation of single crystalline silicon wires. The diameter of the nanowires is determined by the size of the alloy droplet, which in turn is determined by the original Au cluster size.¹² Hence, precise control of the SiNW diameter, which strongly affects the electrical and optical properties of the nanowires,¹³ relies on the ability to prepare Au clusters with homogeneous size. With the exception of Au nanoclusters below 30 nm, SiNW growth occurs preferentially along the [111] direction, leading to vertically aligned nanowires on the Si(111) substrate.¹⁴

The VLS growth of vertically aligned SiNWs with monodispersed diameter has been achieved via e-beam lithography.¹⁵ Although the lithographic method allows for fabrication of nanowires with controlled size and well-defined growth locations through the Au patterned substrate, it involves high processing costs and limits on the nanowire size. Nonlithographic methods employing gold colloids with a narrow size distribution have been successfully used to grow SiNWs with uniform diameter on a Si substrate;^{14,16,17} but in this case, rather low-density nanowire arrays (0.1–1.8 wires/ μm^2) have been achieved, with poor control over nanowire spacing.¹⁷ Dense arrays of SiNWs have been achieved from Au clusters deposited by galvanic displacement from water-in-oil microemulsions,¹⁸ but with limited control over nanowire size uniformity and poor spatial ordering.

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In this article, we describe a nonlithographic technique to synthesize high-density, vertical SiNWs on a Si(111) substrate with well-defined diameter and spacing. Unlike the use of Au colloids for controlled growth of SiNWs, the method described here enables the fabrication of SiNWs with a much higher packing density of up to 60 wires/ μm^2 . Such a high packing density is particularly attractive in nanostructured thermoelectrics and biochemical sensing applications.

A porous anodic alumina (PAA) mask is used for the template growth of vertical SiNWs with homogeneous size on a Si(111) substrate. PAA is a material characterized by a honeycomb pattern of nanometer-sized pores with uniform diameter and spacing.¹⁹ The pores are formed during the electrochemical anodization of aluminum under controlled conditions; different self-ordering conditions yield pores of different diameters and spacing.²⁰ Various semiconductor nanomaterials such as Si, Ge, GaN, and InSb nanowires have been synthesized inside the pores of a PAA membrane.^{21–23} The VLS growth of SiNWs inside the pores of an unsupported PAA template using SiH_4 as the precursor gas has been reported previously.^{24–26} Briefly, gold is deposited inside a free-standing PAA membrane, and the Au loaded template is placed inside the VLS growth furnace where SiNWs with uniform diameter are grown inside the pores of the alumina film. Subsequently, the template is dissolved, leading to a dispersion of nanowires. Although this method demonstrates that a PAA film can be effective in preparing SiNWs with controlled diameter, it produces unsupported nanowires, thus preventing their integration into functional devices. In addition, no control over the growth direction of the SiNWs is achievable in this case, and both single crystalline and bicrystalline SiNWs are observed.²⁵ On the other hand, our approach allows the synthesis of vertically aligned, epitaxial SiNWs on a Si(111) substrate with a tight control over diameter distribution and with high packing density. To our knowledge, the approach reported here leads to the highest reported density of vertical SiNWs on a Si substrate with monodispersed diameter and uniform spacing without lithographic means.

Experimental Section

In this work, a PAA membrane, transferred onto Si, is used as the mask to evaporate ordered arrays of gold nanodots which are subsequently utilized as the catalytic sites for the SiNW growth. The two-step anodization method is employed for the synthesis of the PAA template mask.¹⁹ A high purity Al foil (99.99%) is first electropolished in a solution of ethanol/perchloric acid (5:1, v/v) and then anodized in a 0.3 M oxalic acid solution at 40 V and 0 °C

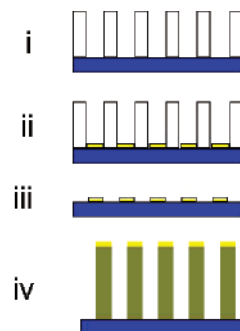


Figure 1. Schematic diagram of the fabrication method used for the PAA template-based growth of SiNWs. (i) Transfer of the PAA mask on Si(111), (ii) evaporation of Au through the PAA pores, (iii) PAA removal, and (iv) growth of SiNWs from the patterned substrate.

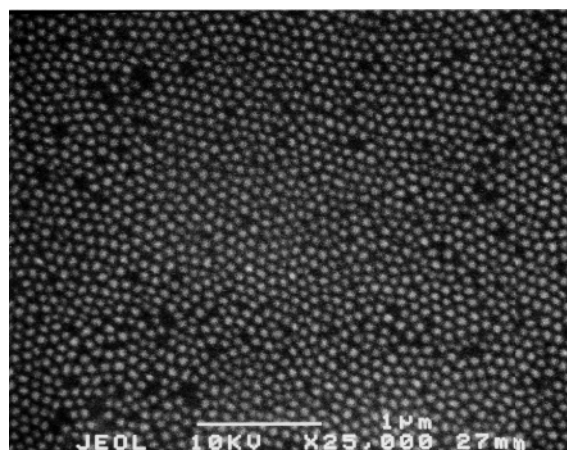


Figure 2. Ordered arrays of Au nanodots evaporated through the nanochannels of the PAA mask. The clusters have an average diameter of 53 nm and a dot-to-dot distance of 100 nm. The height of the dots is 5 nm.

for 8 h. After dissolving the first alumina layer in a phosphochromic solution (H_3PO_4 , 35 mL/L; Cr_2O_3 , 20 g/L) for 2 h at 80 °C, the sample is anodized again under the same conditions for 5 min, and a 200 nm thick PAA layer is obtained. After the second anodization, the PAA membrane is removed from the Al substrate by a lift-off process that involves the selective etching of the unoxidized aluminum in a CuCl_2 -based solution (100 mL of HCl, 100 mL of H_2O , and 3.4 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$). The barrier layer at the bottom of the porous alumina is dissolved in a 5 wt % H_3PO_4 solution at 30 °C for 30 min. The self-ordering anodization regime in oxalic acid produces pores of 45 nm diameter which are widened to 58 nm (with a standard deviation of 4.3%) during the etching of the barrier layer. The average interpore distance is 100 nm. The through-hole membrane obtained is transferred onto the Si(111) substrate via van der Waals bonding.

After evaporating 5 nm of gold through the alumina pores, the PAA layer is removed with commercial tape and the substrate with its hexagonal pattern of gold nanodots is used for the VLS process. The fabrication method is schematically illustrated in Figure 1. The SiNWs growth is carried out in an isothermal 1 in. diameter cylindrical quartz tube fed by SiCl_4 precursor vapor and 10% H_2 in Ar carrier gas.¹⁷ Part of the carrier gas is flown through liquid SiCl_4 to pick up the reactant vapor, and the mixture is introduced in the VLS chamber. Experiments are performed at atmospheric pressure and at temperatures between 800 and 900 °C.

Results and Discussion

Figure 2 shows the ordered pattern of gold nanodots after the thermal evaporation step and PAA mask removal. The

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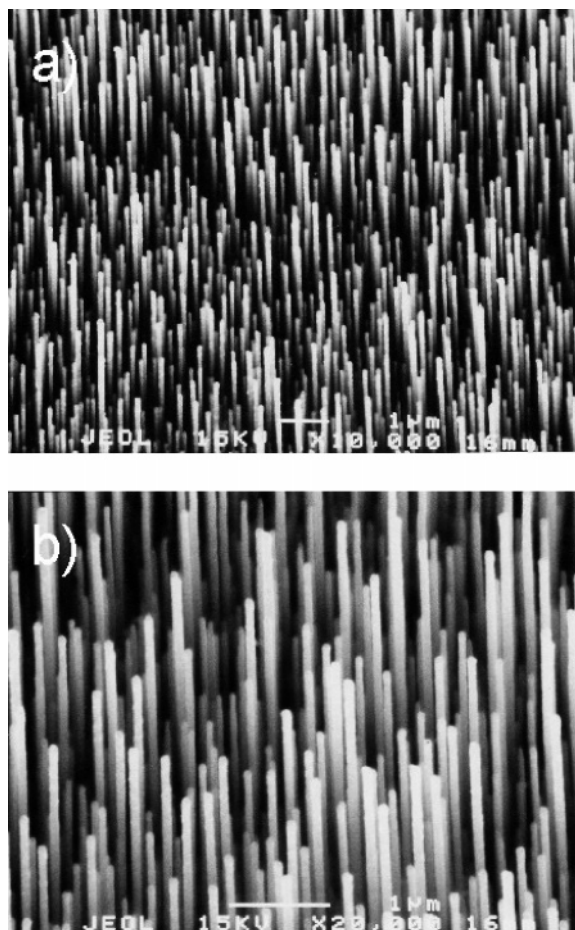


Figure 3. (a) Low magnification and (b) high magnification SEM images of vertically aligned, diameter-controlled SiNWs grown from ordered Au dots on Si(111) substrates: the average diameter of the wires is 72 nm.

size and arrangement of the gold clusters closely match those of the PAA pores. The average diameter of the dots is 53 nm with a standard deviation of 7.2%. The broadening of the size distribution of the Au clusters compared to that of the pores is mainly ascribable to the shadowing effect of the alumina walls as well as to some extent the misalignment of the incident Au beam with the nanoholes. The nanoparticle diameter to interparticle distance ratio can be further increased by simply prolonging the phosphoric acid etch of the PAA film yielding pores up to 80 nm diameter while keeping the distance between pores unchanged and equal to 100 nm. In this work, the etching time of the barrier layer has been adjusted in a way to ensure the opening of the bottom caps without causing excessive enlargement of the pores. The narrowing of the gap between adjacent pores and subsequently between adjacent gold nanoparticles may lead to the agglomeration of the Au–Si droplets, thus preventing the control over the size and growth location of the resulting wires. The average density of the evaporated Au nanoparticles is 93 nanodots/ μm^2 , which is 93% of the PAA pore density (~ 100 pores/ μm^2). Therefore, the use of a PAA film as a nonlithographic evaporation mask provides an effective method to obtain highly ordered arrays of gold nanodots on a silicon substrate with excellent reproducibility.²⁷

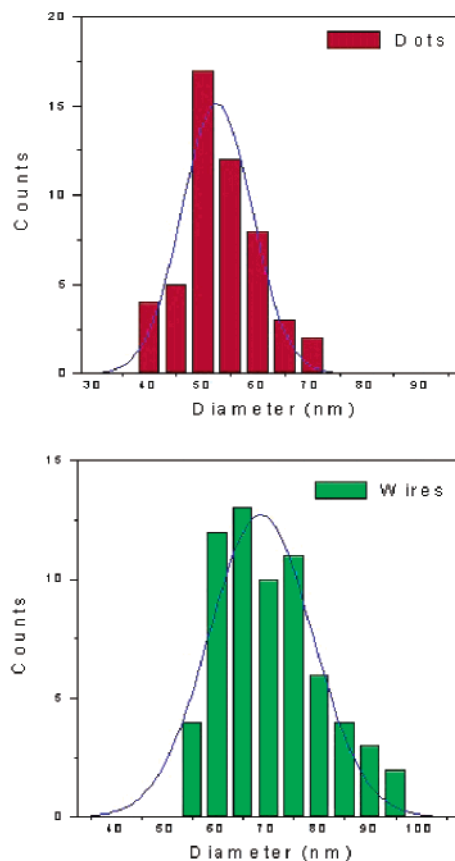


Figure 4. Diameter distribution of the Au cluster (top) and that of the resulting SiNWs (down).

The Si(111) substrates patterned with hexagonally ordered Au seeds are placed in the growth reactor for the VLS synthesis of SiNWs. The scanning electron microscopy (SEM) images of the resulting SiNWs are reported in Figure 3. Vertically aligned SiNWs with a narrow distribution of diameters are obtained for proper precursor/carrier flow ratios at 900 °C. The vertical alignment of the nanowires is achieved by effective anchoring of the PAA template to the substrate and by using SiCl_4 as the precursor gas which forms gaseous HCl as a byproduct upon decomposition. The HCl is believed to etch the native oxide layer on the Si surface causing epitaxial deposition of Si and consequent alignment of the wires with the exposed crystal face of the Si substrate.¹⁷ This is in contrast with SiH_4 as the precursor molecule, which requires additional precautions to remove the native silicon oxide layer before SiNWs growth.¹⁵ The SiNWs have an average diameter of 72 nm with a standard deviation of 10.8%. Figure 4 displays the diameter distribution of the Au clusters as well as that of the obtained SiNWs. As expected, SiNWs are larger in size than the generating catalyst nanoparticles as a result of the expansion of Au clusters as a consequence of the formation of a Au–Si alloy in the early stage of the growth. Given the negligible thickness of the Au dots compared to their diameter, it is most likely the latter value that determines the size of the Au/Si droplet and, therefore, the final SiNW size. In addition, it can be observed that the SiNWs have a wider size dispersion compared to that of the starting Au dots. This can be explained by examining the density of the SiNWs,

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which is approximately two-thirds that of the Au seeds (~ 60 wires/ μm^2).

Hence, some degree of agglomeration of molten Au–Si droplets occurs yielding wires with diameters in the range of 85–95 nm. This phenomenon is likely to be dominant in case of Au nanodots with diameters above 65 nm for which the distance between neighboring particles is too short to prevent agglomeration during the eutectic formation. It is worth noting that no agglomeration of gold clusters is observed when the substrates are heated to the reaction temperatures in the H_2/Ar atmosphere. This may be attributed to the presence of native silicon oxide on the Si(111) surface. The oxide layer, which is not reduced in the H_2/Ar environment, hinders gold mobility and diffusion over the substrate. This observation, which is in agreement with the findings of Ressel et al.,²⁸ demonstrates that the agglomeration of gold particles occurs upon diffusion of Si gaseous reactant into the nanosized liquid droplets of the catalyst metal, followed by nucleation and growth of nanowires. Nonetheless, good control over wire diameter and density can be achieved reproducibly and economically via the PAA template-based placement of Au nanoparticles. Furthermore, among non-lithographic techniques, the PAA method described here provides a unique tool to obtain vertically aligned, diameter-

controlled SiNWs with high packing densities, thus enabling effective nanowire integration into devices such as field emitter arrays as well as vertical field effect transistor arrays with enhanced efficiency.

Conclusions

In this work, we have demonstrated that a PAA template mask can be successfully employed to position the Au catalyst seeds on a Si surface for the VLS synthesis of vertically aligned SiNWs. The gold nanoparticle arrays are arranged in a highly ordered configuration reflecting the hexagonal pattern of the nanopores of the PAA mask. SiNWs with controlled dimensions and spacings are grown in a rather inexpensive manner with this approach over large areas (~ 7 mm \times ~ 7 mm). Additionally, this fabrication method is capable of producing SiNWs with a packing density as high as $6 \times 10^9/\text{cm}^2$, which could be achieved otherwise only with lithographic techniques, entailing serious limits for mass scale production of these nanomaterials. On the contrary, our process allows significant control and affordability toward SiNW synthesis and opens up the possibility of scaling up to high density nanodevice production.

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