Facile and scalable patterning of sublithographic scale uniform nanowires by ultra-thin AAO free-standing membrane

Gang Meng, Takeshi Yanagida, Kazuki Nagashima, Takashi Yanagishita, Masaki Kanai, Keisuke Oka, Annop Klamchuen, Sakon Rahong, Mati Horprathum, Bo Xu, Fuwei Zhuge, Yong He, Hideki Masuda and Tomoji Kawai

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Creating sublithographic scale uniform nanowires for large area is an important issue for nanowire-based various device applications. Although anodic aluminium oxide (AAO) membrane is a promising technique, existing attached AAO membrane mask methods have not been able to fabricate such small nanowires for large areas due to difficulties on transferring a thin membrane. Here we demonstrate a facile and scalable methodology to fabricate sublithographic scale uniformly sized nanowires by introducing ultra-thin AAO free-standing membrane with a rigid Al frame and a hydrophilic contacting method. The present method allows us to fabricate sub 20 nm nanowires with the standard deviations of 1.1 nm via defining the size and spacing of metal catalysts for nanowire growth. We also show the scalability of the present attached AAO membrane mask method for a 4-inch scale wafer.

Introduction

Self-assembled nanowires promise a novel fabrication methodology for nanoscale devices alternative to current lithographic technology because the nanowires can be designed at atomic scale. Among various methodologies to fabricate self-assembled nanowires, metal-catalyzed vapor–liquid–solid (VLS) technique has been proved to be one of the most promising methods since VLS allows us to control precisely the diameter and the spatial location of nanowires via defining the metal catalysts. Within the framework of VLS growth mechanism, the size distribution and the spacing of metal catalysts determine the length and the diameter of nanowires. Many techniques including electron-beam lithography, photolithography, laser interference lithography, nanoimprint lithography, and others have been examined to control the size distribution and the position of metal catalysts for VLS nanowire growth. However creating uniform-sized nanowires at sublithographic scale resolution for a large area is still a challenging issue, although the feasibility of a large quantity of such well-defined small nanowires will induce the breakthrough in the industrial applications using nanowires.

Anodic aluminium oxide (AAO) membrane as a mask for metal catalyst patterning is a promising technique to overcome the above issue. This is because AAO technique is highly scalable, the pore size can be easily at the sublithographic scale down to several tens of nm with the size uniformity, and variable regular spacing between pores. There are two types of AAO mask patterning, such as an attached AAO mask method via a membrane form and a connected AAO mask via a pre-deposited Al layer on the substrate. It has been reported that the regularity of AAO pores in the connected AAO mask method is lower than the attached AAO method due to the limited Al thickness. A barrier layer between AAO pores and substrate was also reported to be an issue in the connected AAO method. In addition, for the connected AAO mask method, a good adhesion between Al layer and a substrate is essential for patterning metal catalysts, in particular an electrode layer is required when electrochemically depositing metal catalysts into a pore with large aspect ratio. These requirements limit the applicable range of materials and substrate employed for a connected AAO method.

Although an attached AAO membrane mask method is applicable to any material and substrate, there are several difficulties to apply the existing attached AAO membrane mask methods for sublithographic scale VLS nanowire growth for large areas. First, there is the lower limitation of nanowire diameter ~50–70 nm. The size limitation in existing attached AAO membrane mask methods is due to the upper limitation on the aspect ratio of AAO membrane mask for metal deposition due to a shadowing effect. This phenomenon determines the lower limitation of AAO pore size used for metal depositions to maintain the low aspect ratio. Second is how to ensure a good contact between the membrane and the substrate,
because an attached AAO membrane mask is normally just maintained on the substrates via a weak Van der Waals surface attachment.\textsuperscript{24,27} Third is a difficulty to transfer completely a large-scale thin AAO membrane onto a substrate without breaking, cracking, folding and ripping, as highlighted in previous works.\textsuperscript{28,29}

Here we demonstrate a facile and scalable methodology to fabricate sublithographic scale uniform-sized nanowires by introducing ultra-thin AAO free-standing membrane less than 200 nm thickness with a rigid Al frame and a hydrophilic contacting method. The present method allows us to apply an attached AAO membrane mask method to a wafer scale large substrate without cracking or folding.

**Experimental section**

**AAO membrane preparation**

First, an ultra-thin AAO layer was formed on high-purity aluminium foil (99.99\%) by a two-step anodizing method.\textsuperscript{30} The details of the two-step anodizing method can be seen in elsewhere.\textsuperscript{13,31} With the precise control of anodizing conditions, well-ordered ca. 20 nm nanopore arrays with controlled pitches of 45, 63, 100 nm can be obtained with the desired thickness.\textsuperscript{30,31}

We have partially removed the oxide layer on the backside of Al foil by mechanical drilling. Then, the exposed Al layer can be etched by dipping into saturated iodine methanol solution at 50 °C for one hour. While the edge of the Al plate under the alumina layer can be retained for further process. For the wet etching of Al, we use a saturated iodine methanol solution\textsuperscript{32} instead of conventional etchants of toxic HgCl\textsubscript{2}\textsuperscript{33} or erosive CuCl\textsubscript{2} solutions\textsuperscript{34,35} because the selectively of iodine methanol to etch Al rather than alumina is much higher than other etchants. This allows us to fabricate a thin free-standing membrane.

**Membrane transfer onto substrate, nanopore fabrication and metal dot formation**

The AAO membrane with remaining Al structure was carefully transferred onto the target substrate. In this study, we used SrTiO\textsubscript{3}, MgO, (La\textsubscript{0.29}Sr\textsubscript{0.71})(Al\textsubscript{0.65}Ta\textsubscript{0.35})O\textsubscript{3} (LSAT) and LaAlO\textsubscript{3} substrates to examine the applicability of the present AAO method for various substrates. Oxygen plasma pre-treatment was employed to make a hydrophilic surface on the substrate by utilizing the plasma conditions of 400 V and 10 mA for 5 min. The hydrophilic surface of the substrate enables a good contact between the AAO membrane and substrate \textit{via} dropping water on the surface. The bottom part of anodic porous alumina can remain on the substrate by removing mechanically only the Al rigid frame, this is because the mechanical removal of Al rigid frame easily causes the separation between the bottom thin AAO membrane and the surrounding Al frame. Since the top of the anodic porous alumina was closed, we have etched the Al\textsubscript{2}O\textsubscript{3} layer by performing argon milling at 5 kV and 3 mA for 40 min. Then the ultra-thin AAO membrane with open-through nanopores was obtained. Au catalysts were then deposited by using ion beam evaporation technique. The depositions were performed at 7 kV and 5 mA under the background pressure of 5.0 × 10\textsuperscript{-4} Pa and the distance between target and substrate of 60 mm to ensure the straightness of supplied flux to the substrate. The AAO membrane was then peeled off by a scotch tape, remaining only as an ordered Au nanodot array.

**Nanowire growth**

VLS nanowire growth was carried out by pulsed laser deposition (PLD) technique (ArF excimer, λ = 193 nm). The detailed conditions and growth mechanisms for VLS oxide nanowire growth can be seen elsewhere.\textsuperscript{36–47} Prior to the nanowire growth, the background pressure of the chamber was 10\textsuperscript{-6} Pa. Then oxygen and argon mixed gas with the ratio of O\textsubscript{2} : Ar = 1 : 1000 was introduced by maintaining the total pressure of 10 Pa. MgO tablet was used as a target for MgO nanowire growth. The substrate temperature, repetition rate, laser energy and growth time were 800 °C, 10 Hz, 40 mJ and 60 min, respectively. The morphology of oxide nanowire was evaluated by field-emission scanning electron microscopy (FESEM) at an accelerating voltage of 30 kV. High-resolution transmission electron microscopy (HRTEM) at an accelerating voltage of 300 kV was utilized to identify the size of the oxide nanowire. X-Ray diffraction (XRD) measurements were performed to study the crystal structures of fabricated nanowires. The structural distribution data of the nanowires were estimated by SEM images for length measurements and HRTEM images for diameter measurements. For statistical reliability, we have averaged the data of 200 samples for size measurements.

**Results and discussion**

Fig. 1(a) shows the proposed process for an attached AAO membrane mask method to fabricate sublithographic scale VLS nanowires. The ultra-thin AAO layer, whose thickness can be controlled down to 50 nm, was formed by a two-step anodizing method. By controlling the anodizing conditions, we can obtain the well-ordered 20 nm nanopore arrays with the controlled pitches and the desired thickness.\textsuperscript{30,31} To support AAO free-standing membrane, we have partially etched Al from the backside to retain the rigid Al frame for further process handling, as shown in Fig. 1(b). For the wet etching of Al, we used a saturated iodine methanol solution\textsuperscript{32} instead of conventional etchants of toxic HgCl\textsubscript{2}\textsuperscript{33} or erosive CuCl\textsubscript{2} solutions\textsuperscript{34,35} because the selectivity of iodine methanol to etch Al rather than alumina is much higher than other etchants. This allows us to fabricate a thin AAO free-standing membrane.

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The details of fabrication conditions can be seen in the experimental section.

Fig. 2(a) shows the SEM image of AAO membrane mask fabricated by the proposed method. The pitch between AAO pores is 63 nm, and the pore size is 20 nm. The SEM images show the good contact by hydrophilic surface treatment. Both membrane and substrate were not treated by oxygen plasma. Cracking and folding can be seen in the image. Both membrane and substrate were treated by oxygen plasma.

Fig. 2(b) shows the relationship between the nanowire yield and the thickness of AAO membrane. (c–e) FESEM images of Au dot patterned by AAO membranes with the thicknesses of (c) 170 nm, (d) 500 nm and (e) 700 nm. Insets show the cross-sectional images of AAO membranes. (f–h) FESEM images of MgO nanowires grown on AAO membranes with the thickness of (f) 170 nm, (g) 500 nm and (h) 700 nm. Insets show top-view images. (i) Typical XRD data of patterned MgO nanowires.

Although the exact upper limitation depends on the straightness of the supplied flux to the substrate, Lei et al. have reported that the upper limitation of aspect ratio is about 10 even in well-controlled deposition configurations, which is clearly consistent with our results. Thus reducing a thickness of an attached AAO free-standing membrane mask is essential to realize VLS nanowires via AAO nanopores with a low aspect ratio.

Fig. 3 shows the structural distribution data (the diameter and the length) of VLS nanowires fabricated by the above AAO membrane of 100 nm thickness. For comparison, the structural distribution data of nanowires fabricated by non-patterned catalysts are shown. Clearly the size distributions of nanowires by the attached AAO membrane mask method are much narrower than those of non-patterned samples. Quantitatively, in non-patterned samples, the standard deviations were 4.8 nm for the diameter and 275.3 nm for the length. Such wide distribution is due to the heterogeneous agglomeration of Au catalysts on the substrate surface in the absence of patterning during high temperature process. On the other hand, the standard deviations for AAO membrane assisted nanowires were greatly improved, 1.1 nm in the diameter, and 84.8 nm in the...
length. Note that the present nanowires of 18.5 nm average diameter with the standard deviation of 1.1 nm for large area had been hardly attainable using the existing attached AAO membrane mask methods. Here we discuss how the nanowires fabricated by AAO membrane exhibit the narrow distributions of the diameter and the length by employing the uniform size and spacing of catalyst array. Within the framework of VLS growth mechanism, the nanowire growth rate is determined by the flux of material supply per unit surface area of catalysts. Thus the size (area) distribution of catalysts on the substrate surface causes the spatial variation of nanowire growth rate by varying the local material supply rate per unit surface area of catalysts.6,46 Thus the size (area) distribution of catalysts on the substrate surface causes the spatial variation of nanowire growth rate by varying the local material supply rate per unit surface area of catalysts.6,46

Fig. 3 Comparison between AAO membrane method and non-patterned catalysts on the structural distributions of the diameter and the length. (a,b) FESEM images of MgO nanowires grown from (a) patterned catalysts by AAO membrane and (b) non-patterned catalysts. SrTiO3(100) substrate was used for the nanowire fabrications. The structural distribution analysis data in (c,d) the diameter and (e,f) the length of MgO nanowires for both patterned and non-patterned samples.

Fig. 4 Controllability of spacing in AAO membrane method. FESEM images of (a–c) AAO membrane and (d–f) MgO nanowires grown on SrTiO3 substrate. The pitches of nanopore arrays are (a,d) 45 nm, (b,e) 63 nm and (c,f) 100 nm. Inset shows FFT images projected by the FESEM images, and FESEM images at near-edge of AAO membrane. (g) Ratio of the pitch of AAO membrane and the spacing of fabricated MgO nanowire array.

63 nm and (c) 100 nm. Inset images show the near-edge of AAO membrane, and the thickness of AAO membrane was ~100 nm. Fig. 4(d–f) show the SEM images of nanowires grown on SrTiO3 substrate by utilizing the spacing-controlled catalyst array. Insets show the FFT data calculated from the top-view images of the nanowires. In the SEM images, the spacing between nanowires seems to correspond to the spacing of AAO pores. More quantitatively, the ratio of AAO pitch to nanowire spacing was calculated and shown in Fig. 4(g). The ratio was found to be almost 1 for all samples, highlighting the feasibility of the present AAO method to control the spacing between nanowires. We attribute the successful spacing defining of nanowires due to a good contact between hydrophilic AAO membrane and hydrophilic substrate, which arises from a strong capillary interaction between them.

Fig. 5 demonstrates the applicability of the presented attached AAO membrane mask method for various substrates. SEM images and XRD data are shown in the figures. Nanowires were grown on various oxide substrates including MgO, LSAT and LaAlO3, whose lattice constants and surface chemical compositions are different.52 The pitches of pores and the thickness of AAO membrane were 63 nm and ~100 nm, respectively. Well-defined nanowires can be grown on any oxide substrates by utilizing the present AAO method. This is because the present method does not require the specific surface chemical modifications to obtain the stuck contact between AAO membrane and substrate. It is noted that for a connected AAO membrane mask method, these highly insulative substrates require the use of electrochemically active electrode layers, for example Ta, Ti or W,27 which are detrimental for VLS nanowire growth with high
temperature process up to 800 °C.\textsuperscript{36–47} Thus the present attached AAO process is a rather versatile method for VLS nanowire growths under various fabrication conditions.

Fig. 6 shows the scalability of the presented attached AAO membrane mask method. The photographic images were shown in the figures. The AAO membrane with 200 nm thickness was formed on a 3 inch Si substrate, and the membrane was not an open-through pore. The large scale AAO free-standing membranes can be seen in the images of Fig. 6(a) and (c), and the AAO membranes can be easily transferred onto the wafer without cracking or folding, as seen in Fig. 6(b) and (d). The feasibility of the AAO free-standing membrane for 4 inch scale is also shown in the Fig. 6(e). Note that the AAO free-standing membrane with 200 nm thickness for 4 inch scale is the largest so far reported. Thus the presented attached AAO membrane mask method is highly scalable, in principle this method can be further extended to a much larger scale substrate.

Conclusion

In summary, we have successfully demonstrated a facile and scalable methodology to fabricate uniform-sized VLS nanowires at sublithographic scale by using ultra-thin AAO free-standing membrane created via a rigid Al frame and a hydrophilic contacting method. Use of the attached AAO free-standing membrane mask with the thickness less than 200 nm allows us to fabricate sub 20 nm nanowires with the standard deviations of 1.1 nm via defining the distributions of both the size and the spacing of the metal catalysts. We also show the scalability of the present attached AAO membrane mask method for a 4-inch scale wafer.

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