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Fabrication and characterization of micropatterned barium titanate ceramics

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Abstract A new patterning method combining electron beam (EB) lithography and electrophoretic deposition (EPD) for fabricating micropatterned barium titanate ($BaTiO_3$) thin films was investigated. At first, resist molds with high resolution were prepared using EB lithography on Pt/Ti/Si substrates. Then $BaTiO_3$ nanoparticles were deposited on the substrates by EPD from a transparent suspension of monodispersed $BaTiO_3$ nanoparticles; a mixed solvent of 2-methoxyethonal and acetylacetone with a 9:1 volumetric ratio was used as a dispersion medium. The nanoparticles with an average size of about 10 nm were synthesized at a low temperature of 90 °C by a high concentration sol-gel process. EPD layers superfluously deposited on the resist molds were mechanically polished away, followed by chemically removing the molds in a resist remover to leave micropatterns of $BaTiO_3$ nanoparticles on the substrates, which were finally sintered to yield micropatterned $BaTiO_3$ ceramic thin films. The method developed may be used to fabricate other micropatterned electroceramic thin films.

Keywords Barium titanate · Micropatterning · Thin film · Electron beam lithography · Electrophoretic deposition · Sol-gel process

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1 Introduction

Recently, patterned/micropatterned electroceramic thin films have attracted growing interest in device applications such as capacitor arrays [1], ferroelectric random access memories (FeRAM) [2], microelectromechanical systems (MEMS) [3], electroluminescent devices [4], and tunable photonic crystals [5]. In addition, the continuing trend of miniaturization in the microelectronics industry requires integration of such electroceramic thin films into electroceramic packages. Due to its electrical (high dielectric constant and relatively low leakage current), ferroelectric and excellent non-linear optical properties, patterned barium titanate ($BaTiO_3$) thin films are promising in memory and electrooptical devices, integrated thin film capacitors and other related applications.

On the other hand, the development of new patterning techniques applicable to electroceramics is desired because sub-micrometer-scale patterning of electroceramics is inherently difficult [6]. Various methods, including top-down and bottom-up approaches have been used to prepare micropatterned electroceramics. Within the top-down approach, focused ion beam patterning, electron beam direct writing, dry-etching, wet-etching, nanoimprint lithography and other lithography techniques have been widely investigated [2, 3, 7–9]. The bottom-up approach can be classified into two main routes, viz., physical and chemical [10, 11]. However, because a relatively high sintering temperature is required to process $BaTiO_3$ ceramics by conventional

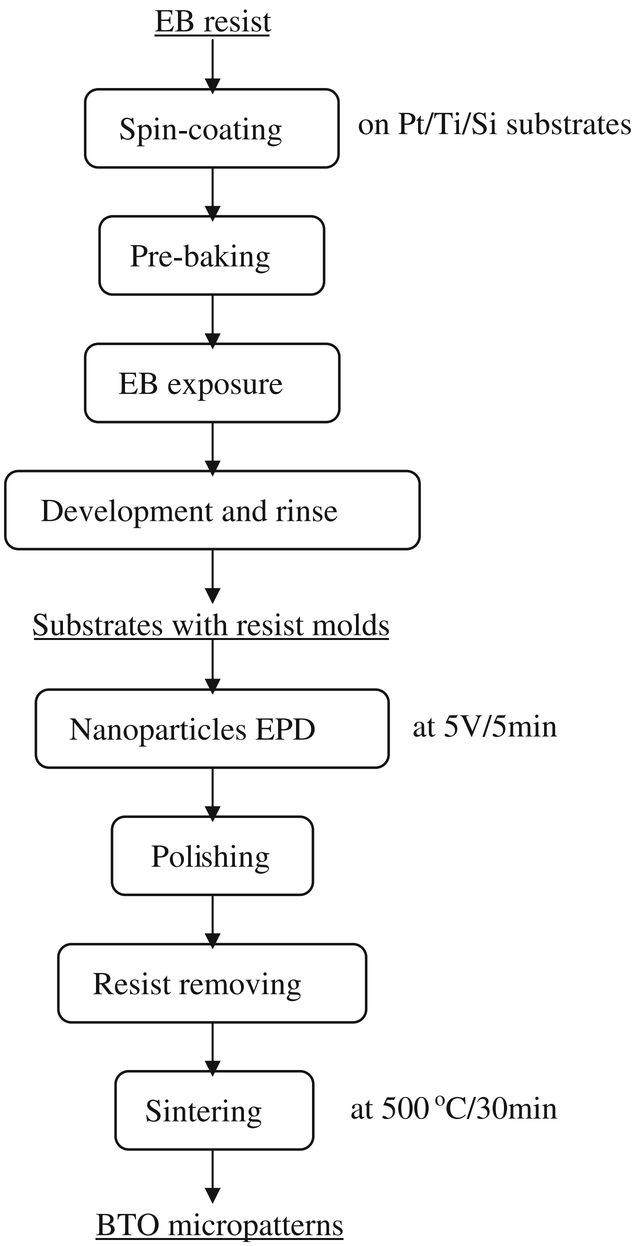


Fig. 1 Micropatterning process of $BaTiO_3$ using electron beam lithography combined with nanoparticles electrophoretic deposition

methods, a low temperature patterning method is needed for preparing micropatterned $BaTiO_3$ thin films.

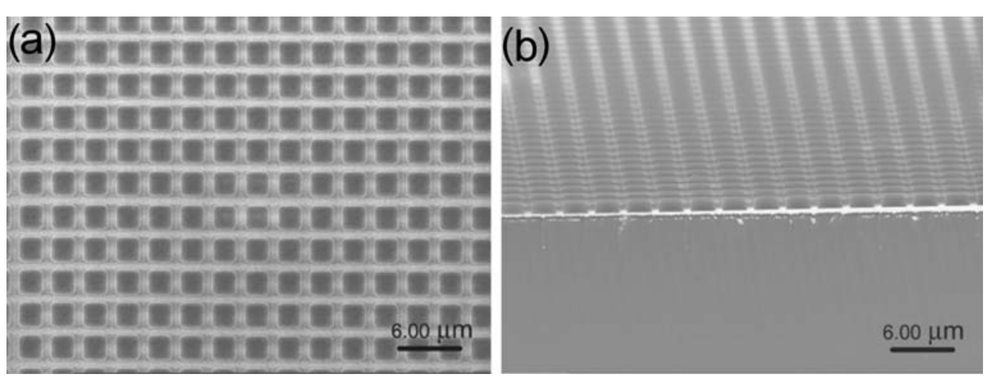
Electron beam (EB) lithography has been widely used for preparing resist molds with high resolution, and the sol-gel process has been used to prepare nanoparticles at low temperatures. Electrophoretic deposition (EPD) offers advantages of depositing films on non-flat and patterned substrates [12]. In this study, we demonstrate that the sol-gel process and electrophoretic deposition can be combined with EB lithography to fabricate micropatterned $BaTiO_3$ thin films at a relatively low temperature.

2 Experimental procedure

Barium titanate nanoparticles with an average size of about 10 nm were synthesized by a high concentration sol-gel process [13] and transparent suspensions of the nanoparticles were prepared by ultra-sonication. The detailed experimental about preparing nanoparticles suspensions was described in our previous paper [14].

Figure 1 shows the micropatterning process of $BaTiO_3$ thin films used in this study, in which EB lithography was combined with nanoparticles electrophoretic deposition. EB resist films were formed on Pt/Ti/Si substrates by spin-coating at 3,000 rpm for 20 s, followed by pre-baking on a hot-plate at 180 °C for 3 min. The spin-coating/pre-baking cycle was repeated several times to obtain resist films with a thickness of about 800 nm. Then an EB lithography system (ELS-5700, Elionex, Japan) was used to create latent micropatterns in the resist films. After developed and baked, resist molds with arrays of square pillars on Pt/Ti/Si substrates were fabricated. These micropatterned substrates were used as cathodes and the same size plates of stainless steel were used as anodes in the EPD process. The distance between the cathode and the anode was 2 cm. A DC voltage of 5 V was applied for EPD. The as-deposited samples were dried in a 50 °C oven in air. After removing $BaTiO_3$ nanoparticles layers super-

Fig. 2 FE-SEM micrographs of the grid resist mold on Pt/Ti/Si substrates: (**a**) top view; (**b**) cross section



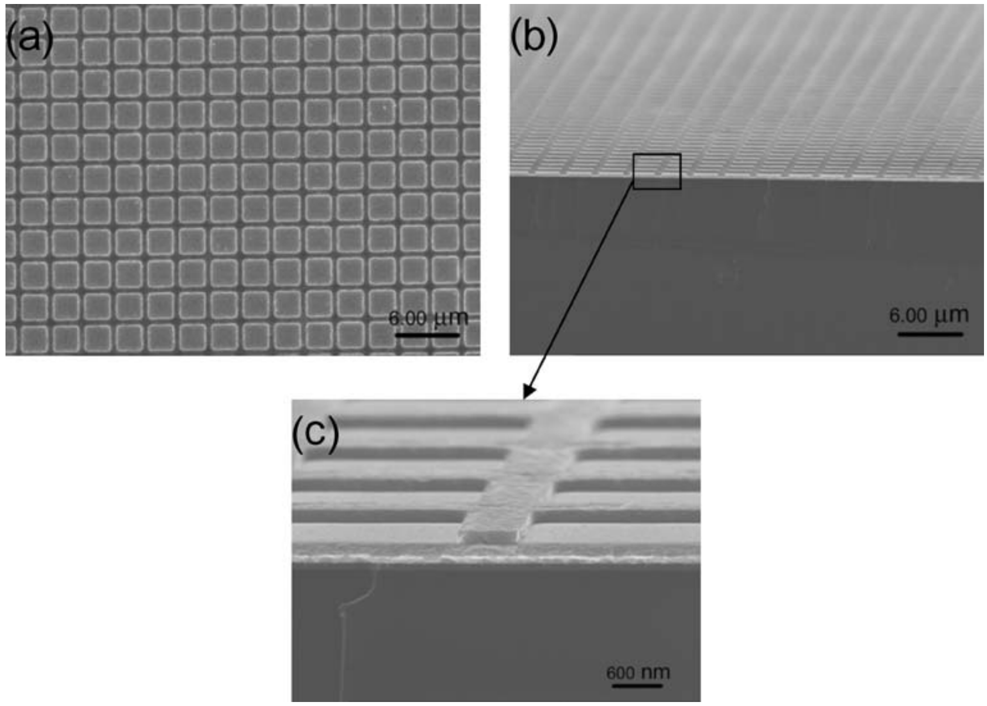


Fig. 3 FE-SEM micrographs of the as-deposited $BaTiO_3$ micropatterns

fluously deposited on the resist molds by mechanical polishing, the resist molds were dissolved in a remover to obtain nanoparticles patterns left on the substrates. The nanoparticles patterns were then calcined at 500 °C for 30 min to yield micropatterned $BaTiO_3$ ceramic thin films.

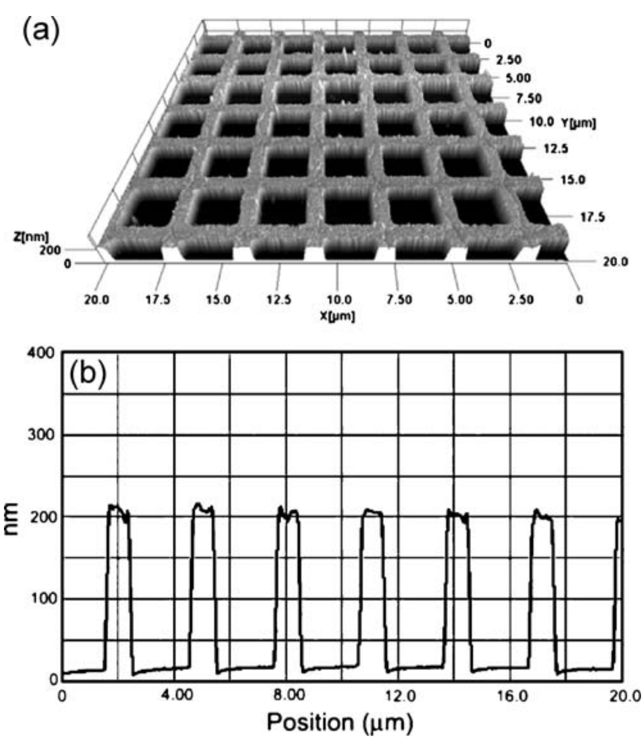


Fig. 4 (**a**) SPM 3D image; (**b**) line cross-section of the as-deposited $BaTiO_3$ micropatterns

The microstructure and surface morphology of EB resist molds and micropatterned $BaTiO_3$ on Pt/Ti/Si substrates were evaluated with a field emission scanning electron microscope (FE-SEM, JSM-6340F, JEOL, Japan). Scanning probe microscopy (SPM, Nano-R system, Pacific Nanotechnology, USA) was used to characterize the surfaces of micropatterned $BaTiO_3$ thin films.

3 Results and discussion

Figure 2 shows FE-SEM micrographs of a resist mold with an array of square pillars formed on a Pt/Ti/Si substrate.

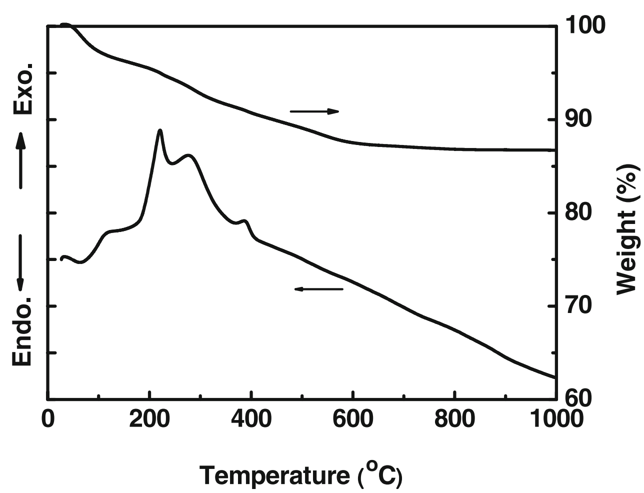


Fig. 5 TG-DTA curve of the dried $BaTiO_3$ gel synthesis at 90 °C for 1 h by the high concentration sol-gel process

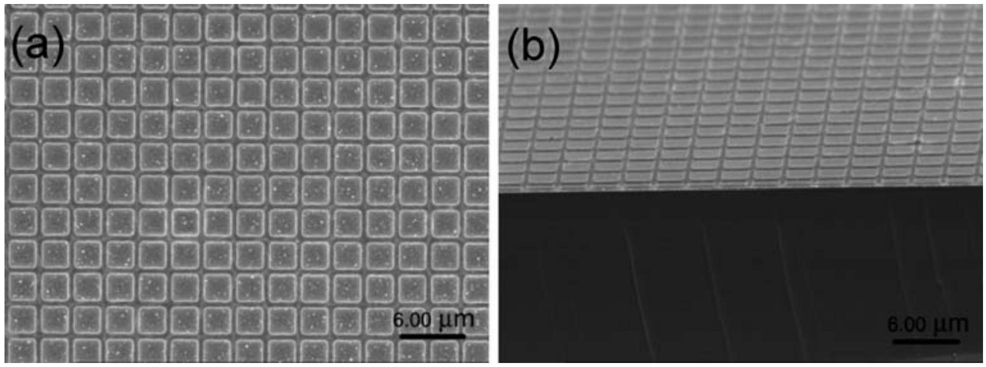


Fig. 6 FE-SEM micrographs of the $BaTiO_3$ micropatterns sintered at 500 °C for 30 min: (**a**) top view; (**b**) cross section

Square resist pillars had a width of 24 µm with a spacing of 600 nm in between. The thickness of the resist film (the height of the resist pillars) was measured to be about 800 nm, and the edge of the resist pillars was confirmed to be very sharp. As shown in Fig. 3, FE-SEM micrographs of an as-deposited $BaTiO_3$ nanoparticles micro-grid, the shape of which was transferred from the resist mold (that is, the inverse shape of the mold), suggests that the method of nanoparticles EPD combined with EB lithography is applicable to prepare micropatterned $BaTiO_3$ thin films.

Good adhesion of the micropattern to the substrate was confirmed. The shape of the micropattern was kept very well although a few nano-cracks were observed. These cracks were introduced during drying or polishing, and addition of some organic binder may help to overcome this problem. We employed a nanoparticles EPD method because it is impossible to deposit nano-structured thin films by traditional EPD, and moreover, the EPD method produces thin films with a higher green density than spin-coating. As reported in our previous paper [13], the success in preparing mono-dispersed $BaTiO_3$ nanoparticles suspension made it possible to deposit nano-structured thin films. A relatively small shrinkage of nanoparticles micropatterns during calcination or sintering benefits preparing crack-free micropatterned ceramics. Figure 4 shows a 3D image and line cross-section of the as-deposited $BaTiO_3$ nanoparticles micro-grid, evaluated with SPM over an area of 20×20 µm. A good feature quality of the $BaTiO_3$ micropatterns was observed. The thickness (or height) of the micropatterns was measured to be about 200 nm and a sharp edge of $BaTiO_3$ micro-grids was observed from the line cross-section.

Figure 5 shows TG-DTA curves of a dried gel synthesized by the high concentration sol-gel process. The weight loss of the material occurred in the range from 100 to 400 °C is due to evaporation and decomposition of organic components. It seems that most of the organic components were burned out up to a temperature of 500 °C. From this result, a heating condition at 500 °C for 30 min was chosen for sintering $BaTiO_3$ nanoparticles micropatterns in this study. FE-SEM micrographs of a sintered micropattern are shown in Fig. 6. It can be seen that the good shape quality of the as-deposited micropattern was remained even after sintering. Good adhesion of the micropattern to the substrate was also confirmed.

4 Conclusions

A high concentration sol-gel process and nanoparticles EPD combined with an EB lithography technique were investigated to prepare $BaTiO_3$ ceramic micropatterns. $BaTiO_3$ micro-grids with a line width of 600 nm and a spacing of 2.4 µm in between were successfully fabricated by this proposed method at a relatively low temperature. The good feature quality and good adhesion between the micropattern and the substrate were confirmed. This method is not only unlimited to the application of $BaTiO_3$ micropatterning but also a promising method for micropatterning other electroceramic thin films on conductive substrates.

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