Electrophoretic deposition and photoluminescent properties of Eu-doped BaTiO₃ thin film from a suspension of monodispersed nanocrystallites

Juan Li⁺⁺, Yong Jun Wu⁺⁺, T. Yamamoto⁺⁺, Makoto Kuwabara⁺⁺

⁺⁺Department of Materials Engineering, University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received 15 November 2003; revised 9 February 2004; accepted 12 February 2004

Available online 28 May 2004

Abstract

Monodispersed Eu-doped BaTiO₃ nanocrystallites with a pseudo-cubic perovskite phase were successfully prepared using highly concentrated alkoxide solution under hydrothermal conditions at temperatures \( \leq 100 \) °C. The obtained nanoparticles had a very narrow particle size distribution and the average value was about 10 nm. By dispersing a piece of BaTiO₃ bulk gel into mixed solvent of 2-methoxyethanol and acetylacetone, we obtained well-dispersed and stable suspensions of Eu-doped BaTiO₃ nanocrystallites with a high transmittance. Using these suspensions, nanostructured thin films with a low porosity and a smooth surface were synthesized on Pt/Ti/SiO₂/Si substrate by electrophoretic deposition. The obtained Eu-doped BaTiO₃ thin films showed strong, visible room temperature photoluminescence (PL) associated with Eu ions. The PL spectra had typical ones for Eu³⁺ band corresponding to \( ^{3}D_{0} \rightarrow ^{7}F_{j} \) electronic transitions with a maximum intensity at 613 nm.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Sol–gel process; Electrophoretic deposition; Eu-doped BaTiO₃; Thin films; Photoluminescence

1. Introduction

As advanced ceramic integration technology is strongly demanded in future markets of devices for information processing, medical and energy related application, electrophoretic deposition (EPD), a process whereby powder particles are deposited from a suspension on to a shaped electrode of opposite charge under application of a d.c. electrical field, becomes a promising method to fabricate such devices [1–7]. Since 1927 when Harsanyi [8] first used EPD to obtain ThO₂ and tungsten deposition on a platinum cathode, the electrophoretic technique has been applied to fabrication of ceramic films and coatings with thickness of a few micrometers to several millimeters. Because the EPD offers many features such as process simplicity, low apparatus cost, applicability for depositing layer on the substrate of complicated shape, easy control of layer thickness and its microstructure, and much higher deposition rate compared to CVD and PVD technique, applications of EPD range from magnetic, electronic, electrolytic, and superconducting ceramic thick films to the coatings of bioceramics, structural and high-temperature ceramics.

However, the conventional EPD uses suspensions of micrometer or submicrometer particles [9–11], which not only makes it impossible to obtain dense thin films and a good surface smoothness, but also hinders EPD applications in fabrication of devices with a submicrometer layer thickness and patterned microstructure.

In our previous work, a new sol–gel process using high concentration of alkoxide precursor solutions has been proved to have a significant advantage in synthesizing BaTiO₃ gel and ceramic materials [12,13]. Transparent, crack-free crystalline BaTiO₃ monolithic gels and thin films have been successfully synthesized at low temperature [14–16]. Eu-doped BaTiO₃ thin films with a pseudo-cubic perovskite structure were successfully fabricated on magnesia substrates at low temperature using a high concentration sol–gel process, in which the newly developed gel-aging process on substrate was employed [17]. In the present study, a developed EPD process with the use of monodispersed nanocrystalline particle synthesized at low
temperature has been proposed. The photoluminescent properties also have been investigated.

2. Experimental

2.1. Preparation of Eu-doped BaTiO$_3$ nanocrystallites

High purity barium diethoxide (Ba(OC$_2$H$_5$)$_2$, purity > 99%), dehydrated europium chloride (EuCl$_3$, purity > 99.99%) and titanium tetra-iso-propoxide (Ti(OiC$_3$H$_7$)$_4$, purity > 99%) were dissolved in a mixed solvent of dehydrated CH$_3$OH and CH$_3$OC$_2$H$_4$OH (purity > 99.8%) with a volume ratio of 3:2. The concentration of barium and europium in the precursor solution was about 1 mol/l and the doping concentration was 5 mol%. After stirring for 24 h in a dry N$_2$ atmosphere at room temperature, the precursor solution was hydrolyzed by spraying mixed solution of distilled water and 2-methoxyethanol (with a volume ratio of 1:1) at ~20 $^\circ$C. After stirring for 10 min, hydrolyzed solution in a glass bottle was put into 90 $^\circ$C-oil bath quickly and aged for several minutes to 12 h. After liquid extraction, the gel was added into a mixed solvent of 2-methoxyethanol and acetylacetone with a volume ratio of 4:1 and then ultrasonically agitated for several hours to form stable suspensions (0.075 mol/l).

2.2. Electrophoretic deposition

Fig. 1 shows a schematic diagram of the EPD system in the present work. A Pt/Ti/SiO$_2$/Si substrate of 1 cm $\times$ 1 cm was used as cathode and a stainless steel plate as the counter-electrode with a distance of 2 cm. Before deposition, the substrates were washed with distilled water, rinsed with ethanol in an ultrasonic bath and dried in air. A d.c. voltage between 1 and 15 V was applied to the electrodes. At current densities higher than approximately 1.0 mA/cm$^2$, hydrogen was evolved at the anode and these gas bubbles may become entrapped between the depositing particles, leading to porosity in the final compact. Thus, the applied voltage was kept to minimize the gas evolution in the electrode. The deposits were dried in air at 50 $^\circ$C and some of them were heat-treated up to 600 $^\circ$C for 3 h.

2.3. Characterization

Particle size and crystal structure were measured by a high-resolution transmission electron microscopy and X-ray diffractometry (XRD, Mac Science, M18XHF). The particle size distribution was characterized by a particle size analyzer (Nikkiso, UPA250). Surface morphology and film thickness were evaluated by field emission scanning electron microscopy (FE-SEM, HITACHI, S5000). The excitation and emission spectra were recorded using a JASCO FP-750 spectrophotometer. All the measurements were carried out at room temperature with a band width of 10 nm for emission and excitation.

3. Results and discussion

Crystal structure characterization of the gel nanoparticles was provided by TEM. Fig. 2a shows that these particles consist of regularly shaped near-spherical monodispersed crystalline particles with the particle diameter of 8–12 nm. The particle size distribution measured by a particle size analyzer using dynamic light scattering technique indicated
that the obtained crystallites had a very narrow distribution and the average diameter is 9.8 nm. The electron diffraction pattern (Fig. 2a) could be indexed to cubic symmetry, indicating BaTiO$_3$ to be in the perovskite cubic phase. In our previous paper [18], the crystallinity of Eu-doped BaTiO$_3$ thin films prepared by GAP on substrate at 50°C decreased with increasing Eu concentration. When Eu doping concentration is about 5%, very weak peaks of cubic phase were observed. Fig. 3 is the XRD patterns of 5% Eu-doped BaTiO$_3$ gel crystallites hydrolyzed with $R_w = 10$ and aged at 90°C for 30, 60, 200 min and 12 h, respectively. In agreement with the results of TEM, the obtained crystallites tended to crystallize a pseudo-cubic perovskite phase. The nanoparticles had a good crystallinity and with increasing aging time the crystallinity slightly improved. A high-resolution micrograph shown in Fig. 1b demonstrated that the crystallites were structurally perfect. The planes visible are the 2.85 Å (110) planes.

Because EPD utilizes the phenomenon of the movement of colloidal particles suspended in a medium under a d.c. electric field, it is important to choose suitable suspension mediums to obtain stable suspension. Lamb and Salmon [19] dispersed BaTiO$_3$ powder (1–10 mm) in di(ethylene glycol)dimethyl ether and an anionic wetting agent and deposited $\sim$380 nm thick coatings at 200 V/cm for 45 s. Nagai et al. [20] utilize a mixed ethanol-acetylacetone suspension as the dispersive medium. A solution of 20–80% ethanol gave a constant and high deposition rate, where no deposition was observed from pure ethanol or acetylacetone. Okamura et al. [9] deposited 0.1-μm BaTiO$_3$ from acetone with iodine. We here selected a mixed solution of 2-methoxyethanol and acetylacetone as dispersive medium, and found a volume ratio of 2-methoxyethanal and acetylacetone, as 80–20% results a good stability of suspensions and high EPD rate, which is discussed in our other paper [21]. The free hydrogen ions were produced in the suspensions as by-products of the intermediate species

$$\text{CH}_3\text{C} = \text{C} = \text{CH}_2 + \text{CH}_3\text{C} = \text{C} = \text{CH}_2\rightarrow \text{CH}_3\text{C} = \text{C} = \text{CH}_2 + \text{H}_2\text{O}$$

So the Eu-doped BaTiO$_3$ nanoparticles surrounded by the free hydrogen ions were positively charged. The transmission spectra of Eu-doped BaTiO$_3$ suspensions aged for different time are shown in Fig. 4. After sonication for several hours, the suspensions of nanocrystallites aged for $\geq$30 min at 90°C were transparent and remained stable for several months without stirring or sonicating. On the other hand when gel particles aged for short time $\leq$30 min were dispersed into the dispersive medium, some unknown needle-like precipitation was observed. When gel nanoparticles were dispersed with 2-methoxyethanol or acetylacetone separately, the precipitation was discovered only in the latter case. As shown in Fig. 5, the crystallinity estimated from the peak intensity of (110) increased with increasing aging time. The formation of these unknown precipitations has some relationship with the poor crystallinity of

![Fig. 3. X-ray diffraction patterns of 5% Eu-doped BaTiO$_3$ crystallites aged for different time.](image1)

![Fig. 4. Transmittance of suspensions of 5% Eu-doped BaTiO$_3$ crystallites aged for different time.](image2)

![Fig. 5. The dependence of transmission of suspension at 600 nm and XRD intensity of peak (110) on aging time.](image3)
nanoparticles aged for <30 min, which would be discussed in detail in our other paper. Fig. 5 also showed that the transmittance at 600 nm of suspensions decreased with the increase of aging time. Because almost no change was observed in particle size of nanocrystallites aged for 30 min to 12 h from 8.2 to 11.8 nm, which was calculated by the half-width of X-ray diffraction peaks, the decrease of transmittance could be mainly attributed to the aggregation of the nanoparticles during aging.

Nanostructured Eu-doped BaTiO$_3$ thin films were successfully fabricated via EPD. Because the Eu-doped BaTiO$_3$ nanocrystallites were positively charged in the suspensions, thin films were deposited at the cathode and no deposition was observed at the anode. Many previous researches on EPD showed that the electroporetic deposited films were very porous with a rough surface because of use of the micrometer or submicrometer particles and the bubble generation on electrodes during filming. In the present work, the obtained thin films have a relative low porosity and a smooth surface due to incorporation of the nanosized particle and well-dispersion of the particles in suspensions, which is shown in Fig. 6.

Fig. 7 shows the deposition time dependence of the deposition current density when applying a constant voltage at 5 V. The deposition current density decreased with deposition time and resulted in a decreased deposition rate, which may be attributed to the electrode polarization, the formation of an insulating deposit layer, and the decrease of suspension concentration. The voltage drop due to electrode polarization should reach a steady value very fast, but the resistance due to the build up of an insulating deposit and influence of the concentration will increase continuously as deposition progresses. Thus, with increasing deposition time, the thickness increase of films deposited under constant voltage and variable concentration condition should deviated from the linear increase of those deposited under constant-current and constant concentration [3]. Here, because we only deposited very thin films with a thickness less than 300 nm, these influences are not so significant that an almost linearly increased film thickness with increasing deposition time from 1 to 5 min were obtained, which is shown in Fig. 6.

The Eu-doped BaTiO$_3$ thin films fabricated by EPD showed strong room temperature photoluminescence (PL) visible to the naked eye associated with Eu ions. The photoluminescence spectrum of the 5%Eu-doped BaTiO$_3$ thin films excited at 275 nm shown in Fig. 8a represents europium luminescence peaks in the investigated spectral range arising from $^5\text{D}_0 - ^7\text{F}_j$ ($j = 0-4$) transitions of Eu$^{3+}$ ions. The dominating peak at around 613 nm corresponds to $^5\text{D}_0 - ^7\text{F}_2$ electronic transitions of Eu$^{3+}$ ions. As discussed in...
our previous paper [17], thin films sintered at temperatures below 600 °C showed an improved PL of Eu³⁺ ions with increasing sintering temperature. However, a rapid quenching of Eu³⁺ emission due to reduction of europium ions from trivalent state to divalent state occurred when thin films were sintered above 600 °C. The dependence of emission intensity at 613 nm of thin films electrophoretically deposited by nanocrystallites aged for different time on sintering temperature up to 600 °C is shown in Fig. 8b. The thin films of nanocrystallites aged for 60 min had a highest PL intensity compared to those aged for 30, 200 min and 12 h. This may attribute to a relative better crystallinity of the nanocrystallites aged for 60 min than those aged for 30 min and a smaller particle and a slighter agglomeration than those aged for 200 min and 12 h.

4. Conclusions

Although EPD has been used for many years to fabricate ceramics films and coatings, there are few papers reporting fabrication of ceramic thin films (thickness < 1 μm) by this method. In the present paper, dispersing monodispersed single crystal nanoparticles of Eu-doped BaTiO₃ aged at hydrothermal condition at temperature <100 °C by high-concentration sol–gel process in to a mixed solvent of 2-methoxyethanol and acetylacetone, clear and very stable suspensions were synthesized. Using these suspensions, Eu-doped BaTiO₃ thin films with a low porosity and a smooth surface were electrophoretically deposited on the Pt/Ti/SiO₂/Si substrates. The film thickness, which was controlled by varying the deposition time when a constant voltage 5 V was applied, increased with increasing duration. The obtained films exhibit strong room temperature photoluminescence of Eu ions with a predominant band at 613 nm, and the PL intensity increased with increasing sintering temperature up to 600 °C. The thin film of nanocrystallites aged for 60 min showed a highest photoluminescence because of their relative better crystallinity than those aged for 30 min and a smaller particle size than those aged for 200 min and 12 h.

Acknowledgements

The study was financially supported by a Grant-in-Aid for Scientific Research (No. 12305042) and a Grant for 21st Century COE Program ‘Human-Friendly Materials based on Chemistry’ from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] C.T. Chu, B. Dunn, Fabrication of YBa₂Cu₃O₇₋ₓ superconducting coatings by electrophoretic deposition, Appl. Phys. Lett. 55 (1989) 492–494.
[2] Z. Zhang, Y. Huang, Z. Jiang, Electrophoretic deposition forming of SiC-TZP composites in nonaqueous sol media, J. Am. Ceram. Soc. 77 (1994) 1949–1964.
[3] P. Sarkar, P.S. Nicholson, Electrophoretic deposition (EPD): mechanism, kinetics, and application to ceramics, J. Am. Ceram. Soc. 79 (1996) 1987–2002.
[4] P.S. Nicholson, P. Sarkar, S. Datta, Producing ceramic laminate composites by EPD, Am. Ceram. Soc. Bull. 75 (11) (1996) 48–51.
[5] R.C. Hayward, D.A. Saville, L.A. Aksay, Electrophoretic assembly of colloidal crystals with optically tunable micropatterns, Nature 404 (2000) 56–59.
[6] Z. Wang, J. Shemilt, P. Xiao, Fabrication of ceramic composite coatings using electrophoretic deposition, reaction bonding and low temperature sintering, J. Eur. Ceram. Soc. 22 (2002) 183–189.
[7] R.N. Basu, M.J. Mayo, C.A. Randall, Free standing sintered ceramic films from electrophoretic deposition, Jpn. J. Appl. Phys. 38 (1999) 6462–6465.
[8] E. Harsanyi. US Patent No. 1897902, 1993.
[9] S. Okamura, T. Tsukamoto, N. Koura, Fabrication of ferroelectric BaTiO₃ films by electrophoretic deposition, Jpn. J. Appl. Phys. 32 (1993) 4182–4185.
[10] P.S. Nicholson, P. Sarkar, X. Huang, Electrophoretic deposition and its use to synthesize ZrO₂/Al₂O₃ micro-laminate ceramic/ceramic composites, J. Mater. Sci. 28 (1993) 6274–6278.

[11] G. Wang, P. Sarkar, P.S. Nicholson, Influence of acidity on the electrostatic stability of alumina suspensions in ethanol, J. Am. Ceram. Soc. 80 (1997) 965–972.

[12] H. Shimooka, M. Kuwabara, Preparation of dense BaTiO₃ ceramics from sol–gel-derived monolithic gels, J. Am. Ceram. Soc. 78 (1995) 2849–2852.

[13] H. Shimooka, M. Kuwabara, Crystallinity and stoichiometry of nanostructured sol–gel-derived BaTiO₃ monolithic gels, J. Am. Ceram. Soc. 79 (1996) 2983–2985.

[14] H. Shimooka, S. Kohki, T. Kobayashi, M. Kuwabara, Preparation of translucent barium titanate ceramics from sol–gel-derived transparent monolithic gels, J. Mater. Chem. 10 (2000) 1511–1512.

[15] J.-H. Cho, K. Miyazwa, M. Kuwabara, Influence of hydrolysis water content on the microstructure of BaTiO₃ xerogels prepared from high concentration metal alkoxide solutions, J. Sol–Gel Sci. Technol. 23 (2002) 9–14.

[16] H. Matsuda, N. Kobayashi, T. Kobayashi, K. Miyazawa, M. Kuwabara, Room-temperature synthesis of crystalline barium titanate thin films by high-concentration sol–gel method, J. Non-Cryst. Solids 271 (2000) 162–166.

[17] J. Li, M. Kuwabara, Preparation and luminescent properties of Eu-doped BaTiO₃ thin films by sol–gel process, Sci. Tech. Adv. Mater. 4 (2003) 143–148.

[18] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallogr. A 32 (1976) 751–767.

[19] V.A. Lamb, H.I. Salmon, Electrophoretic deposits of barium titanate, Am. Ceram. Soc. Bull. 41 (1962) 781–782.

[20] M. Nagai, K. Yamashita, T. Umegaki, Y. Takuma, Electrophoretic deposition of ferroelectric barium titanate thick films and their dielectric properties, J. Am. Ceram. Soc. 76 (1993) 253–255.

[21] J. Li, Y.J. Wu, H. Tanaka, T. Yamamoto, M. Kuwabara, Preparation of mono-dispersed suspensions of barium titanate nanoparticles and electrophoretic Deposition of thin films towards ceramic integration. J. Am. Ceram. Soc., in press.