Preparation of Si Nanocrystals Using Anodic Porous Alumina Template Formed on Silicon Substrate

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A novel technique to extend template application of anodic porous alumina to Si has been reported. First, porous alumina template about 400 nm thick was prepared on silicon substrate by anodizing thin aluminum film with high purity of 99.99% in 15 wt.% sulfuric acid under a constant voltage of 20 V and at an electrolyte temperature of 5°C. Then, amorphous Si layer approximately 50 nm in thickness was deposited onto the surface of template by using electron beam evaporation technique followed by an Xe ion beam bombardment, upon which as-coated Si layer at the pore mouth could be removed into pores smoothly. Three runs were performed by repeating above process of deposition and post bombardment. Finally, samples were annealed at 800°C for 30 min in nitrogen. Transmission electron microscopy and x-ray diffraction analysis reveal Si nanocrystals with a size of 15–20 nm being formed in the pores of template.

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It is well known that a porous structure with pore diameter varying over a very wide range from nanometer scale up to the micro scale depending on the electrochemical parameters used, can be obtained when aluminum with high purity is treated anodically in moderate acid solutions such as sulfuric acid, phosphoric acid, and oxalic acid.[1] As a result of naturally occurring self-organized process during anodization,[2–5] anodic porous alumina shows a quite different structure from that of extensively studied porous silicon.[6,7] It has several unique structural properties such as controllable pore diameter (4–250 nm), extremely narrow size distribution for pores diameter and their interval, ideally cylindrical shape of pores. During last decades anodic porous alumina has attracted considerable research attention due to not only its widespread industrial applications but also great complexity involved in its growth process. Recently, there has been a renewed interest in this material being used as templates for fabrication of other metal or semiconductor nanostuctures.[8–12]

Among previous studies on template application of anodic porous alumina, a majority of papers were focused on the use of dc or ac electrochemical deposition methods, whereas only a few employed the chemical or physical vapor deposition ones.[13,14] This mainly resulted from the advantage shown in the use of electrochemical methods over that vapor deposition ones. In detail, the electrochemical deposition worked in the state of fluid and the pores were easily filled out by the electrochemically reduced products. On the contrary, the chemical or physical vapor deposition worked in the vapor phase and the deposited films were easily coated at the pore mouth instead of expected piling up from the pore bottom progressively. However, the electrochemical deposition methods compared to vapor ones have their inherent difficulties of depositing those materials whose relative salt solutions are difficult to find, for example, Si. Therefore, the aim of present letter is to overcome above problems faced by both types of deposition method and to carry out the template application of anodic porous alumina to Si. To accomplish this aim, we propose a novel technique, that is, electron beam deposition combined with post Xe ion beam bombardment.

Template application of anodic porous alumina to Si for fabrication of Si nanostructure via electron beam deposition and post Xe ion bombardment technique is described schematically in Fig. 1. Overall process consists of three main steps. First, anodic porous alumina template was prepared by anodizing aluminum with purity 99.99% in 15 wt.% sulfuric acid solution under a constant voltage of 20 V and an electrolyte temperature of 5°C, respectively. To avoid any effects possibly caused by remaining aluminum to final annealing treatment, we employed a controlled anodization and did not terminate the anodization process until the aluminum metal had been totally anodized. In other words, the alumina template was fabricated directly on silicon substrate.[15] Thickness of the template was about 400 nm checked by scanning electron microscopy. Then, amorphous silicon film about 50 nm in thickness was deposited onto the template surface by electron beam evaporation. Prior to the deposition, the surface of the template had been cleaned with 20 keV ions for the dose of $2 \times 10^{15}/\text{cm}^3$ in order to remove the organic and carbon contamination. Subsequently, Xe ion beam was introduced in the deposition chamber to bombard the films at a fixed energy of 80 keV with an incidence direction perpendicular

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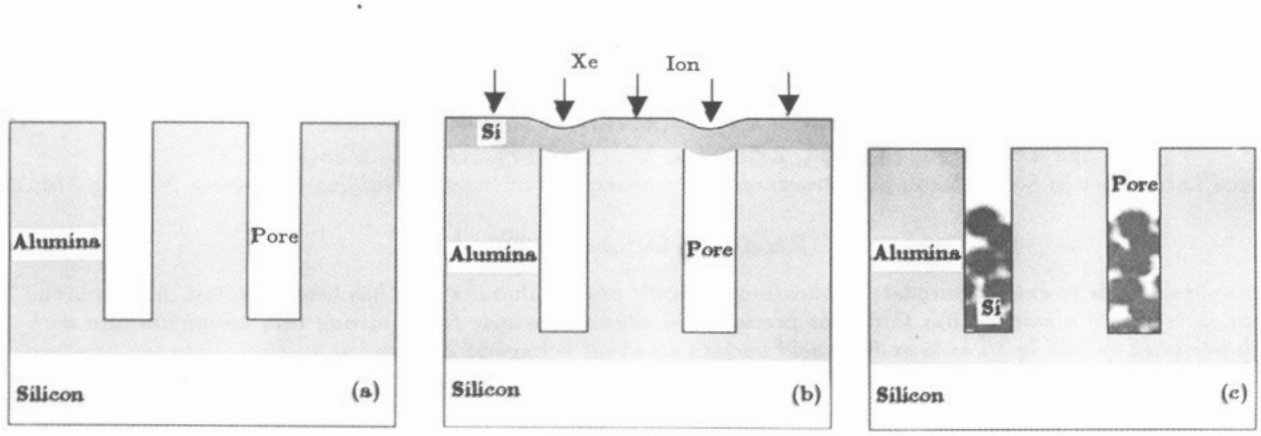

Fig. 1. Schematic diagram of three main steps included in the template application of anodic porous alumina to Si.

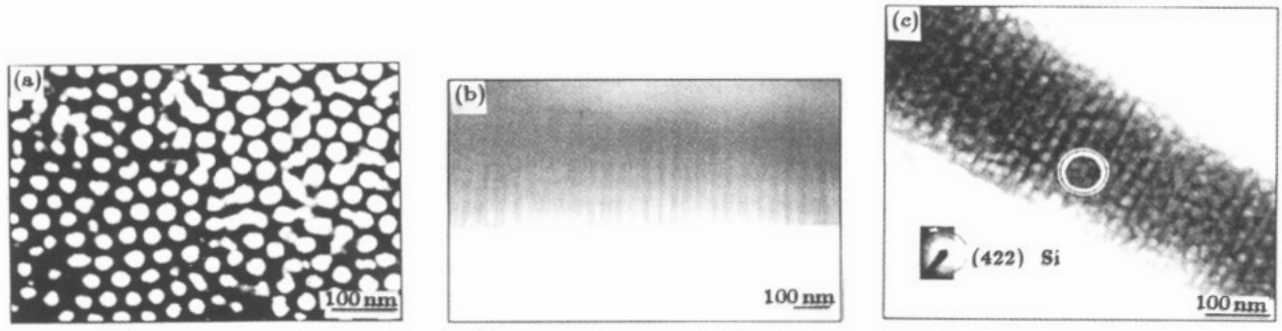

Fig. 2. (a) Planar and (b) cross-sectional TEM images of the original template of anodic porous alumina and (c) cross-sectional TEM image of the annealed sample at 800°C for 30 min. The inset in (c) is the electron diffraction pattern from the marked cycle.

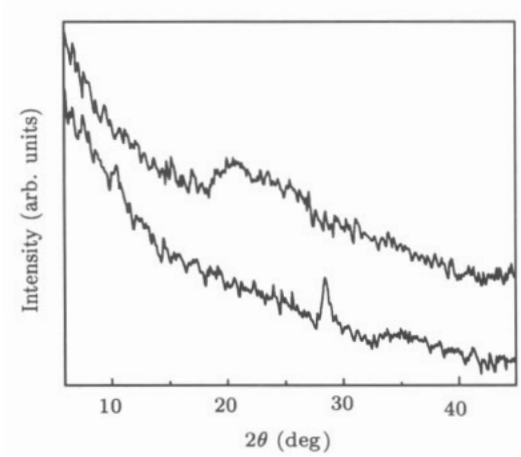

Fig. 3. XRD pattern for as-bombarded sample (upper) and annealed one at 800°C for 30 min (lower).

to the template surface. After the accumulated dose of Xe ion was up to $5 \times 10^{16}/\text{cm}^2$, the second run of deposition and post bombardment began. All three runs were performed by repeating above process of deposition and post bombardment. Finally, thermal annealing procedure took place in a quartz tube infrared furnace flushed with nitrogen at 800°C for 30 min. On annealing as-bombarded amorphous Si in the pores tended to crystallize into nanocrystals. Cross-sectional microstructure of the annealed sample was studied by using a Hitachi H-800-NA microscope operated at 200 keV. X-ray diffraction (XRD) pattern was also measured using Cu K_α x-rays from a rotating cathode operated at 40 kV and 180 mA.

Figures 2 (a) and 2(b) show planar and cross-sectional transmission electron microscope images of the original template of anodic porous alumina. In Fig. 2(a), local domains in the range of $1-2\,\mu$m with quasi-hexagonal arrangement can be identified. Mean diameter and spacing of the pores are approximately 24 and 37 nm, respectively. It is noteworthy that the pores in Fig. 2 (b) are significantly vertical to the substrate surface. This is a favorable feature for post Xe ion bombardment that ensures the Si coated at the pore mouth to be removed into the pores. Figure 2(c) shows the cross-sectional transmission electron microscope (TEM) image of the sample after annealing at 800°C for 30 min. Nanoparticles appeared in bright contrast with a size of 15–20 nm can be clearly observed in the pores of template. Most of them seem to align in a similar direction along the pores, which is

certainly correlated to the spatial confinement effect of the pores. To further confirm those nanoparticles are exactly Si nanocrystals, we studied the electron diffraction pattern from a selected area (marked by a circle). As shown in the inset of Fig. 2(c), typical halo ring (indicated by the arrow) on the diffraction pattern corresponds to that particular set of (422) reflections for Si. The evident four bright spots superposed on the halo ring are attributed to the reflection of Si nanocrystals having preferential directions and thereby expected nanocrystalline Si is evidenced.

Figure 3 (lower) shows the XRD pattern of the annealed sample at 800°C for 30 min. A small peak corresponding to (111) orientation can be seen at $2\theta = 28.4°$ indicating a preferential (111) crystallization of Si nanocrystals. Using Scherrer formula: $L = 0.9\lambda/\cos\theta \cdot \Delta(2\theta)$ the average size of nanocrystals is calculated to be approximately 16 nm which is slightly smaller than the mean value measured from the TEM image. This difference in size may be caused by an oxide-capping layer usually contained on the surface of the nanocrystals. Figure 3 (upper) also displays a typical amorphous pattern of Si with a broad peak in the range of $10° - 25°$ for the as-bombarded sample without any annealing treatment for comparison.

In summary, we have demonstrated for the first time the template application of anodic porous alumina to Si via electron beam deposition and post Xe ion beam bombardment technique. TEM and XRD analysis of the annealed sample at 800°C in nitrogen for 30 min reveal the presence of Si nanocrystals in the pores of the sample. It proves that the Xe ion beam bombardment is an effective technique to remove the coated Si layer into the pores. This technique to great extent makes a good deficiency of the electrochemical deposition method for depositing those materials whose relative salt solutions are difficult to find. Furthermore, great potential applications of this technique can be anticipated particularly in microelectronics or nanoelectronics since it has successfully broken through the limitation of the template application of anodic porous alumina to those important semiconductors such as Si.

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