Available online at www.sciencedirect.com

ScienceDirect

Journal of the European Ceramic Society 28 (2008) 101–108

www.elsevier.com/locate/jeurceramsoc

Electrophoretic deposition of $BaTiO_3$ films on a Si substrate coated with conducting polyaniline layers

J.Q. Wang [a,b], M. Kuwabara [a,*]

[a] Department of Applied Science for Electronics and Materials, Kyushu University, 6-1 Kasuga-kouen, Kasuga 816-8580, Japan
[b] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

Received 20 January 2007; received in revised form 7 May 2007; accepted 13 May 2007
Available online 3 August 2007

Abstract

In this work, electrophoretic deposition (EPD) technique was employed for fabricating the barium titanate ($BaTiO_3$) films on the Si substrate modified with the ordered conducting polyaniline (PANI) layers. Firstly, surface polymerization of ordered conducting PANI layers on the Si substrate modified with the aniline-bearing silane self-assembled monolayer was performed by polymerization of aniline monomer in an acidic aqueous solution. Then, EPD of $BaTiO_3$ films was fulfilled using the conducting PANI layers coated Si wafer as the cathode. The analytical results demonstrate that the crack-free, relatively dense and smooth $BaTiO_3$ films have been accomplished on the PANI layers modified Si substrate with the appropriate suspension concentration and the deposited film thickness can be changed expediently by adjusting EPD process parameters. This method provides a potential route for fabricating ceramic films on the non-conductive Si or glass substrates using EPD technique.

Keywords: $BaTiO_3$ thin films; Self-assembled monolayer; Surface polymerization; Polyaniline; Electrophoretic deposition

1. Introduction

Barium titanate ($BaTiO_3$) ceramic films have gained much attention for applications in the optoelectronic devices, dynamic random access memory, non-volatile memory, multilayer capacitors, and tunable microwave devices, etc.[1,2] Various methods have been developed to fabricate thin and/or thick $BaTiO_3$ films such as sputtering, spin-coating, dip-coating, metallorganic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), sol–gel, and electrophoretic deposition (EPD).[3–5] Among these, EPD technique is attracting considerable research interest in the area of ceramic integration for several advantages such as process simplicity, low raw material and equipment cost, high deposition rate, and ease to deposition of multilayer films with controlled thickness on complex-shaped or -patterned substrates.[6–8] As well known, EPD is a colloidal process wherein ceramic bodies are directly shaped from a stable colloidal suspension by a dc electric field. Therefore, only electrically conductive materials, such as metals or graphite, are commonly used as electrodes for EPD deposition.[9,10] Nowadays, the fast developing micro-electromechanical systems (MEMs) are focused for their superior performance with low unit cost and silicon, polysilicon, silicon carbide, and other functional ceramic materials are the main elements for building this systems.[11] Therefore, it will be a promising research innovation how to use EPD technique to fabricate ceramic coatings (for example $BaTiO_3$ films) on these semi- or non-conductive substrates.

Recently, polyaniline (PANI), owing to its promising electronic and optical properties, as well as the ease of synthesis and relative environment stability, has been extensively investigated in conductive polymers and can be prepared by chemical or electrochemical polymerization.[12,13] Specially, the chemical deposition of conducting PANI thin layers on various materials, such as plastics, glass, metals, as well as on micro- and nano-porous materials finds extensive applications in the fields of optoelectronics, microelectronics, MEMs, sensors, and so on.[14] Wu et al.[15,16] have reported that ordered PANI layers with good adhesion and excellent conductivity can be synthesized on aniline-primed Si substrate by electroless surface polymerization. However, up to now, relatively little work has been published on the fabrication of ceramic films using the ordered PANI layers as the electrode material by EPD technique except

---

[*] Corresponding author. Tel.: +81 92 583 7528; fax: +81 92 583 7528.
E-mail addresses: wangj@asem.kyushu-u.ac.jp (J.Q. Wang), Kuwabara@asem.kyushu-u.ac.jp (M. Kuwabara).

0955-2219/$ – see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2007.05.020

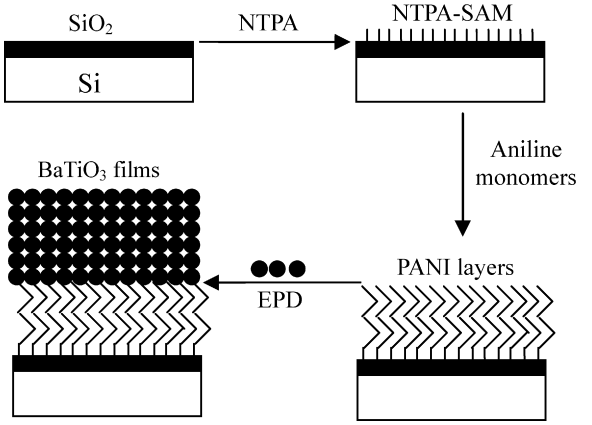

Fig. 1. Schematic illustration of the fabricating process for $BaTiO_3$ films on a Si substrate.

that Al_2O_3 coating has been achieved by EPD process using the conductive polypyrrole layers coated ceramic substrates as the cathode.[9] In this paper, a monolayer of $C_6H_5NHC_3H_6Si(OMe)_3$ was firstly formed on the single crystal Si substrate via molecular self-assembly technique. Then, the chemical polymerization of conducting PANI layers was carried out by reaction of the aniline-bearing silane self-assembled monolayer with aniline in an acidic aqueous solution in the presence of an oxidant of $(NH_4)_2S_2O_8$. At last, EPD of $BaTiO_3$ films was performed using the synthesized conducting PANI layers as the cathode. The detailed experimental process for fabricating $BaTiO_3$ films on the Si substrate is schematically shown in Fig. 1. The structure of the as-deposited $BaTiO_3$ films was determined with the X-ray diffraction analysis (XRD), while the thickness and morphology of the films were analyzed by means of surface profiler and field emission scanning electron microscopy (FE-SEM), respectively.

2. Experimental

2.1. Materials

Ammonium persulfate, $(NH_4)_2S_2O_8$, and pure aniline monomers (>99%) were obtained from the Wako Co. and used as received. *N*-[3-(Trimethoxysilyl)-propyl]aniline ($C_6H_5NHC_3H_6Si(OMe)_3$, coded as NTPA) and barium titanate nanosize powders ($BaTiO_3$, 99%) were purchased from the Aldrich Co. 1-Methyl-2-pyrrolidinone (NMP, >99%, HPLC grade) was received from the Sigma–Aldrich Co. Ultrapure water and reagent grade solvents were used in the experiments.

2.2. Preparation of conducting PANI layers

The self-assembled NTPA monolayer (for short NTPA-SAM) was prepared according to the literatures,[15,16] using single-crystal silicon wafers polished on one side and cleaned sequentially with chloroform, acetone, and ethanol as the substrates. After immersing in the mixed solution of 30% H_2O_2 and concentrated H_2SO_4 (“Piranha” solution) at 90 °C for 40 min, the wafers were placed into the methanol solution containing 11 mM of NTPA at room temperature for 20 h, to allow the formation of self-assembled NTPA-SAM. Finally, the wafers were washed sequentially with methanol, followed by drying in nitrogen. Chemical synthesis of the PANI layers on NTPA-SAM (coded as PANI/NTPA-SAM) modified Si substrates was performed by dipping the substrates in aniline/HCl aqueous solution and then $(NH_4)_2S_2O_8$ was added. After polymerization (5 min–5 h) at 0 °C, the PANI films were dipped in ethanol (EtOH) and undergone an ultrasonic treatment for 1 min, then washed with copious amounts of water and blown dried with nitrogen gas.

2.3. Fabrication of $BaTiO_3$ films on the as-synthesized PANI layers coated Si substrate using EPD technique

Suspensions for the EPD experiments were prepared as follows. Two types of organic solvent mixtures, EtOH/acetylacetone (Acac) and 2-methoxyethanol (EGMME)/Acac, were used as the suspension media, respectively. The suspensions (3.0–30.0 g/L) were prepared by ultrasonically dispersing $BaTiO_3$ powders in the mixed solvents. The $BaTiO_3$ films were electrophoretically deposited from the prepared suspension. A Si wafer modified with conducting PANI layers after protonation with 0.5 M H_2SO_4 in a size of 1 cm × 1.5 cm was used as cathode and the same size plate of stainless steel was used as anode. The separating distance between the cathode and the anode was 1–2 cm. A dc voltage ranging from 0 to 30 V provided by a dc voltage source (HP4140B, Hewlett-Packard, Japan) was applied to the electrodes to electrophoretically deposit $BaTiO_3$ thin films and the varied thickness of films was obtained by changing the EPD process parameters. The as-deposited $BaTiO_3$ films were dried in a 40 °C oven in air for several hours.

2.4. Characterization of the prepared samples

Surface morphology and thickness of the prepared samples were evaluated by field emission scanning electron microscopy (FE-SEM, JEOL JSM-6340F). The microstructure and surface morphology of PANI layers were also investigated using scanning probe microscopy (SPM, Nano-R system, Pacific Nanotechnology, USA) in “close contact” mode. All scans were taken at room temperature in air. The zeta potential measurement and particle size distribution analysis of the $BaTiO_3$ particles in the suspensions were performed using a Zetasizer Nano Instrument (Nano-ZS, United Kingdom Malvern Instruments Ltd.) and the final data were obtained by averaging 10 measurements for each sample. The phase structure of the $BaTiO_3$ powders and the as-deposited $BaTiO_3$ films were determined on a D/max-RB X-ray diffractometer (XRD, Rigaku Corp., Tokyo, Japan) with Cu Kα radiation at 40 kV and 40 mA with a scanning step of $2\theta = 2.0°$/min. The thickness of the prepared PANI layers and $BaTiO_3$ films was measured with an Alpha-Step IQ Surface Profiler (KLA-Tencor Corp. USA) and the final thickness data were obtained by averaging five to six measurements at different spots of each sample surface.

3. Results and discussion

3.1. Characterization of the synthesized PANI layers

For comparison, the PANI layers are also prepared on the bared Si substrate under the same experimental conditions. It can be obtained that the PANI layers grown on NTPA-SAM primed substrates have much better adhesion compared to those grown on unmodified Si substrates and PANI layers deposited on unmodified substrates are easily washed off with splash water, while PANI layers on NTPA-SAM modified Si substrate pass the peeling test.[16] In addition, the synthesized PANI layers cannot be wiped out by solubility test with NMP solution or ultrasonic treatment process, which indicates that the resulting PANI layers have excellent adhesion due to the covalent anchor between PANI chain and the Si substrate.

The thickness of the as-synthesized PANI layers on the NTPA-SAM modified Si wafer is measured with the surface profiler and the relationship curve between the thickness of PANI layers and the polymerization time is shown in Fig. 2. When the concentration of aniline monomer is 0.15 M and the molar ration of aniline to oxidant $(NH_4)_2S_2O_8$ is kept constant value of 1, the thickness of the PANI layers increases when the polymerization time is increased up to 25 min, then it approaches a saturation value of 220 nm for a much longer polymerization time of 5 h, which corresponds to 440 aniline units.[15]

The top views and cross-sectional view of FE-SEM micrographs for the as-synthesized PANI layers on the NTPA-SAM modified Si wafer are shown in Fig. 3. From the micrograph of low magnification (Fig. 3a), it is obvious that a crack-free PANI layer is compactly synthesized on the NTPA-SAM modified Si substrate and the surface is fairly uniform and smooth with a little of aggregated polymer particles. Moreover, it can be seen from the high magnification micrograph (Fig. 3b) that the PANI layers is composed of tightly packed spherical polymer particles and displays scalelike morphology, and there is no fibril morphology, which has been observed previously in electrochemical polymerized polymer.[17] From the view of cross-section (Fig. 3c), a visible PANI layer with the thickness of about

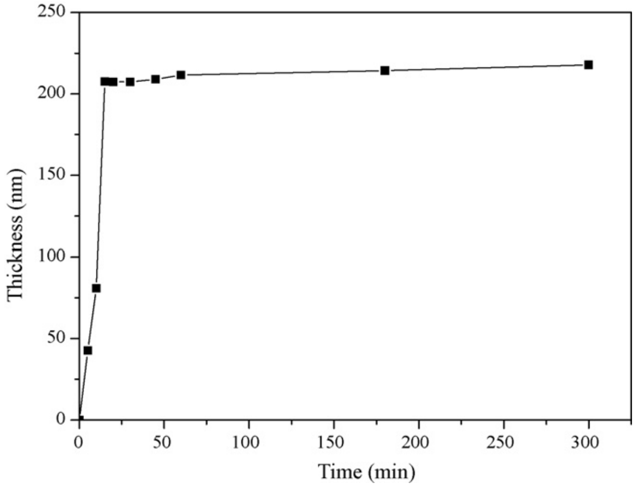

Fig. 2. Effect of polymerization time on the thickness of PANI layers synthesized on the NTPA-SAM modified Si substrate.

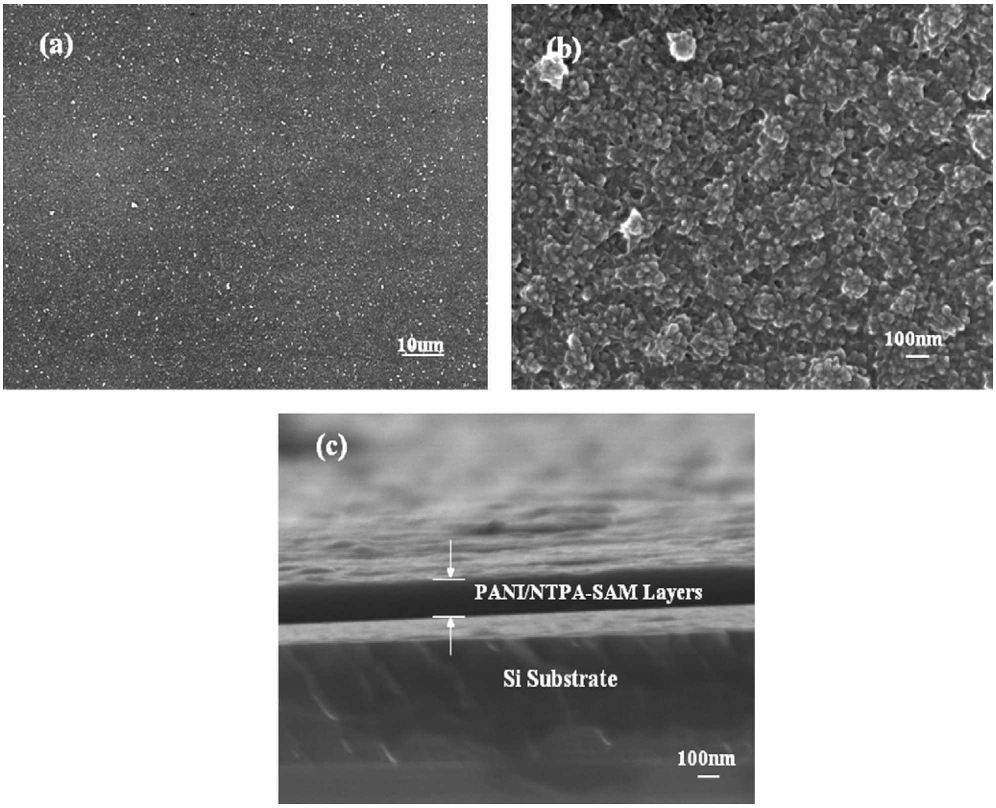

Fig. 3. FE-SEM micrographs of PANI layers on NTPA-SAM modified Si substrate.

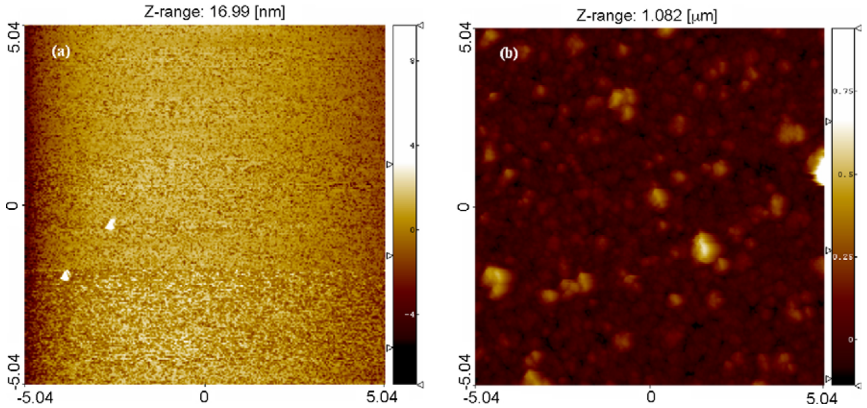

Fig. 4. AFM images (10 µm × 10 µm) of (a) NTPA-SAM on Si and (b) as-synthesized PANI layers on NTPA-SAM.

220 nm has been achieved under the deposition conditions of 0 °C and 5 h.

In order to get more detailed information on the microstructures, the surface morphologies on the process of synthesizing PANI layers are also observed by using AFM. Fig. 4 shows the AFM images taken over regions 10 µm × 10 µm, where (a) refers to the NTPA-SAM on the oxidized Si wafer and (b) to the as-synthesized PANI layers on NTPA-SAM. It is clearly shown that the surface of the NTPA-SAM (Fig. 4a) is very smooth and homogeneous with lower surface root-mean-square (RMS) roughness of 1 nm. After the synthesis of the PANI layers on the NTPA-SAM under the polymerization conditions of 0 °C and 5 h, significant differences are visible in the corresponding AFM image (see Fig. 4b). Namely, the as-synthesized PANI layers are constitutive of spherical polymer particles and the surface of PANI layers is bumpy with a higher RMS roughness of 55.5 nm, which is almost consonant with the morphology determined by SEM analysis.

Regarding the conductivity of the synthesized PANI layers in the protonated state, the surface resistance measured with multimeter changes from a big surface resistance of about 1 MΩ/□ (where the □ is 1 cm wide and 1 cm long) for the pristine silicon wafer to a surface resistance of 2155 Ω/□ for the PANI layers with a thickness of 220 nm after protonation with 0.5 M H_2SO_4. Using the average thickness of 220 nm for the PANI layers prepared on the silicon surface, a surface conductivity of 21.1 S/cm can be calculated, which is similar with the results reported by other researchers.[14,18] Therefore, the as-synthesized PANI layers have the excellent conductivity and can be used as the electrode material for the following EPD experiment.

3.2. *EPD of $BaTiO_3$ films on the as-synthesized conducting PANI layers*

The XRD pattern (dotted line) of the $BaTiO_3$ nanosize powders after being dried at 100 °C in oven for 2 h is shown in Fig. 5. Peaks at $2\theta = 22.1°$, 31.6°, 39.1°, 45.4°, 51.1°, 56.3°, 66.1°, 70.4°, and 75.0° are ascribed to the (1 0 0), (1 1 0), (1 1 1), (2 0 0), (2 1 0), (2 1 1), (2 2 0), (3 0 0), and (3 1 0) lattice planes of pure cubic perovskite phase $BaTiO_3$ (JCPDS card no. 31-0174). A typical micrograph of the $BaTiO_3$ powders is presented in Fig. 6, which shows that the $BaTiO_3$ particle has an average size of about 50 nm and is roughly spherical in shape with some apparent particle agglomerations.

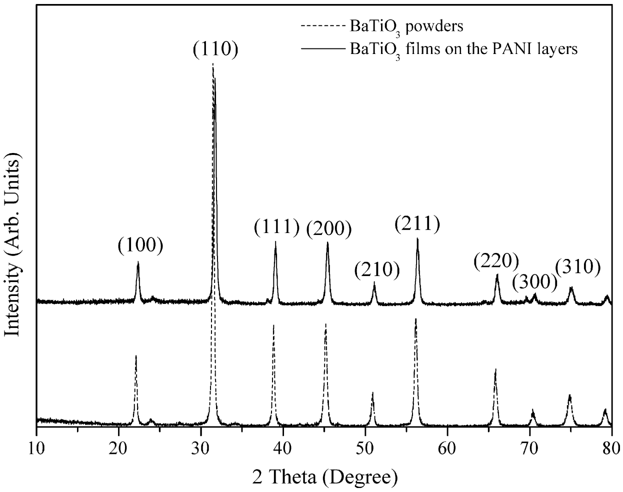

Fig. 5. XRD pattern of $BaTiO_3$ powder (dotted line) and $BaTiO_3$ films (solid line) deposited on the PANI/NTPA-SAM layers modified Si substrate using EPD method.

It is well known that the EPD technique utilizes the phenomenon of the movement of colloidal particles suspended in a

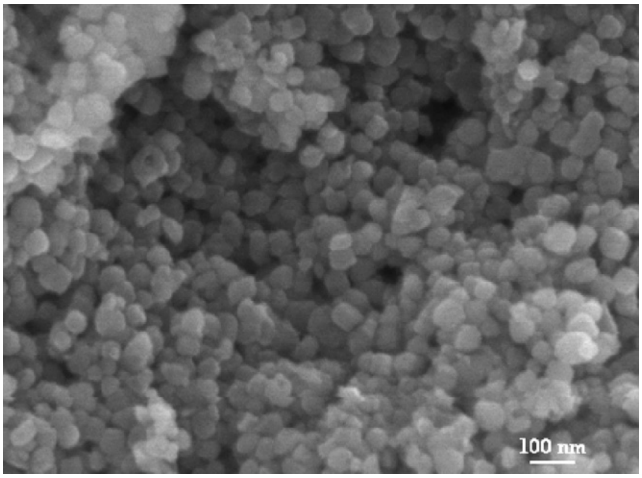

Fig. 6. SEM image of $BaTiO_3$ powders.

dispersive medium under a dc electric field. So, it is of great significance to select a suitable suspension medium for the $BaTiO_3$ powders.[19] $BaTiO_3$ films deposited through EPD technique were attained by using some inappropriate organic solvents such as diethylene glycol dimethylether, 1-nitropropane, and pyridine due to their chemical toxicity.[19,20] Recently, some environment beneficial and cost-effective organic solvents such as acetone, EtOH, Acac, isopropyl alcohol/ethyl acetate, EGMME/Acac, chloroform/methylene chloride, EtOH/acetone, etc. have been used as the dispersive media for preparing $BaTiO_3$ EPD suspensions and validated availability.[6,8,19,20] Nagai et al.[19] and Louh et al.[20] reported that the mixed solvent of EtOH/Acac had a better dispersive performance for the micrometer or submicrometer scale $BaTiO_3$ particles and the optimal volumetric ratio of EtOH and Acac for obtaining the maximum EPD efficiency was 1: 1. While in our previous work,[4,6] the mixed solvent of EGMME/Acac with a volume ratio of 9: 1 was proved possessing an ideal dispersive capability for the 10 nm $BaTiO_3$ particles. In the present study, in order to obtain a relatively stable and well dispersed $BaTiO_3$ suspension for the EPD experiment, two kinds of mixed suspension media, EGMME/Acac with a volume ratio of 9: 1, or EtOH/Acac with a volume ratio of 1: 1, have been tested. After two kinds of suspensions with the concentration of 3 g/L were prepared and held still for several hours, the supernatant fluid was extracted and used for the measurement of particle size distribution with the Zetasizer Nano Instrument, and the result is presented in Fig. 7. It is noted that the size distribution of $BaTiO_3$ particles in the suspension media of EtOH/Acac is approximately between 50 and 350 nm (see Fig. 7a), and the average particle size is about 96 nm. It can be concluded that, according to the estimation from SEM analysis and the reported size of 30–50 nm provided by the vendor, the most of $BaTiO_3$ accumulations in the suspension media of EtOH/Acac exists in the accumulated state of 2–3 single $BaTiO_3$ particle. While the size distribution of $BaTiO_3$ particles in the suspension media of EGMME/Acac is approximately between 400 and 2000 nm (see Fig. 7b), and the average particle size is about 685 nm, revealing that serious agglomeration of $BaTiO_3$ particles has been happened in this case. So, the suspension media of EtOH/Acac has a better dispersive performance for the employed $BaTiO_3$ particles than that of EGMME/Acac. Moreover, the zeta potential value of $BaTiO_3$ particles dispersed in suspension media of EtOH/Acac is about 37 mV, determined by the laser electrophoresis zeta-potential analyzer, indicating that the $BaTiO_3$ particle is positively charged. The surface charging mechanism of $BaTiO_3$ particles in the suspension media of EtOH/Acac can be explained with the DLVO theory.[10] The measured operational pH reading of $BaTiO_3$ particles in the suspension media of EtOH/Acac is ~5.5, mensurated with a pH meter (PC 300 series, Asone Ltd.). The operational pH reading in a non-aqueous solvent can be defined by the following equation[8,10]:

$$p\alpha_{\mathrm{H}} = \frac{\mathrm{pH} - \Delta E_j}{0.05916} \quad (25^\circ\mathrm{C})$$

where pH is the operational pH reading measured in the non-aqueous solvent, and $p\alpha_{\mathrm{H}}$ is the negative logarithm of proton activity in the non-aqueous solvent, or the pH in an equivalent aqueous medium; ΔE_j is the difference between the liquid-junction potentials encountered in the standardization and testing step of a standard pH meter, which has a positive value for the EtOH/Acac solvent mixture. Therefore, the equivalent aqueous pH value in the suspension media of EtOH/Acac is less than 5.5. While Paik et al.[21] have pointed out that the isoelectric point ($\mathrm{pH_{IEP}}$) of $BaTiO_3$ particles in water is ~9.8 in non-dilute solid concentrations. Consequently, it can be concluded that the zeta potential value of $BaTiO_3$ particles in the suspension media is positive and high because the equivalent aqueous pH value of 5.5 in the suspension media of EtOH/Acac is far lower than the $\mathrm{pH_{IEP}}$ of 9.8, which agrees well with the measured higher value of 37 mV. So, the $BaTiO_3$ suspension prepared in the suspension media of EtOH/Acac is employed for depositing $BaTiO_3$ films by EPD technique.

During the EPD process, it was seen that the $BaTiO_3$ particles were only deposited on the cathode and no deposition occurred on the anode, which also demonstrated that the $BaTiO_3$ particles were positively charged in the prepared suspension. The effects of some parameters such as applied voltage, deposition time, suspension concentration and separating distance between two electrodes, on the thickness of the as-deposited $BaTiO_3$ films were investigated and the measurement was performed with the surface profiler. When the suspension concentration and electrode distance are kept at constant values of 9 g/L and 2 cm, respectively, the effect of applied voltage and deposition time on the $BaTiO_3$ films thickness is shown in Fig. 8a. It is evident

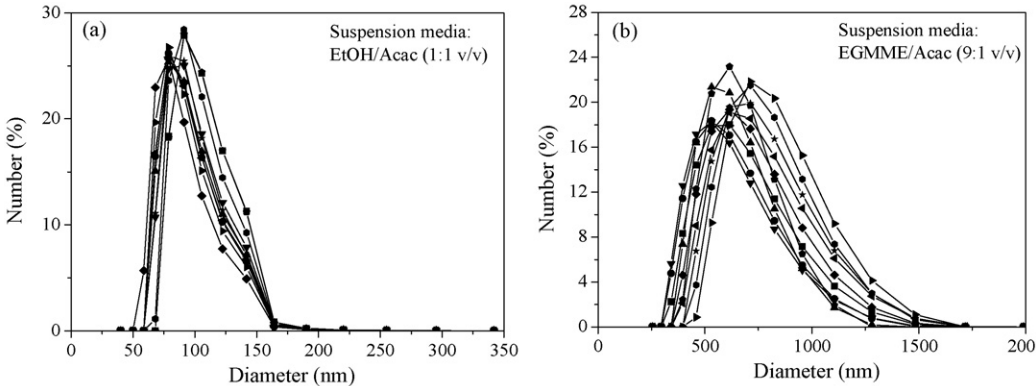

Fig. 7. Size distribution of $BaTiO_3$ particles in the different suspension media.

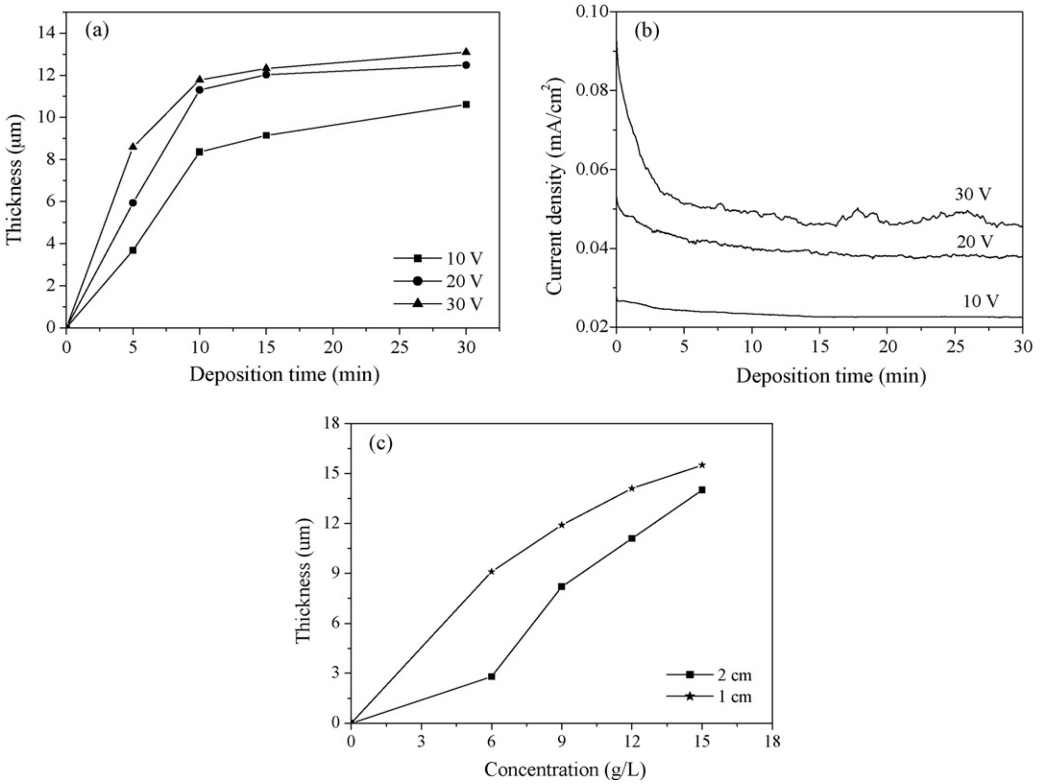

Fig. 8. (a) Effects of EPD voltage and deposition time on the thickness of deposited $BaTiO_3$ films, (b) dependence of the deposition current density with the deposition time at the different applied voltages, and (c) thickness variation of the deposited $BaTiO_3$ films against various suspension concentrations at the different electrode distances.

that, for each applied voltage, the thickness change of deposited $BaTiO_3$ films with deposition time can be divided into two regions. First, the film thickness increases quickly and almost linearly with the increase of deposition time when the time is less than 10 min. Then, the thickness of deposited films increases slowly with the increase of deposition time and approaches a saturation value for a much longer deposition time. The change trend of the deposited $BaTiO_3$ film thickness with the deposition time is correlative with the variation of deposition current density with the deposition time and the dependent curves at the different applied voltages are exhibited in Fig. 8b. It reveals distinctly that the change process of current density with the deposition time also can be separated into two major sections for each applied voltage. First, as the deposition time increases, the current density decreases quickly when the deposition time is less than 10 min. Thereafter, with increasing the deposition time, the current density decreases slowly and reaches a steady value, which can be attributable to these effects, the resistance of substrate is enhanced as long as more of $BaTiO_3$ particles are deposited on the substrate to build thicker layer, the electrode polarization, and the decrease of suspension concentration.[5,7,8] Furthermore, under the same deposition time, it is displayed obviously in Fig. 8a that the thickness of deposited $BaTiO_3$ films increases with the increase of applied voltage. Since the thickness of deposited $BaTiO_3$ films gets the saturation value after 10 min deposition at different applied voltages, the deposition time will be kept at constant value of 10 min for the rest of experiments. When the applied voltage is set at 10 V, the relationship between the film thickness and suspension concentration at different electrode distances is depicted in Fig. 8c. It indicates that the thickness of deposited $BaTiO_3$ films increases with the increase of suspension concentration at each electrode distance. On the other hand, for a given suspension concentration and applied voltage, the higher deposition thickness can be achieved when the smaller separating distance between two electrodes is employed. So, the thickness of deposited $BaTiO_3$ films can be controlled easily by changing EPD process parameters and the similar experimental phenomena has also been reported by Zhang and Lee[8] and other researchers.[5,20]

For the sake of obtaining the smooth, dense, and crack-free $BaTiO_3$ films on the conducting PANI layers coated Si substrate, EPD process was carried out with various concentration $BaTiO_3$ suspensions, while the applied voltage, deposition time, and the separating distance between two electrodes were kept at 10 V, 10 min, and 2 cm, respectively, and the SEM micrographs of the deposited $BaTiO_3$ films are shown in Fig. 9. It is clear that a half-baked $BaTiO_3$ film is presented with the lower suspension concentration of 3 g/L (see Fig. 9a), indicating that no enough $BaTiO_3$ particles are absorbed on the surface of PANI layers to form a complete $BaTiO_3$ film under so low suspension concentration. While with higher suspension concentration of 30 g/L, there are obvious cracks appeared on the film surface (see Fig. 9b), although the deposited $BaTiO_3$ film is so dense and smooth. However, in virtue of suspensions with the appropriate concentrations of 6–15 g/L, an integrated and crack-free film can be fabricated and the typical SEM micrographs of the

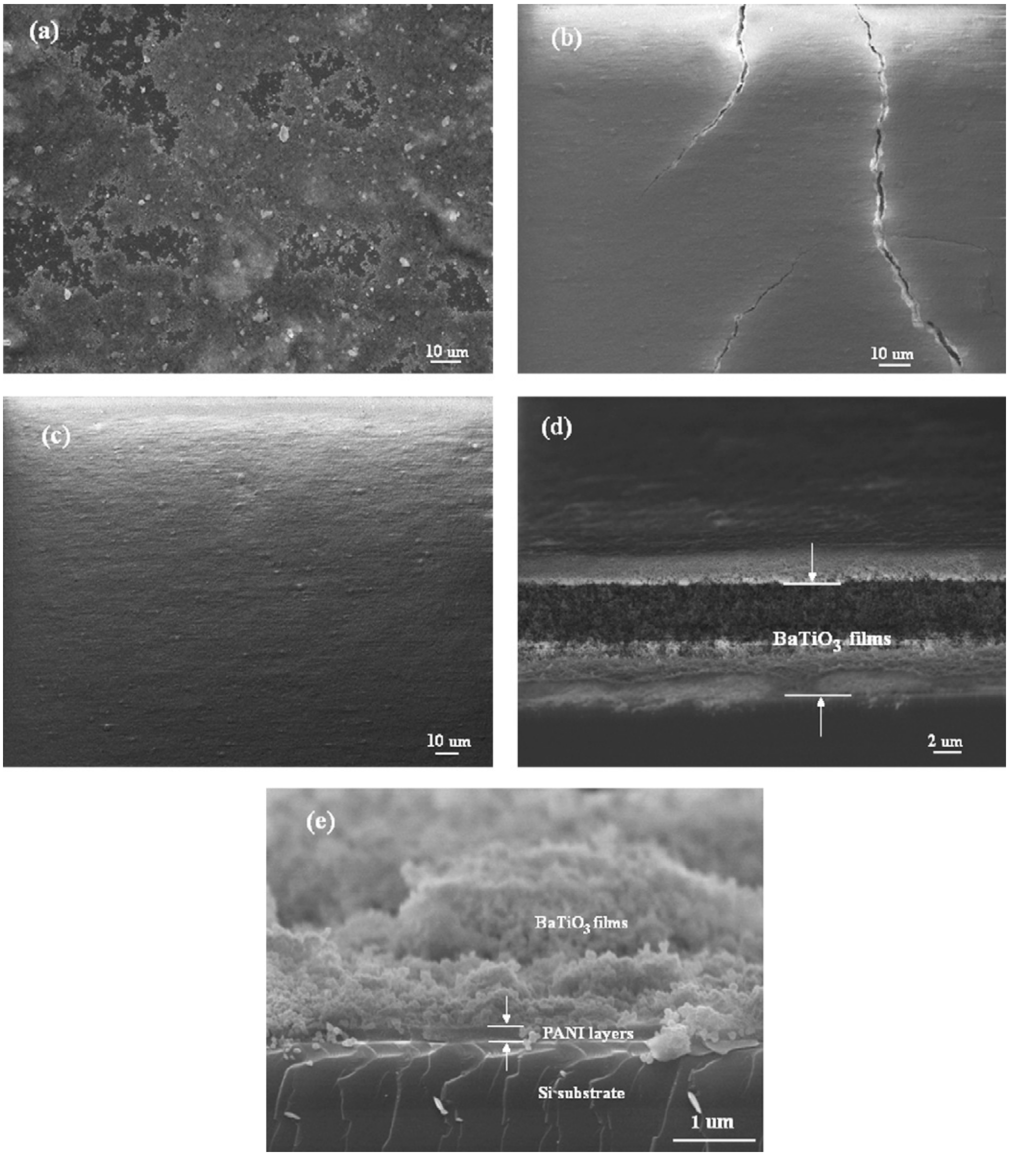

Fig. 9. FE-SEM micrographs of $BaTiO_3$ films deposited by EPD process.

$BaTiO_3$ films deposited with the suspension concentration of 9 g/L are shown in Fig. 9c–e. From the top surface micrograph (Fig. 9c), it can be found that a flat and smooth $BaTiO_3$ film has been deposited compactly on the PANI layers and no obvious cracks are observed. From the cross-sectional micrograph at different magnifications (Fig. 9d and e), it is obvious that the $BaTiO_3$ film is formed by the deposition of $BaTiO_3$ particles on the surface of conducting PANI layers (see Fig. 9e) and a relatively dense $BaTiO_3$ film with a uniform thickness of about 8 μm (see Fig. 9d) has been achieved, which accords with the thickness value determined by the surface profiler. The microstructure of above mentioned $BaTiO_3$ film is also characterized by XRD analysis and is indexed as pure cubic $BaTiO_3$ (see solid line in Fig. 5). Moreover, the absence of a typical diffraction peak from the single crystal Si substrate indicates that the as-deposited $BaTiO_3$ film is so integrated and thick enough that the underlying Si substrate is covered completely.

4. Conclusions

In this work, EPD technique was employed for fabricating the $BaTiO_3$ films on the Si substrate modified with the ordered conducting PANI layers. Firstly, surface polymerization of ordered conducting PANI layers on aniline-primed Si substrate was performed by polymerization of aniline monomer in an aqueous solution. It could be found that a dense, smooth, and strong adhered PANI layer had been executed on the aniline-primed Si substrate and the synthesized PANI layers had an excellent conductivity. Secondly, EPD of $BaTiO_3$ films was fulfilled using the PANI/NTPA-SAM layers modified Si wafer as the cathode. The effects of some parameters such as applied voltage, deposition time, suspension concentration, and separating distance between two electrodes, on the thickness of the as-deposited $BaTiO_3$ films were investigated. It was obtained that, when the suspension concentration and electrode distance were kept constant, the thickness of deposited films increased quickly and almost linearly with the increase of deposition time when the time was less than 10 min. Under the same deposition time, the deposited film thickness increased with the increase of applied voltage. On the other hand, when the applied voltage and deposition time were kept constant, the thickness of deposited $BaTiO_3$ films increased with the increase of suspension concentration at each electrode distance. Furthermore, for a given suspension concentration and applied voltage, the higher thickness could be achieved when the smaller separating distance between two electrodes was employed. All these results demonstrated that the thickness of the as-deposited $BaTiO_3$ films could be changed expediently by adjusting EPD process parameters. The analytical results from SEM images indicated that a relatively dense and smooth $BaTiO_3$ films with the uniform thickness could be attained on the PANI layers modified Si substrate when applying an appropriate concentration suspension. The advantage of this method is focused on the fact that the EPD technique can be employed for the fabrication of ceramic films on the non-conductive Si or glass substrates, which is expected to be a potential fabricating route in micro-electronic devices and other areas.

Acknowledgements

The research project is supported by the Japanese Society of the Promotion of Science (JSPS: P05418). The authors are grateful to Ms. T. Kuga, Ms. S. Murakami, and Mr. R. Fujiwara, et al. for assistance with the experiment.

References

1. Wu, Y. J., Li, J. and Kuwabara, M., Barium titanate micropatterns prepared by electron beam lithography and electrophoretic deposition. *Key Eng. Mater.*, 2006, **301**, 247–250.
2. Hu, Z. G., Wang, G. S., Huang, Z. M. and Chu, J. H., Structure-related infrared optical properties of $BaTiO_3$ thin films grown on Pt/Ti/SiO_2/Si substrates. *Phys. Chem. Solids*, 2003, **64**, 2445–2450.
3. Wu, Z. B., Kumagai, N. and Yoshimura, M., Hydrothermal formation and growth of single- and double-layer $BaTiO_3$ and $SrTiO_3$ films on the flexible polymer film substrates from sol–gel amorphous titanium oxide films. *Chem. Mater.*, 2000, **12**, 3356–3361.
4. Wu, Y. J., Li, J., Tanaka, H. and Kuwabara, M., Preparation of nano-structured $BaTiO_3$ thin film by electrophoretic deposition and its characterization. *J. Eur. Ceram. Soc.*, 2005, **25**, 2041–2044.
5. Okamura, S., Tsukamoto, T. and Koura, N., Fabrication of ferroelectric $BaTiO_3$ films by electrophoretic deposition. *Jpn. J. Appl. Phys.*, 1993, **32**, 4182–4185.
6. Li, J., Wu, Y. J., Tanaka, H., Yamamoto, T. and Kuwabara, M., Preparation of a monodispersed suspension of barium titanate nanoparticles and electrophoretic deposition of thin films. *J. Am. Ceram. Soc.*, 2004, **87**, 1578–1581.
7. Li, J., Wu, Y. J., Yamamoto, T. and Kuwabara, M., Electrophoretic deposition and photoluminescent properties of Eu-doped $BaTiO_3$ thin film from a suspension of monodispersed nanocrystallites. *Sci. Technol. Adv. Mater.*, 2004, **5**, 393–398.
8. Zhang, J. P. and Lee, B. I., Electrophoretic deposition and characterization of micrometer-scale $BaTiO_3$ based X7R dielectric thick films. *J. Am. Ceram. Soc.*, 2000, **83**, 2417–2422.
9. Uchikoshi, T., Furumi, S., Suzuki, T. S. and Sakka, Y., Electrophoretic deposition of alumina on conductive polymer-coated ceramic substrates. *J. Ceram. Soc. Jpn.*, 2006, **114**, 55–58.
10. Sarkar, P. and Nicholson, P. S., Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics. *J. Am. Ceram. Soc.*, 1996, **79**, 1987–2002.
11. Ren, S. L., Yang, S. R. and Zhao, Y. P., Micro- and macro-tribological study on a self-assembled dual-layer film. *Langmuir*, 2003, **19**, 2763–2767.
12. Madathil, R., Multilayer growth of conductive polyaniline: a two-pot, alternate, oxidation and reduction strategy. *Synthetic Met.*, 2005, **150**, 123–126.
13. Gemeay, A. H., Mansour, I. A., El-Sharkawy, R. G. and Zaki, A. B., Preparation and characterization of polyaniline/manganese dioxide composites via oxidative polymerization: effect of acids. *Eur. Polym. J.*, 2005, **41**, 2575–2583.
14. Li, Z. F. and Ruckenstein, E., Patterned conductive polyaniline on Si(1 0 0) surface via self-assembly and graft polymerization. *Macromolecules*, 2002, **35**, 9506–9512.
15. Wu, C.-G. and Chen, J.-Y., Chemical deposition of ordered conducting polyaniline film via molecular self-assembly. *Chem. Mater.*, 1997, **9**, 399–402.
16. Wu, C.-G., Yeh, Y.-R., Chen, J.-Y. and Chiou, Y.-H., Electroless surface polymerization of ordered conducting polyaniline films on aniline-primed substrates. *Polymer*, 2001, **42**, 2877–2885.
17. Kanamura, K., Kawai, Y., Yonezawa, S. and Takehara, Z., Diffusion behavior of anions in polyaniline during electrochemical undoping. 2. Effect of the preparation conditions of polyaniline on the diffusion-coefficient of $BF4^-$. *J. Phys. Chem.*, 1994, **98**, 2174–2179.
18. Li, Z. F. and Ruckenstein, E., Conductive surface via graft polymerization of aniline on a modified glass surface. *Synthetic Met.*, 2002, **129**, 73–78.
19. Nagai, M., Yamashita, K., Umegaki, T. and Takuma, Y., Electrophoretic deposition of ferroelectric barium titanate thick films and their dielectric properties. *J. Am. Ceram. Soc.*, 1993, **76**, 253–255.
20. Louh, R. F. and Hsu, Y. H., Fabrication of barium titanate ferroelectric layers by electrophoretic deposition technique. *Mater. Chem. Phys.*, 2003, **79**, 226–229.
21. Paik, U. and Hackley, V. A., Influence of solids concentration on the isoelectric point of aqueous barium titanate. *J. Am. Ceram. Soc.*, 2000, **83**, 2381–2384.