Journal of Ceramic Processing Research. Vol. 7, No. 3, pp. 253~255 (2006)

JOURNAL OF
Ceramic Processing Research

The array growth of ferroelectric nanotubes in anodic porous alumina nanoholes on silicon

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A highly self-ordered hexagonal array of cylindrical pores has been fabricated by anodizing a thin film of Al on Si substrate and subsequent growth of $PbZrTiO_3$(PZT) in these nanoholes has been performed sol-gel solution infiltration method. The diameter and the aspect ratio of vertically aligned AAO nanopores are about 40 nm and 9:1, respectively. The ferroelectric properties of PZT nanotubes were observed by an electrostatic force microscope (EFM). These nanotubes should provide promising materials for fundamental investigations on nanoscale ferroelectricity, and be useful in ferroelectric nanostorage media.

Key words: Anodized aluminum oxide, $PbZrTiO_3$, Ferroelectric, Nanotube arrays, Nano storage.

Introduction

The fabrication of ordered fine patterns of nanometer dimensions is of growing importance for preparing various types of nanometer-scale devices. The most common technique used for electron-beam lithography. However, it involves several disadvantages such as high cost and scaled down due to the increase in the number of defects in the pattern. To overcome these drawbacks in conventional lithographic techniques, other types of processes based on the self-organization of materials have attracted considerable interest [1].

Exhibiting both a very high aspect ratio (~1000) and a high pore density of 10^{11} pores/cm^2, AAO arrays may find applications in the area of nanotechnology. Aluminum anodization is one of the most controllable self-ordered processes, and nanoporous anodic aluminum oxide has been employed to synthesize a variety of nanoparticles and nanowires through a template-mediated approach [2]. Anodic aluminum oxide (AAO) membranes and self ordered nanoporous arrays are suitable for many technical applications. AAO arrays have been used as templates for synthesis of diverse nano-structures and as replicas for fabrication of membranes from other materials (e.g. polymers and metals). In addition, a modification of pores of AAO membranes provides the possibility of the design of materials and devices with new properties and functions. This modification can be accomplished by a number of methods, including electro-deposition, chemical vapor deposition, and sol-gel deposition [3-6]. Recently, aluminum anodization has been combined with traditional silicon processing to fabricate uniform anodic aluminum oxide thin films directly onto a silicon substrate.

Ferroelectric oxides, which exhibit a spontaneous electric polarization that can be reoriented with an external field, have received considerable attention because of their utilization in nonvolatile memory devices. These oxides also exhibit other related properties, including piezoelectricity, pyroelectricity, and large dielectric constants, and they have been used in fabricating micro-actuators, sensors, and capacitors [7-11]. With the miniaturization trend in device size, the size-dependent evolution of ferroelectricity in nanocrystalline and thin film samples has been the focus of much research effort. Nanoscale oxides have been shown to exhibit many unique properties, such as a size-induced depression of the phase transition temperature and the emergence of ferroelectricity in thin antiferroelectric films [12].

In this research, we report the synthesis of lead zirconium titanium (PZT) nanotubes by using anodic aluminum oxide on silicon substrates. The ferroelectric properties of PZT nanotubes were observed by an electrostatic force microscope (EFM).

Experimental

A layer of aluminum with a thickness of 500 nm was deposited by electron beam evaporation onto a p-type Si substrate (0-10 Ωcm, (100) crystal orientation). The porous anodic aluminum oxide (AAO) can be fabricated via a two-step anodizing process. The anodization process was carried out at room temperature. The electrolytic solution was 0.3 M sulfuric acid and the

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bias voltage was set at a constant DC voltage of 25V for several minutes. After anodization, the sample was rinsed completely in de-ionized water. The reference electrode was graphite. The anodic oxide layer was then removed in a mixture of 0.2 M chromic acid and 0.4 M phosphoric acid for 4 hours at 60 °C. This regularly marked AAO films were anodized again under the same conditions as the first step. Anodized aluminum oxides were widened in a saturated 1 M NaOH solution. They were then washed in de-ionized water for several times to remove the NaOH solution.

Lead zirconate titanate ($PbZr_{0.52}Ti_{0.48}O_3$, PZT) nanotubes were fabricated by wetting on the nanopore walls by using a commercial PZT precursor solution (*Inostek Inc.*). Dried gel was subsequently crystallized by a thermal treatment at 580 °C in air. By selective etching of half of the AAO nanopore mold with 1 M NaOH solution, PZT nanotube arrays were obtained.

The surface microstructure of AAO films and PZT nanotube arrays were observed using scanning electron microscope (SEM). Ferroelectric properties of the PZT nanotube arrays have been investigated using an electrostatic force microscope (EFM).

Results and Discussion

Anodized aluminum oxide (AAO) arrays were fabricated by applying the two step anodizing procedure for an aluminum film deposited on a silicon wafer as shown in Fig. 1. Figure 1(a) shows the anodized aluminum oxide film before using the pore widening process. The figure shows a small diameter pores distributed over the surface, where the dark areas are the pores with an irregular characteristic pattern with an average diameter of 10 nm and the surrounding areas are aluminum oxide. Figure 1(b) and (c) shows the porous alumina after the second anodization and widening processes. The diameter and the aspect ratio of vertically aligned nanopores are about 40 nm and 9:1, respectively.

PZT layers were successfully embedded in the alumina nano pores as shown in Fig. 2. PZT nano layers were formed on the alumina nano pore walls as shown in Fig. 2(b). PZT layers were fabricated by wetting on the nano pore walls using a commercial PZT precursor solution.

Figure 3(a) shows that almost all the pores are filled with PZT nanotubes. After the alumina wall had been partly dissolved away, aligned PZT nanotube arrays were implanted into the remaining alumina as shown in Fig. 3(b). Ferroelectric nanotubes were grown at 580 °C for 5 hr. Ferroelectric nanotubes were grown vertically on the AAO. PZT nanotubes their diameter and tube-wall thickness were about 60 nm and 5 nm, respectively.

Figure 4(a) shows representatively atomic force microscope (AFM) and EFM images. The diameter of PZT nanotubes were about 40 nm as shown in Fig. 4(a). The bright part shows the polarization behavior and the dark part were polarized in the opposite direction at 0V as shown in Fig. 4(b). On the other hand, the bright part increased after applying +2V as shown in Fig. 4(c). However, a reverse bias such as –2V changes the bight part as shown in Fig. 4(d). Comparison of the EFM images of Fig. 4(c) and (d)

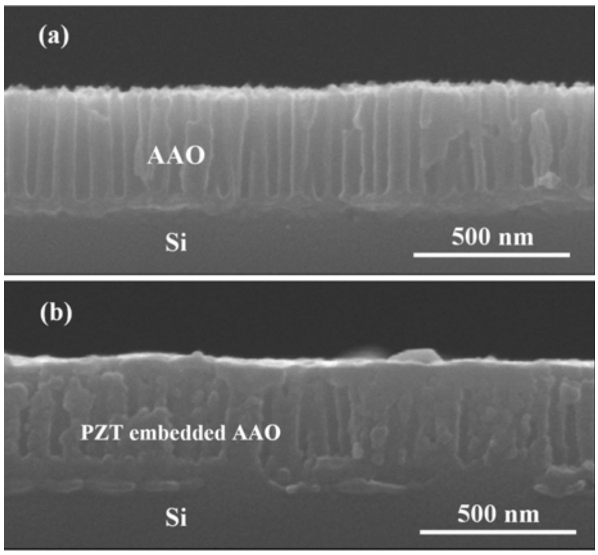

Fig 2. Cross sectional view of nanostructures for (a) as received alumina nano pores and (b) PZT embedded alumina nano pores.

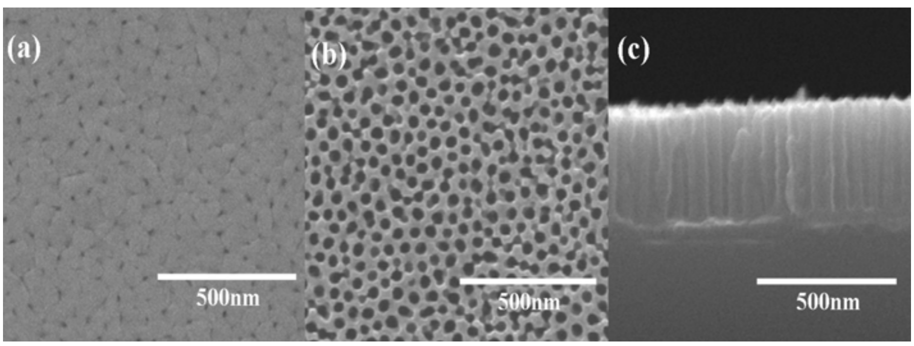

Fig. 1. SEM microphotographs of porous alumina after the second anodization and widening processes (a) view of the surface (after the second anodization) (b) view of the surface (after the widening process) and (c) cross sectional view.

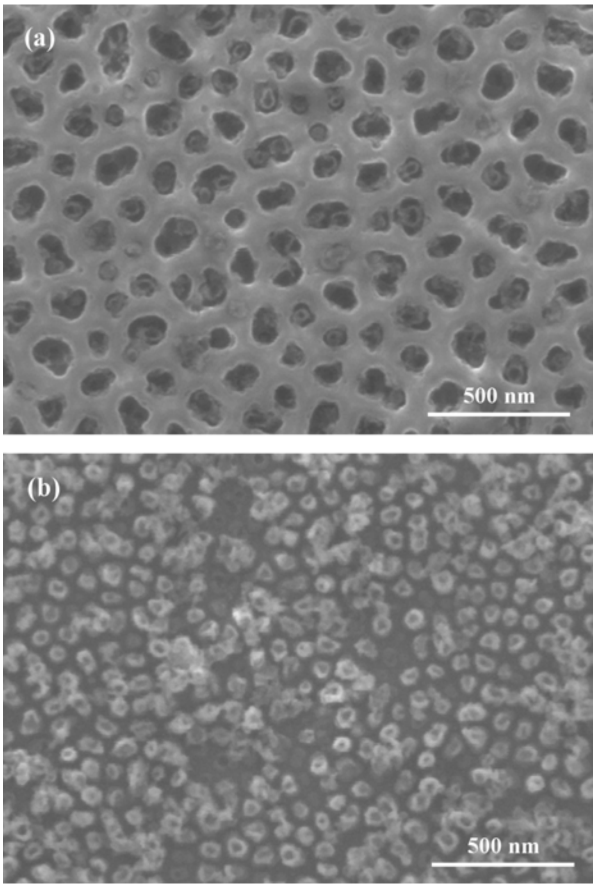

Fig. 3. SEM images of the PZT nonotube arrays: (a) top view of the nano porous alumina filled with PZT nonotubes, and (b) aligned PZT nanotube arrays by removal of part of the alumina.

shows a reversal of the ferroelectric dipole by changing the bias voltage from 2V to −2V. It is suggested that the ferroelectric polarization reversal behavior of PZT nanotubes is attributed to the change of external bias. In ferroelectric nanostorage, bits of information are coded as (+) or (–) states which correspond to opposite orientations of spontaneous polarization. Therefore, an individual domain can be considered as a bit data. The smaller the domain, the higher the storage density that can be achieved [12-14].

Conclusions

AAO arrays were fabricated by applying the two step anodizing procedure and widening processes for an aluminum film deposited on a silicon wafer. The PZT nanotube arrays were successfully fabricated in the AAO pore by a sol-gel solution infiltration method. The PZT nanotubes had a pore diameter and tube-wall thickness where were about 60 nm and 5 nm, respectively. By EFM, ferroelectric responses of aligned ferroelectric nanotubes were observed. These nanotubes should provide promising materials for fundamental investigations on nanoscale ferroelectricity, and be useful in ferroelectric nanostoragie media.

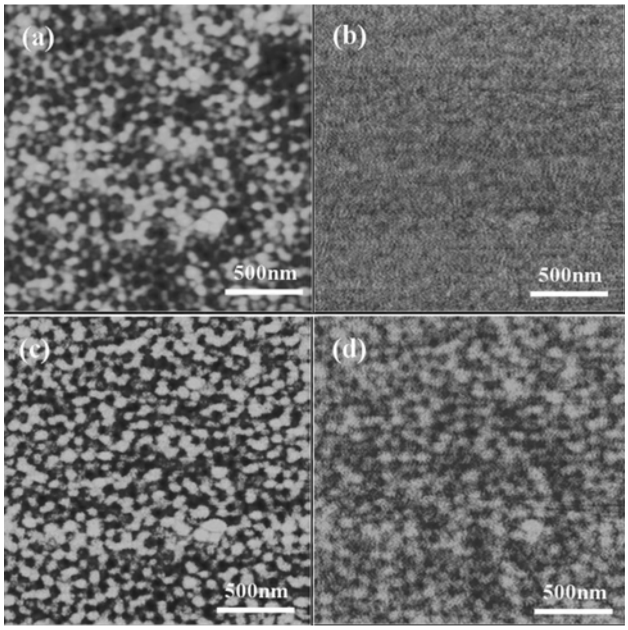

Fig. 4. Ferroelectric responses of nanotubes: (a) AFM image, (b) EFM image after applying V=0V, (c) V=+2V and (d) V=−2V.

Acknowledgement

This work was supported by Korea Materials & Components Industry Agency (KMAC), Korea.

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