Fabrication and characterization of barium titanate nanocube ordered assemblies on micro-patterned substrates

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Single-crystalline BaTiO₃ nanocubes were synthesized by hydrothermal method using water-soluble titanium complex and surfactants. The highly-ordered assemblies of BaTiO₃ nanocubes were directly fabricated on the substrates with micro-patterns by the dip coating method with a low upstroke operation rate. The micro-patterns which had micro-trenches parallel to the upstroke operation direction affected the formation of nanocube assemblies and enabled to fabricate assemblies with average size of about 40 μm in length and width of 2 μm. The micro-patterned polyimide substrate affected the capillary force and enhanced the ordering degree and density of the nanocube packing. This method has an advantage to suppress generation of micro-cracks and to form micro-patterning the BaTiO₃ nanocube assemblies.

Key-words : Barium titanate, Nanocube, Self-assembly, Dielectrics, Micro-patterning

1. Introduction

Electronic devices become more and more accurate and miniaturized according with the growth of the communication tools in recent years. Moreover, the wearable electronic tools will be developed in near future. Therefore, development of further miniaturized and high-performance electronic devices are strongly demanded. However, conventional materials and fabrication methods of these devices will meet the limitation on above rigorous demands. To satisfy these demands, developments of the entirely new nano-sized materials and technologies are necessary. Nanocrystals have great potentials to obtain enhanced and/or unique properties compared with conventional materials and to become one of the key engineering for device applications.1),2) Barium titanate (BaTiO₃, BT) is commonly used for the dielectric materials such as multi-layered ceramic capacitors, positive temperature coefficient thermistors, etc. However, the dielectric properties of BT particles decrease when the size of the BT particles decrease in nanometer region because its ferroelectricity is disappeared.3),4) When the particle size decreases in several tens nanometer region, the crystallographic phase of BT nanoparticles becomes cubic phase and does not have phase transitions. The origin of extinction of tetragonal phase is explained with that the surface energy is enhanced and lattice relaxation occurs. The thickness of surface cubic phase layer is considered to be about 10–15 nm. Therefore, the critical size which maintained ferroelectricity in BT nanoparticles is estimated about 20 nm. This is the so-called “nanosize effect”. However, the authors and other groups reported that the cubic-shaped BT nanocrystals (BT nanocubes) which had been synthesized by hydrothermal and solvothermal method with surfactants were able to maintain ferroelectricity even in the size of sub-10 and 15 nm.5),6) These reports indicated that the shape of nanocrystals played an important role to achieve high properties such as ferroelectricity. Moreover, the highly-ordered assemblies of these nanocubes are necessary for the application of the devices. Solution based self-assembled bottom-up process of the nanocrystals is the most suitable technique to obtain the large scale assemblies of highly ordered 2D or 3D nano-architectures on desirable substrates directly.7),8) The precise control of the size distribution and shape of the BT nanocubes was absolutely imperative for enlargement of assembly area with highly-ordered structure. The authors have already reported fabrication of the highly-ordered BT nanocube assembly by using capillary force assisted self-assembly method and dip-coating method.9),10),11) In addition, it has been also reported that the dielectric constant of BT nanocube assemblies were enhanced to above 3000 with relatively low loss tangent and the behaviors were considered to be attributed to its interfacial structure.12),13) Therefore, it is becoming clearer that the BT nanocube 3D architectures have a great potential to improve the properties or miniaturizations of dielectric devices. However, there still remain some issues to be resolved. As a lot of micro-cracks are usually generated through self-assembly process, the high ordering assembled area is limited. In this study, the BT nanocube assemblies with high ordering were directly fabricated on micro-patterned substrates. The patterns are expected to suppress generation of micro-cracks and to fabricate the assemblies in desired pattern directly on the substrate.

2. Experimental procedure

The BT nanocubes were prepared by the hydrothermal method at 220°C with optimized composition of Ba(OH)₂·8H₂O, titanium (IV) bis(ammonium lactate) dihydroxide (TALH), NaOH, tert-butylamine, and oleic acid.6) The BT nanocube assemblies were fabricated by the dip-coating method.10),11) As-synthesized BT nanocubes were washed by ethanol several times and then the nanocubes were ultrasonically dispersed in mesitylene (1,3,5-trimetylbenzene, boiling point: 165°C) and centrifuged. 6 ml of the supernatant colloidal solution was transferred into a cylindrical glass vial (16 mm in inner diameter and 40 mm in height). The micro-patterned Si, micro-patterned Pt with Pt partially-coatings (micro-patterned Pt/Si), and polyimide micro-patterned Si (micro-patterned Pt/Si) were chosen as the sub-

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The micro-patterned Si substrate has line and space patterns with the width of from 0.5 to 5 µm and the depth of 500 nm. The micro-patterned Pt/Si substrate has line and space micro-patterns, where the bottom of the trench structure with the width of 2 µm and the depth of 500 nm was coated with Pt as bottom electrodes. Thickness of Pt bottom electrode was about 200 nm. The cross-sectional image of the micro-patterned Pt/Si substrate was shown in Fig. 1. The micro-patterned Pt/Si has line and space micro-patterns with the width of from 2 to 4 µm and the depth of about 1 µm. To confirm the influences of materials being the constituents of micro-patterns, the identically-shaped patterns were made by Si substrate itself. These substrates were cleaned by UV irradiation before dip-coating. The upstroke operating rate was set at constant of 0.01 µm/s and the operation temperature was about 25°C. The as-assembled structures were irradiated by UV light for 2 h and dried at 200°C for 5 h to remove residual organics. BT nanocubes assemblies fabricated on micro-patterned Pt/Si substrate were calcined at 400°C for 1 h and sintered at 850°C for 1 h in O2 atmosphere. The microstructures of these assemblies were observed by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-6335FM).

3. Results and discussion

Figure 2 shows FE-SEM images of as-assembled films of BT nanocubes on micro-patterned Si substrates. The line direction of micro-patterns was set to parallel or to perpendicular to the operating direction of dip-coating, as illustrated in Fig. 2(a). Both of them, the BT nanocubes were filled into the line patterns and assembled with high ordering. However, in the case of micro-patterns perpendicular against to the operating direction, a lot of micro-cracks were generated in the assembly independent of the existence of micro-patterns as shown in Fig. 2(b). On the other hand, the generation of micro-cracks were limited to the across direction of the micro-trench width in the case of micro-patterns parallel to the operating direction of dip-coating. Furthermore, the long range assembly of about 40 µm in length and 2 µm in width was obtained into the micro-patterns as shown in Fig. 2(d).

The microstructure of BT nanocube assembly in the micro-pattern [Fig. 2(e)] was highly ordered structure similar to the case using the substrates without micro-patterns. Figure 2(f) shows the cross-sectional image of BT nanocube assembly in the micro-pattern parallel to the operating direction. The micro-trenches were filled by the nanocubes and assembly had a highly ordered inner structure. These results meant that highly ordered structures of BT nanocube assemblies in the long range were obtained into the micro-patterns parallel to the operating direction. The effect of micro-patterns was illustrated in Fig. 3. In the case of dip-coating direction parallel to the micro-patterns, as shown in Fig. 3(a), the capillary force, which works at the interface between the colloidal solution and the substrate to make a liquid film, was enhanced by the fine-shaped surface and local space of the micro-patterns of the substrate. Moreover, the colloidal solution effectively remained for a long time in the micro-trenches. The solvent of the remaining colloidal solution in the pattern might be slowly evaporated along to the edge of micro-trenches, and thereby the anisotropic drying was promoted to form close-packing structures in long range. On the other hand, in the case of perpendicular type, the effect of the micro-trenches did not work effectively. As the result, a lot of micro-cracks appeared in the...
coating area similar to the case of the substrate without micro-patterns in our previous work. It was revealed that the direction of line patterns parallel to the operating direction was effective to suppress generation of micro-cracks.

**Figure 4** shows the microstructures of BT nanocube assembly in the micro-patterned Pt/Si substrate. The range of the assembly was shorter about 10 μm than that on the micro-patterned substrates without Pt coating. Because the effective trench depth decreased to about 300 nm due to the thickness of bottom Pt layer, the enhancement of capillary force might not work enough. This result meant the aspect ratio of the trench shape in the micro-pattern was quite important to obtain the long range assembly without micro-cracks. On the other hand, as the surface and inner structure had also high ordering degrees as shown in Figs. 4(b) and 4(c), the degree of ordering of BT nanocube assembly was considered to be almost independent on the aspect ratio of micro-patterns. It had been found that the degree of ordering depended on the size and shape distribution of nanocubes. The narrow size distribution, 90 degree corners, and flat surfaces of BT nanocubes were the most important factors to assemble high ordering structures similar to results of our previous works.14-18) The microstructure of BT nanocube assembly in the micro-pattern after sintering 850°C was shown in Fig. 4(d). The assembly area had no change after sintering, and the nanocubes maintained its shape and high ordering with the across direction of the micro-trench, which were same as on the micro-patterned Si substrate as shown in Fig. 2. Moreover, for the detail structure, it was found that the ordering of BT nanocube assembly in polyimide micro-patterns was much higher than that in Si micro-patterns from cross-sectional image as shown in Fig. 5(d). It has been already mentioned that the degree of ordering of the assembly has strongly depended on the size and shape distribution. It was inferred that the further effective factor was added by existence of polyimide patterns. Instead of using the micro-patterns of rigid materials such as Si, polyimide was chosen as a relatively soft patterning material in this process. It is considered that this high ordering structure was yielded under the influence of swelling of polyimide through the dip-coating process. The schematic image of this process was illustrated in Fig. 5(d). As polyimide has a high chemical resistance against toluene or mesitylene, it does not dissolve in the colloidal solution at the conventional conditions. However, it might be swollen in the solvents as the polymers or gels commonly involve solvents. So, the micro-trenches decreased in width, the capillary force worked strongly to take up the colloidal solution into the trenches effectively. And then, the much slower evaporation and anisotropic drying occurred in the polyimide patterns to lead nanocube assemblies in higher ordering. As the result, the high ordering structure was yielded in the polyimide micro-patterns. To confirm the effect of polymer mold pattern, the identically-shaped patterns were made by Si substrate itself and BT nanocube assemblies were fabricated on this micro-patterned substrate. **Figure 6** shows microstructures of BT nanocube assemblies fabricated on the identical micro-patterned Si and PI/Si substrates. Both substrates had same width of micro-patterns about 5 μm as shown in Figs. 6(a)–6(d). In spite of the identical pattern, the generating of micro-cracks of BT nanocubes in both assemblies was quite different. In the case of PI/Si substrate, the cracks were only generated in perpendicular direction of trench patterns. However, the cracks were generated in random direction in Si patterns as shown in Fig. 6(b). When the width of Si patterns were narrow as shown in Fig. 2, the capillary force worked effectively and strongly to soak up the colloidal solution...
in the local space as mentioned above. As a result, the generation of micro-cracks were limited in the perpendicular direction of trench patterns, and nanocube assemblies became dense and high ordering structure over long range. However, when the width of Si patterns became wider, there seemed to be no effect to suppress generation of the micro-cracks. In the meanwhile, the PI patterns were totally different from the case of Si patterns. The polyimide is swelled through the dip-coating process. The width of micro-patterns temporarily becomes narrow. Therefore, the micro-cracks were suppressed in the wider patterns. Moreover, the cross-sectional microstructures of BT nanocube assemblies in micro-patterned PI/Si and micro-patterned Si substrates had also different appearances except thickness as shown in Figs. 6(c) and 6(d), respectively. In the case of Si patterns, the nanocube assembly was closed to the side wall and almost filled in the trench because the Si side walls are rigid. And also, the assembly has slight curvature surface caused by the surface tension which was generated when the solvent evaporated. In contrast, in the case of PI/Si micro-patterns, there are some gaps between the assembly and the PI side wall. Furthermore, the cross-section of the assembly in the trench of PI micro-pattern was almost rectangular shape. These appearances supported the swelling effect of polyimide patterns. Additionally, using micro-pattern substrate for dip-coating assembly process supports that the nanocrystals can be directly assembled in desired micro-design. The advanced results will be reported in future.

4. Conclusions

In order to suppress generation of many micro-cracks during the evaporation of the solvent through solution based self-assembly process, the substrates with micro-patterns were used. Highly ordered BT nanocube assembled films were fabricated by the dip-coating self-assembly method on micro-patterned Si, micro-patterned Pt/Si and micro-patterned PI/Si substrates. The long range coating area about 40 μm in length and 2 μm in width was yielded by using the micro-patterned Si substrates being set with the micro-patterns parallel to the operating direction. The surface and inner structures of BT nanocube assembly were also dense and close packing structure. On the other hand, generation of micro-cracks did not suppress well in the case of using the substrates being set with the micro-patterns perpendicular to the operating direction. These results suggested that the slow evaporation of the solvent and the anisotropic drying were induced by the micro-patterns parallel to the operating direction. BT nanocube assemblies fabricated on micro-patterned Pt/Si substrate were sintered at 850°C. The microstructures of these assemblies kept the high ordering and cubic shapes without grain growth in the micro-pattern. In the case of micro-patterned PI/Si substrate, the BT nanocubes were assembled with much higher ordering compared with being assembled in the micro-patterned Si and micro-patterned Pt/Si substrates. This result was considered to be stem from that polyimide was swollen by the solvent in the dip-coating assembly process. It reveals that the micro-patterned PI/Si substrate becomes a powerful tool to suppress the generation of micro-cracks and to make micro-patterned nanocube films with dense and high-ordering. Although dielectric properties of these BT nanocube micro-patterned assembly films have not been clarified yet and must be discussed as soon as possible, this micro-patterning method has a great potential for the new approach of minimum and high performance electronic devices.

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References