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COMMUNICATIONS

Two-dimensional lateral superlattices of nanostructures: Nonlithographic formation by anodic membrane template

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A nonlithographic technique that utilizes highly ordered anodized aluminum oxide porous membrane as template is presented as a general fabrication means for the formation of an array of vastly different two-dimensional lateral superlattices structures. Hexagonal close-packed nanopore arrays were fabricated on Si, GaAs, and GaN substrates via reactive ion etching. Quantum dot arrays of various metals and semiconductors were formed through evaporation and subsequent etching. The two-dimensional lateral superlattice structures fabricated using this method are of a high level of ordering, uniformity, and packing density. The diameter and periodicity of the nanostructures are determined by the features of the original alumina membrane, which can be adjusted by varying the anodization conditions. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1433173]

The development of quantum well and superlattice structures has greatly enhanced the performance of a variety of electronic and optoelectronic devices. However, it has been known for quite some time that the venture towards lower dimensions such as quantum wires and quantum dots will lead to even greater benefits. Thus, much attention has been directed towards fabricating well-patterned semiconductor nanostructures. Conventional patterning by electron-beam lithography is workable, but impractical for large array sizes. Self-assembly of quantum dots by heteroepitaxial growth yields a sparse packing density, achieves only partial ordering with a broad distribution of dot sizes. Also, the technique is specific to a particular material system.

An alternative path to the formation of low-dimensional structures, especially well-ordered and densely packed arrays of such nanostructures, is via self-organization in electrochemistry. This nonlithographic technique that utilizes anodized aluminum oxide (AAO) in its porous form, i.e., nanoporous alumina, has attracted considerable interest recently built on original explorations a decade earlier.[1–6] The nanopores in the AAO formed under carefully controlled conditions can self-organize into highly ordered arrays, be uniform in diameter and in spacing, and oriented normal to the plane.[6,7]

In this article, demonstrate the versatile utilizations of the highly ordered AAO template and present it as a general fabrication tool for templating formations of various two-dimensional lateral superlattice structures in semiconductors, metals, or other composite materials. We show that one can transfer the nanopore array directly onto a semiconductor or metal substrate via etching (positive transfer) and/or form their inverse structures (negative transfer) such as array of pillars and dots via evaporation of masking caps through the nanopores followed by a subsequent etch. The fabrication process flow is described below and is illustrated in Fig. 1.

Anodized porous alumina has been studied for many years. And it is well established that by a carefully controlled two step anodize process, high purity (99.999%) aluminum foil will self-organize into densely packed, highly ordered, vertically oriented, straight nanopores. Details on the anodization process are published elsewhere.[7] The periodic porous array has a very narrow pore diameter distribution and found to be defect free over microscopically large areas.[7–10] After nanopore array formation by anodization, the AAO membrane can be separated from the aluminum foil using a 2% $HgCl_2$ solution. The obtained nanoporous array in the membrane is hexagonally ordered with the nanopore diameter typically around 40 nm and periodicity around 100 nm, both adjustable to some extent by varying the anodization conditions. The packing density is of the order of 10^{10} cm^{-2}. The nanopores are open on one side of the membrane while a thin Al_2O_3 barrier layer exists on the opposite side. Two different ways are tried to remove this barrier layer and form a through-pore membrane. Etching the membrane in a 0.1 M phosphoric acid solution for 3 h at room temperature forms a through-pore membrane as shown in the scanning electron microscope (SEM) image in Fig. 2. The diameter of the nanopores after removing the barrier layer becomes slightly larger and the pore diameter can be widened further by extending the wet etch time in the phosphoric acid solution without affecting the periodicity. The pore diameter standard deviation throughout the array is better than 5% of the mean diameter. Plasma etching with CF_4+O_2 gas system is also effective for removing the barrier layer without changing either the pore diameter or the period. The flow rates of CF_4 and O_2 are 18 and 8 sccm, respectively. The pressure is 100 mTorr with a power of 250 W. An etching time of 10 min. is

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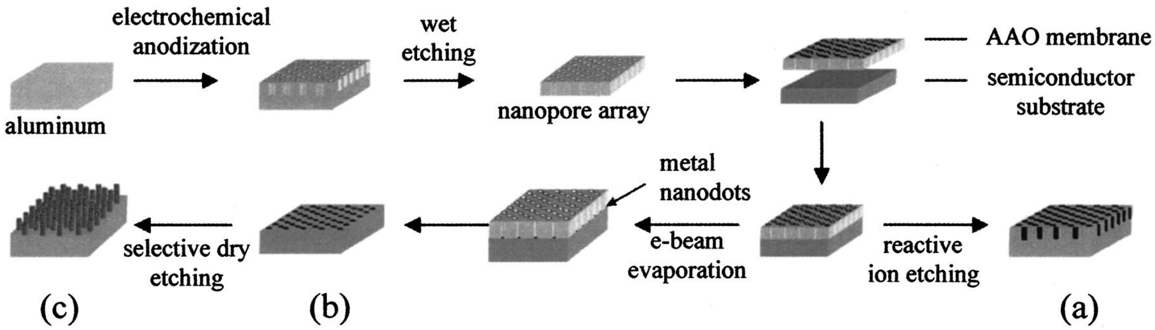

FIG. 1. Schematic of the fabrication of lateral two-dimensional superlattice structures: (a) semiconductor with nanopore array; (b) semiconductor with metal nanodot array; and (c) an ordered semiconductor nanopillar array.

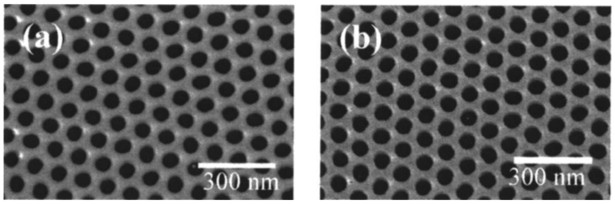

FIG. 2. SEM views of an anodized aluminum oxide membrane from (a) the top and (b) the bottom.

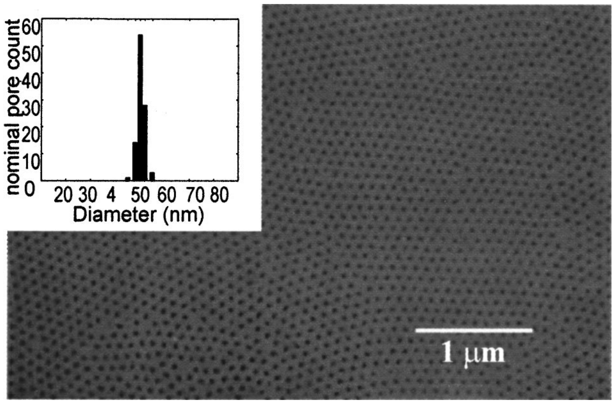

FIG. 3. SEM image of Si with nanopore arrays after AAO mask removal.

TABLE I. Dry etching conditions for nanopore fabrication.

Substrate	Si	GaAs	GaN
Gas	$CBrF_3+CF_4$	BCl_3	Cl_2
Flow rate (sccm)	10+2	20	60
Pressure (mTorr)	70	15	80
Power (W)	80	100	200

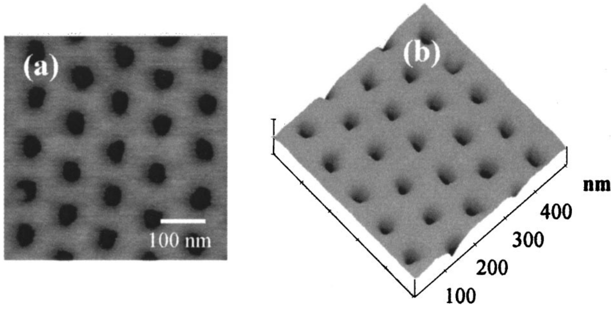

FIG. 4. AFM images of nanopore arrays on GaAs after AAO mask removal: (a) top view and (b) surface graph.

enough to fully open the nanopores. Through-pore membranes made by dry etching maintain all the characteristics of the original membrane.

The plasma etched through-pore membrane of up to 1 cm^2 in area and approximately 500 nm thick can easily be placed directly onto a semiconductor substrate as an etch mask to form the first type of two-dimensional lateral superlattice—nanopore (or, nanomesh) superlattice. Plasma etching (Plasma Therm 790 Series) with $CBrF_3$ and CF_4 gas systems was used to form nanopores on Si as an example of the first type. The flow rate of $CBrF_3$ and CF_4 was 10 and 2 sccm, respectively. The pressure of the chamber was 70 mTorr with a rf power of 80 W. A SEM image in Fig. 3 shows the nanopore array pattern on Si after a 15 min etch and after the removal of the alumina membrane. The etched pore depth is about 100 nm for this etch duration. The mean pore diameter is approximately 40 nm and the period is 100 nm: all the same as in the original AAO membrane. The results represent a significant advance over the prior effort with a similar goal.[1] The resultant nanopore diameter distribution remains narrow (inset in Fig. 3) as it should be because both the Si surface and the membrane surface are flat and smooth.

Reactive ion etching (Trion Minilock II) with a BCl_3 and Cl_2 gas system was used to transfer the AAO nanopore array pattern onto GaAs and GaN. The typical conditions are listed in Table I. After etching, the alumina membrane was physically removed. Figure 4 shows the atomic force microscope (AFM) images of the resultant nanopore arrays on GaAs. For an etching time of 15 min, the etched pore depth is about 120 nm in GaAs, as determined by SEM rather than AFM, which is constrained by probe size and shape. The diameter of the semiconductor holes is approximately 40 nm for both and the period is 100 nm, the same as in the original AAO membrane mask. However, we noticed that in the case of GaN, the nanopore diameter distribution is noticeably broader than that of the membrane. This is understandable given that the surface roughness of GaN wafer is normally greater than that of GaAs and more so than in the case of Si.

From the above results it is clear that highly ordered, densely packed nanopore superlattice can be readily fabricated using this nonlithographic templating technique on different semiconductor substrates or other materials. The resultant pore diameter is about the same as the original AAO

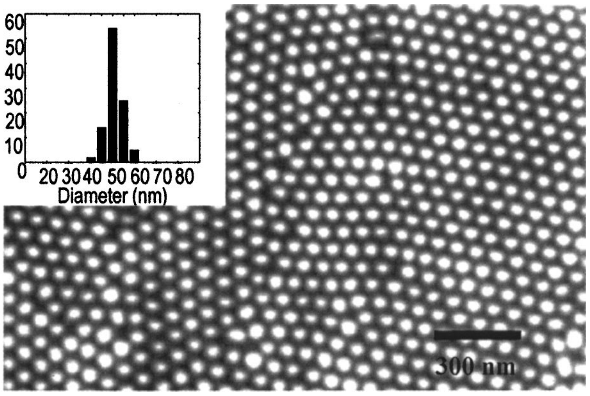

FIG. 5. SEM image of a Ni nanodot array on Si.

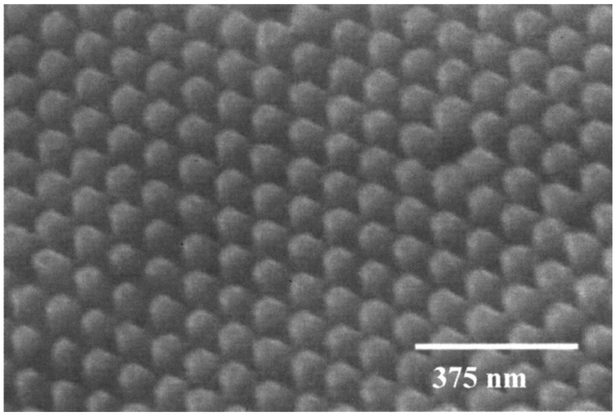

FIG. 6. An oblique view SEM image of a Si nanodot array.

mask. The uniformity and the packing density are determined by the original AAO membranes.

Next, we show that the two-dimensional lateral superlattice of quantum dots can also be made using AAO membrane. Through-pore alumina membranes made by etching in phosphoric acid were placed on Si and GaAs substrates. Electronic beam evaporation in a vacuum of 2×10^{-6} Torr was employed to deposit metal nanodot arrays through the membrane. The process is nonselective to either target metal materials or substrate materials. The typical evaporation rate used was 0.03 nm/s for bulk metal films. Different metals, such as Au, Ni, Co, and Fe, were deposited on Si and GaAs substrates. Figure 5 shows the e-beam evaporated Ni nanodot array on Si substrate. The height of the Ni cap is around 20 nm for an evaporation time of 60 min. The mean diameter of the nanodots is approximately 55 nm, the same as in the AAO membrane used. The nanodot diameter distribution is typically 10% of the mean diameter, which is wider than that of the AAO membrane and can be attributed to the evaporated metals' lateral diffusion and the surface roughness.

The Si wafer patterned with evaporated highly ordered Ni nanocaps was then selective etched by plasma etching using the same recipe listed in Table I for Si nanopore etching. Figure 6 is the oblique view of resulted Si nanodot array. After 5 min of etching, dots of 30 nm in height were obtained. The dot diameter is approximately 50 nm, the same as that of the metal dot mask formed via the AAO template. Thus, it is apparent that this technique can be applied in various ways to form semiconductor quantum-dot arrays, metallic dot arrays, or other more complex composite nanostructures arrays.

In summary, we have fabricated a variety of two-dimensional lateral superlattice structures using a highly ordered alumina through-hole membrane as a template. Arrays of nanopores, nanopillars, and metallic dots on Si, GaAs, and GaN have been shown with the use of the AAO membrane combined with conventional dry etching and evaporation methods. The transferred nanostructures are shown to be highly ordered with a narrow size distribution and high packing density.

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