Fabrication of Inverse Opal Structure of Silica by Si Anodization

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Three-dimensional (3D) porous materials that are formed using spherical colloidal particles as templates have attracted considerable attention because of their potential for application in unique optical devices such as photonic crystals. Using an inverse opal structure, which could be produced only in the voids between the particles, it has been possible to fabricate various types of porous material by changing matrix materials, such as organic prepolymer or monomer, a sol-gel precursor, a solution containing an inorganic salt and metal alkoxides. That is, 3D porous materials can be obtained from a wide variety of materials, including polymers, ceramic materials, inorganic semiconductors and metals. The common methods used in templating are based on high-temperature "dry" processes, such as polymerization, sol-gel hydrolysis, thermal decomposition and reduction. On the other hand, several studies have been reported on the low-temperature "wet" process using electrodeposition or electroless deposition. In the case of the electrochemical process, the dimensions of the desired structures can be adjusted easily by controlling electrolytic conditions in comparison with the conventional "dry" process. Here we present a novel approach to the fabrication of 3D porous structures using spherical colloidal particles as templates for the anodization of the underlying substrate in an aqueous solution. In this process, the void can be filled with the silicon oxide produced on a Si substrate by localized anodization.

Figure 1 shows the schematic of the templating of the colloidal crystal structure on a Si substrate. The templating process used to fabricate the 3D porous structure was carried out as described previously.[1)] A *p*-type Si wafer (0.005-0.01 Ω cm, (100) crystal orientation) was used as the substrate. The monodisperse suspension of polystyrene beads (PS, 0.2% solids) was dropped onto the substrate. The suspension drop was dried in air, and the nanospheres self-assembled into a closely packed structure with 3D ordered lattices via attractive capillary forces [Fig. 1(a)]. After the complete evaporation of the solvent, the Si substrate with the colloidal crystal structure of PS beads was anodized at a constant current density in 0.3 mol dm^{-3} oxalic acid at 20℃ [Fig. 1(b)]. The formation behavior of silicon oxide on the Si substrate was examined by measuring voltage transient at a constant current density and observing the obtained structure at different stages after dissolving the PS beads in toluene [Fig. 1(c)]. The ordered geometric structure formed on the Si substrate was evaluated by field-emission scanning electron microscopy.

From the SEM image in Fig. 2, it was confirmed that the networks of silicon oxide, that is, the hollow spaces of air spheres were ordered in a triangular lattice, the interval of which was in good agreement with the diameter (474 nm) of the PS beads used as a template. The three dark spots inside each hole indicate the air spheres of the underlying layer, which were formed at spots of contact between beads. That is, the voids between the particles were filled with the silicon oxide produced on the Si substrate by anodization. According to a previous report using PS beads as templates, the center-to-center distance between the holes is reduced by about 30 % less than the initial size of the PS beads owing to the shrinkage during the drying and heat treatment process. The decreasing in hole distance in our process is small in comparison with that achieved using high-temperature "dry" processes, such as polymerization, sol-gel hydrolysis, thermal decomposition, and calcination.

The obtained porous silica has potential technological or scientific applications as catalysis, supports, and sensors that need a tailored space of controlled 3D periodicity. In addition, the preparation of porous oxides based on this process is applicable to different types of substrate including other semiconductors and metals.

[1] H. Asoh, A. Uehara and S. Ono, *Jpn. J. Appl. Phys.* in press.

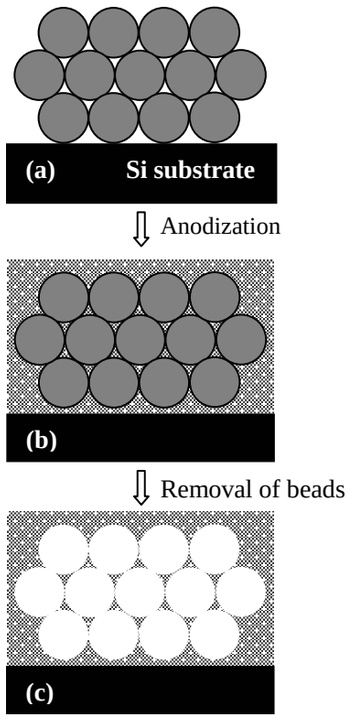

Fig. 1 Schematic of templating process. (a) Template, (b) PS beads/Oxide composite, (c) 3D inverse opal structure

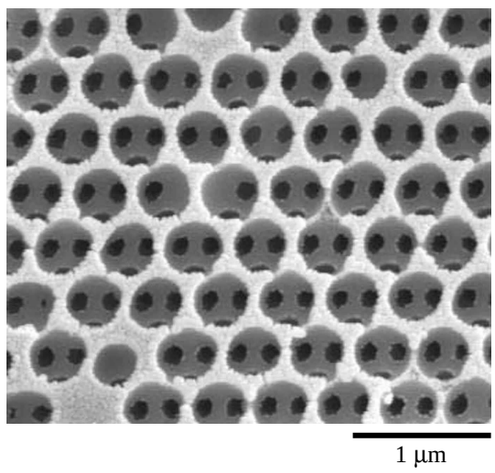

Fig. 2 SEM image of the surface of the anodized Si after removal of PS beads. Anodization was conducted in 0.3 mol dm^{-3} oxalic acid at 10 mA cm^{-2} up to 20 V.