Growth of copper-indium nanorods on Si substrate using porous anodic alumina as template

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Abstract. Copper-indium nanorod arrays have been synthesized by electrodeposition using porous anodic alumina nano template supported on a silicon substrate. Porous anodic alumina template was fabricated by evaporating aluminium film onto silicon substrate and then anodizing the aluminium film in dilute phosphoric acid. The approach employs a plasma etching to penetrate the alumina pore barrier layer before electrodeposition, which enables direct electrical and chemical contact with the silicon substrate electrode. The resulting template and copper-indium nanorods obtained were characterized using scanning electron microscopy (SEM) and energy-dispersed X-ray spectroscopic analyzer (EDS), the pores of alumina are found to have dimensions of 150–250 nm pore diameters and 330–510 nm pore spacings, partial filling of the pores of the alumina template by Cu-In is achieved. The results of this work reveal that the alumina nano template is particularly well suited to the etching mask and template-assisted growth of nanostructures to be integrated into rigid substrate.

1. Introduction
Ordered one-dimensional nanorods have attracted considerable interests recently for their fundamental importance and potential applications in many fields, such as data storage, field emission display, light-emission diodes and energy conversion [1-3]. To fabricate the nanorod arrays, it has been considered that the template-directed synthesis method is the simplest and convenient pathway as an inexpensive alternative to lithographic patterning method. Porous anodic alumina (PAA) has been frequently used for the templated synthesis of nanorods, since this porous template material is consisted of a self-assembled honeycomb array of uniform size parallel channels [4,5], pores with different diameters and pore interval distance can be created by choosing the proper anodization condition of the aluminium layer. The majority of previous studies used Al foils to prepare PAA films, which must eventually be separated from the Al foil for later applications, and the separated PAA film is brittle, so great care needs to be exercised in the preparation and manipulation of the PAA film. This is apparently not suitable for most integrated device applications. Recently, nanoporous PAA has been prepared directly by Al films coated on silicon wafers for integrated micro-electronic applications [6,7]. Moreover, in PAA membrane, there is a continuous and dense alumina barrier layer at the pore base, which prevents the direct electrical and chemical contact between the pore and the base conducting
substrate. Therefore, it is necessary to develop low-cost and simple methods to remove the barrier layer and get throughout channels to the substrate.

Figure 1. Schematic diagram describing the fabrication of PAA films and nanorod arrays on silicon substrate and other rigid substrates.

In this paper, we present a procedure that combines an anodization process to produce template arrays and a reactive ion plasma etching (RIE) method to get throughout channels to the substrate. Large-area PAA membranes with large cells on silicon substrate were prepared by anodizing evaporated aluminium film in phosphoric acid solution at 160V. RIE was employed to remove the barrier layer in the channel base, and copper-indium nanorods were fabricated by electrodeposition in the PAA template. Figure 1 illustrates the fabrication process in this work.

2. Experiment

An aluminium film with thickness approximately 2 μm was deposited on an N type silicon substrate with resistivity of 1–3 Ω·cm by electron-beam evaporation. A two-step anodization was then carried out in a 5wt% phosphoric acid solution at 1 °C and a DC potential of 160 V. The alumina yielded in the first anodization step was dissolved by immersing the sample in a mixed acid solution with phosphoric acid and chromic oxide solution (6wt%H₃PO₄+1.8wt%H₂CrO₄) at 60 °C. The second anodization was then carried out until the current in the circuit dropped significantly. To ensure complete conversion of the entire aluminium film into its oxide, the voltage was maintained for 60 s after the current had stabilized at this low value. By controlling the time of the second step, we can control the ultimate thickness of the PAA film. Subsequently, the AAO sample was subjected to chemical etching (in 5wt. % H₃PO₄ for 30–50min at 30°C) to enlarge the pores and thin the barrier layer at the bottom of PAA template. Next, the sample with the pore widened alumina on the silicon substrate was subjected to reactive ion etching. The gases used were CHF₃ and Ar with flow rates of 5 sccm each. The power was set at 250 W and the chamber pressure was maintained at 25 mTorr. The etching duration was 5 min. Co-depositions of copper and indium through the nanometer-scale windows in the PAA were performed by electrodeposition technique. A three electrode system with platinum counter electrode and silver chloride reference electrode was used. An aqueous solution contains 3mM CuCl₂, 10mM InCl₃, the solution pH was adjusted to 1.8 with HCL solution. The electrodeposition process was conducted in constant voltage mode at 0.63V at room temperature, and the deposition time was 15 min.

The morphology and composition of the PAA and Cu-In nanorods were characterized, respectively, by a JEOL JSM-6390LA scanning electron microscope (SEM) and a JED-2300 energy dispersive X-ray analyzer (EDS).

3. Results and discussion

To obtain a PAA template with straight channels, Al film of a high purity and smooth surface is needed, so the substrate was rotated and no heating was applied during e-beam evaporation. In the case of phosphoric acid electrolyte, it was not easy to continue electrolysis for a long time without
burning, namely. The temperature of the electrolyte need to be maintained at 1℃ during anodization using a cooling system and the solution was stirred vigorously using a stirrer in order to accelerate the diffusion of the heat that evolved from the sample, which is important or preventing localized temperature increases and to maintain the stable growth of the anodic oxide film.

Figure 2. PAA film anodized by Al film on Si with subsequent chemical widen (5wt% H3PO4, at 30℃, 30min.) (a) plane view, (b) cross-sectional view, (c) after RIE etching, and (d) top-view of PAA template filled by Cu-In nanorods.

Figure 2(a) and (b) show the surface morphologies and cross-sectional images of the prepared PAA that were widened in 5wt% H3PO4 solution at 30℃ for 30 min, respectively. The diameters of the nanopores are around 150-250 nm and pore interval distances are 330-520 nm, while the template thickness is approximate 1200 nm. The homogeneity of cell arrangement is rather inferior to those produced in other electrolytes, such as oxalic and sulfuric acid solutions [8,9], because the high voltage tends to induce local events such as electric breakdown, local thickening of the barrier layer and pore branching.

Figure 3. Cu-In nanorods synthesized in PAA template (a) top view and (b) corresponding EDX spectroscopy of the template and nanorods.

Figure 2(c) shows SEM cross-sectional image of the PAA template on silicon after RIE etching. It is obvious that the barrier layer was etched away and the substrate also was etched due to long etching
duration. Cu-In alloy nanorods were deposited in the PAA template on Si substrate as shown in figure 2(d). From the experimental results on EDS measurement in figure 3(a) and (b), the peaks of the Cu and In component were observed confirms that the nanorods are Cu-In alloy. The experimental data above clearly show that the incorporation of porous anodic alumina membrane and the template-assist growth of nanorods arrays were achieved, also the PAA template is a good etching mask for fabrication of other nanostructures. For future work a better control of the etching and electrodeposition would be desirable.

4. Conclusion
We report a simple approach for the synthesis copper-indium nanorods on rigid substrate, by combing the direct anodization of aluminum on Si substrate, RIE etching and electrodeposition technique. The pore diameter, interval distance and thickness of the PAA template can be controlled by selecting proper anodization conditions, which makes the alumina nano template particularly well suited to the etching mask and template-assisted growth of nanostructures to be integrated into rigid substrate. Since there is a support of substrate, the resulting structure is robust enough to be grown in large area. The Cu-In nanorods grown on the substrate also have the potential applications in copper indium diselenide based solar cells.

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