J Electroceram (2010) 24:104–109
DOI 10.1007/s10832-008-9556-5

Moldless micropatterning of $BaTiO_3$ nanoparticles via electrophoretic deposition: A simple and feasible method

J. Q. Wang · M. Kuwabara

Received: 12 November 2007 / Accepted: 29 September 2008 / Published online: 5 November 2008

Abstract In this work, a simple, reproducible, and inexpensive fabrication route for moldless micropatterning of a colloidal assembly on a conducting substrate surface is actualized by means of electrophoretic deposition (EPD) technique. A synergetic combination of photolithography and EPD is employed for fabricating micropatterns of barium titanate ($BaTiO_3$) nanoparticles on an indium-tin-oxide (ITO) coated glass slide or a Pt/ITO substrate. At first, high quality resist molds with various micropatterns are fabricated on ITO glass slide by photolithography technique, which is used for providing a controlled local electric field during the EPD process. Then, $BaTiO_3$ nanoparticles suspension is prepared in KCl aqueous solution and is demonstrated the $BaTiO_3$ nanoparticles are negative charged in the suspension. At last, EPD of various $BaTiO_3$ micropatterns is accomplished successfully on the anodic ITO glass slide or Pt/ITO substrate using the micropatterned ITO glass slide as the cathode, indicating that it is a simple and potential route for micropatterning of colloidal assembly on a non-modified conducting substrate by virtue of EPD process.

Keywords Micropatterning · Barium titanate · Photolithography · Electrophoretic deposition · Nanoparticles

J. Q. Wang · M. Kuwabara (✉)
Department of Applied Science for Electronics and Materials,
Kyushu University,
6-1 Kasuga-kouen,
Kasuga 816-8580, Japan
e-mail: kuwabara@asem.kyushu-u.ac.jp

J. Q. Wang
State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou 730000, China

1 Introduction

In recent years, more and more researchers have come to recognize that the development of microfabrication techniques for particle assembly processing is of great importance for producing micro- and nano-scale materials or devices with a high performance [1]. In particular, the technique for fabricating patterned colloidal microstructures from particle suspensions has the promising purposes in the materials processing [2]. Very recently, a great deal of attention has been focused on the fabrication of patterned electroceramic materials due to the increasing demands for integrating them into microelectronic devices, and their potential applications as sensing, optical, and photonic band-gap materials [3, 4]. Specially, deposition of micropatterned barium titanate ($BaTiO_3$) films onto metal electrodes has attracted significant interest for its conspicuous technological applications in both the electronic and optical component industries. Various strategies, basing on gravity-sedimentation, electrostatic interaction, nanosphere lithography, electrophoresis, have been explored to fabricate $BaTiO_3$ and other colloidal particle micropatterns on a solid substrate [4–6]. Among these techniques, the electrophoretic deposition (EPD) process has been demonstrated to be a promising method for its extensive employments not only in ceramic film forming but also in particle alignment for microscale ceramic or polymer spherical particles on planar or patterned substrates [1, 3, 7]. Furthermore, lithography (including electron beam lithography and photolithography) has been utilized for fabricating very high resolution resist molds with nano- or mico-scale structures [8]. Nowadays, some results have been reported that confinement from lithographically defined electrode can be used for enhancing colloid crystal growth and producing patterned microstructures by dint of EPD process [9, 10]. For example, Xiong et al. [10] and

Winkleman et al. [11] attested that the micrometer and nanometer scaled micropatterns were electrophoretically achieved by selective deposition of the spherical latex particles in the predesigned trenches, respectively. In our lab, Dr. Wu et al. [3, 4] also proved previously that electron beam lithography and EPD could be combined and employed for selective deposition of nanoscale $BaTiO_3$ micropatterns with the microarrays of lines, grids, and dots. On the other hand, it has been demonstrated that an important challenge in micromanufacturing is the direct growth or assembly of nanoelements over macroscopic length scales [12]. However, up to now, no interrelated work has been published on fabricating micropatterns of $BaTiO_3$ and other electroceramic nanoparticles on the moldless substrate using EPD technique. Herein, a different kind of assembly technique was presented and a combination of photolithography and EPD was employed for fabricating micropatterns of $BaTiO_3$ nanaoparticles on a moldless conductive substrate. At first, high quality resist molds with various micropatterns were prepared on ITO glass substrate by photolithography technique, which was used for providing a controlled local electric field during EPD process. Then, commercial spherical shape $BaTiO_3$ nanoparticles with an average size of about 50 nm were adopted for preparing EPD suspension in KCl aqueous solution. At last, $BaTiO_3$ micropatterns were electrophoretically deposited on a moldless substrate. The microstructures and surface morphologies of the fabricated microelectrode and the as-deposited $BaTiO_3$ micropatterns were observed by an optical microscope and a field emission scanning electron microscopy.

2 Experimental

Schematic representation for fabricating micropatterns of $BaTiO_3$ nanoparticles is displayed in Fig. 1. The commercial positive photoresist (OFPR-8600 LB, Tokyo Ohka Kogyo Co., Ltd., Japan) was spin-coated on an ITO glass slide for several times and a photoresist film with a thickness of about 5 μm was obtained. Then, a mask was covered onto the photoresist film and this set was placed into the exposal system (Mask Alignment M-1S, Mikasa Co., Ltd., Japan) to be exposed under 405 nm UV light for a certain time. After developed and baked, a patterned microelectrode for providing a controlled local electric field during the EPD process was fabricated.

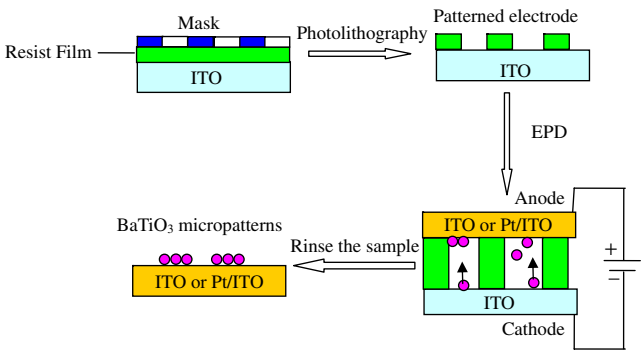

Fig. 1 Schematic illustration of the fabrication procedures for micropatterning of the $BaTiO_3$ colloidal nanoparticles

Barium titanate nanosize powders ($BaTiO_3$, 99%) were purchased from the Aldrich Co. and water (>18.0 MΩ/cm) used for all experiments and for all cleaning steps was obtained from a Millipore Milli-Q Plus water purification system. The suspension with a concentration of 0.25 g L^{-1} was obtained by ultrasonically dispersing appropriate $BaTiO_3$ powders in 1×10^{-5} M KCl aqueous solution. The $BaTiO_3$ micropatterns were electrophoretically deposited from the prepared suspension. In order to avoid any effects associated with gravity-sedimentation of particles, EPD was carried out against gravity. An ITO glass slide or a Pt/ITO sheet (aforehand, a 60 nm Pt layer was coated on the ITO glass slide with a JEOL JFC-1200 Fine Coater) in a size of 1×1.5 cm was used as the top electrode (anode) and the prepared ITO microelectrode with the same size was employed as the bottom electrode (cathode). A dc voltage ranging from 0-30 V provided by a dc voltage source (HP4140B, Hewlett-Packard, Japan) was applied to the two electrodes separated by the resist film, in which appropriate volumes of suspension were injected in advance, to electrophoretically deposit $BaTiO_3$ micropatterns on the top electrode. Following EPD, the samples were rinsed with water for removing any loose particles and dried.

The particle size distribution and zeta potential measurement analysis of the $BaTiO_3$ particles in the KCl aqueous suspension 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 microstructures and surface morphology of the prepared microelectrodes and the as-deposited $BaTiO_3$ micropatterns were observed by an optical microscope (Eclipse E600 POL, Nikon, Tokyo, Japan) and a field emission scanning electron microscopy (FE-SEM, JEOL JSM-6340F).

3 Results and discussion

In this experiment, ultrapure water was employed as the dispersive medium for preparing $BaTiO_3$ suspension because, to our best of knowledge, the patterned photoresist film only could be existed in the aqueous solution and would be dissolved quickly by some common organic dispersive media such as methanol, ethanol, acetone, etc.

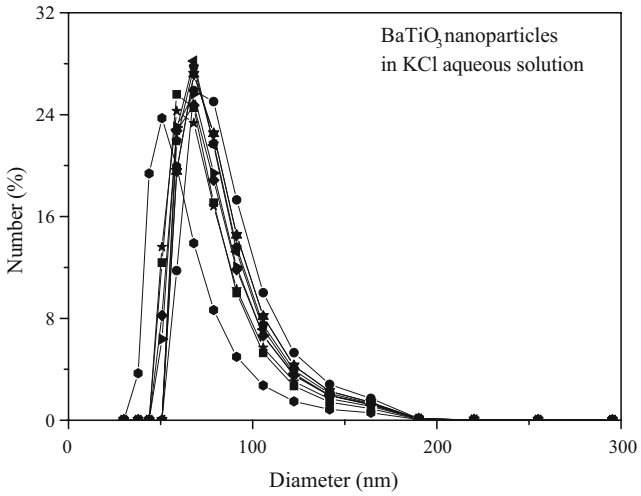

Fig. 2 $BaTiO_3$ particle size distribution in KCl aqueous solution

Moreover, a little KCl was added for improving the stability of the aqueous suspension, the deposition rate in EPD process, and the adhesion of $BaTiO_3$ particles to the substrates [13, 14]. The size distribution of $BaTiO_3$ particles in KCl aqueous solution was measured with the Zetasizer Nano Instrument and the result was shown in Fig. 2. It is noted that the size distribution of $BaTiO_3$ particles in suspension is approximately between 30 and 300 nm, and the average particle size is about 78 nm, which reveals that, according to the estimation from SEM analysis (Figure is omitted) and the reported size of 30-50 nm provided by the vendor, the most of $BaTiO_3$ particle aggregations in KCl aqueous suspension exists in the aggregated state of 2-3 single $BaTiO_3$ particle. In addition, the zeta potential value of $BaTiO_3$ particles dispersed in KCl aqueous suspension is about -33 mV at pH=7.10, determined by the laser electrophoresis zeta-potential analyzer, indicating that the $BaTiO_3$ particles are negatively charged in this case and the prepared suspension is normally considered stable according to the definition of zeta potential. So, the $BaTiO_3$ particles will be deposited on the anode (top electrode) during the EPD process.

Before EPD process, the patterned ITO glass microelectrodes with different shapes and sizes were firstly fabricated by use of photolithography technique, which would be used for providing a local electric field for the following EPD experiment. The typical optical microscopy photographs of the prepared microelectrodes with the zonal and circular shapes are presented in Fig. 3, combining the information from the surface profile curves (Figures are omitted) obtained by an Alpha-Step IQ Surface Profiler (KLA-Tencor Corp. USA), illuminating that high quality microelectrodes, which not only possess the sharp edges but also the walls of resist molds are almost perpendicular to the bottom of ITO sheet, have been fabricated successfully. It also can be seen that the zonal trenches have a width of 50 μm with a spacing of 50 μm in between [see Fig. 3(a)], while circular holes have a diameter of 50 μm with a spacing of 100 μm in between [see Fig. 3(b)].

The typical FE-SEM micrographs of the as-deposited $BaTiO_3$ micropatterns with the zonal and circular microstructures, the shapes of which are almost complementary with the corresponding resist molds, are shown in Figs. 4 and 5, respectively, suggesting that the means of EPD $BaTiO_3$ nanoparticles, using the photolithographic ITO microelectrodes to provide the local micro-electrical field, is feasible to fabricate patterned $BaTiO_3$ microstructures with different shapes on various substrates under the appropriate EPD conditions (the zonal micropatterns are deposited on ITO glass slide under the EPD conditions of 3 V and 5 min, see Fig. 4(b) and (c); while the circular micropatterns are obtained on Pt/ITO substrate under the EPD conditions of 4 V and 5 min, see Fig. 5. Moreover, it is also clear from Figs. 4(c) and 5(d), owning to the inhomogeneity of electric field caused by surface roughness, irregular shape and non-uniform size of $BaTiO_3$ particles, that the particles are attached incompletely on the substrates with disordered structures.

During the EPD process for fabricating the circular $BaTiO_3$ micropatterns on different substrates, the assembly currents as a function of time at different voltages were measured using a picoammeter and the results were

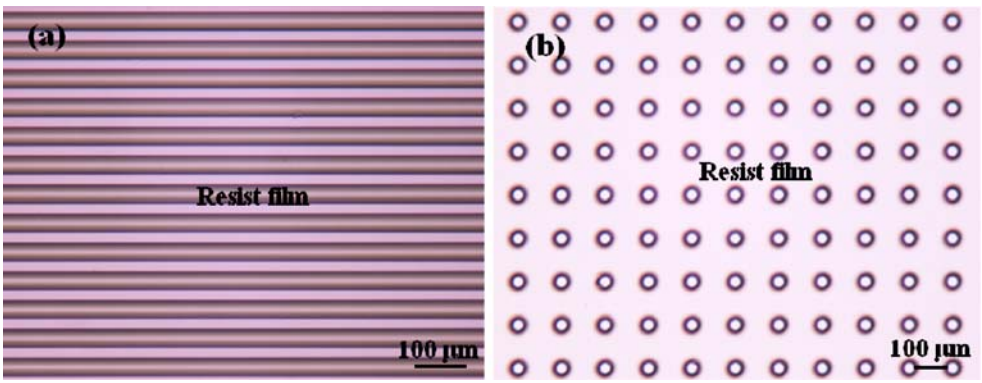

Fig. 3 Optical microscopy photographs of the prepared microelectrodes with the zonal (**a**) and circular (**b**) microstructures

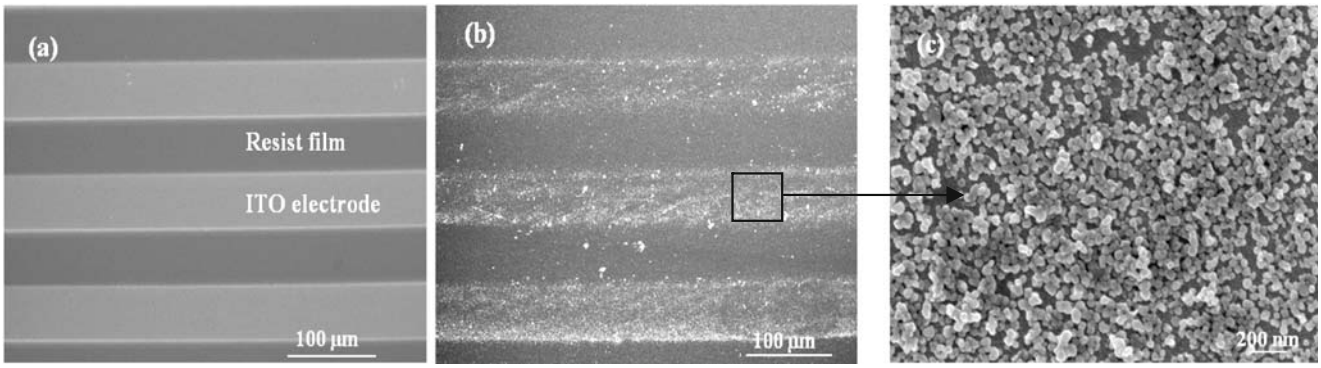

Fig. 4 FE-SEM photographs of the prepared ITO microelectrode (**a**), the as-deposited $BaTiO_3$ micropatterns (**b**), and the accumulated states of $BaTiO_3$ particles (**c**) on ITO glass slide

exhibited in Fig. 6. It reveals distinctly from Fig. 6(a) and (b) that the assembly current initially decreases rapidly, then decreases slowly and almost reaches a steady value with time, which can be attributable to the effects of enhancement of substrate resistance, electrode polarization, and decrease of suspension concentration as the EPD process progresses [15, 16]. On the other hand, it is seen that no obvious assembly is observed at a dc voltage of less than 2 V on both types of substrates, consistent with the measured lower assembly current. For the ITO glass slide, the optimal assembly voltages are in the range of 3–5 V, while for the Pt/ITO substrate, the optimal assembly voltages are in the range of 2.5–4 V, with relatively higher current induced.

Recurring to the similar procedures, the $BaTiO_3$ micropatterns with the smaller size also can be accomplished making use of the downsizing microelectrodes and the typical FE-SEM photographs are shown in Fig. 7. Using 5 V for 5 min, the circular micropatterns of $BaTiO_3$ nanoparticles with a diameter of 20 μm and a spacing of 40 μm are fabricated on the ITO glass slide [see Fig. 7(b) and (c)]. It is obvious from Fig. 7(c) that the most of $BaTiO_3$ particles are located on the areas demarcated by the borderline of patterned photoresist film and several layer aggregations of $BaTiO_3$ particles are mainly assembled on the center of circular microstructure [see Fig. 7(d)].

To gain more insights into the $BaTiO_3$ particle assembly process using electrophoresis, it is helpful to explore the particle transport mechanism under the influences of electrostatic and other forces such as capillary force, electrostatic force, gravitation, etc. [10]. During the EPD process, the applied voltages were in the range of 2.5–5 V, while the distance between two electrodes (corresponding

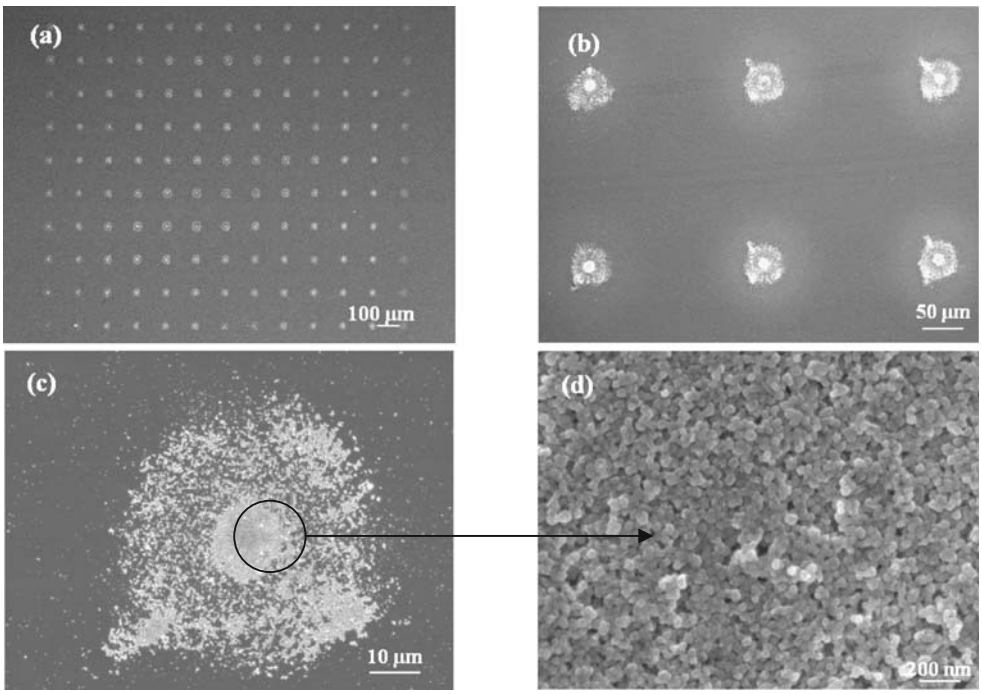

Fig. 5 FE-SEM photographs of the deposited $BaTiO_3$ micropatterns on Pt/ITO sheet at different magnification

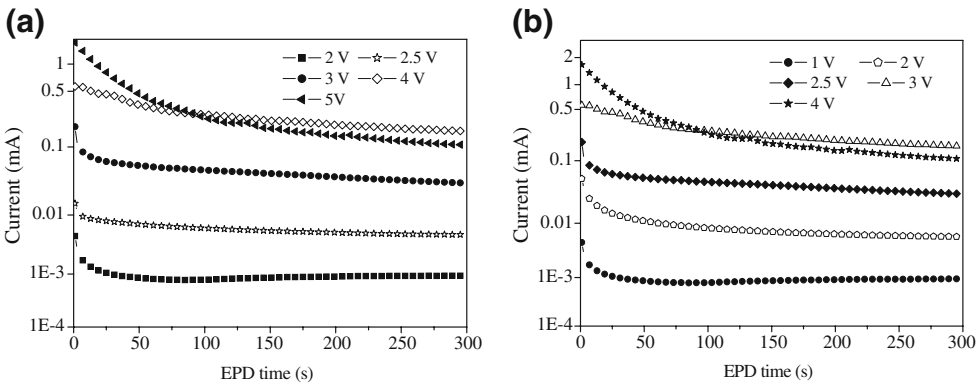

Fig. 6 Assembly current variation as a function of deposition time during EPD process on ITO glass (**a**) and Pt/ITO (**b**) substrates

to the thickness of resist film) was about 5 μm, so the electric fields were in the range of 5,000–10,000 V cm^{-1}, indicating that the role of applied electric fields was dominant over the effects from the capillary force, electrostatic force, gravitation, etc., and the applied electric field was strong enough for effective assembly of $BaTiO_3$ particles on both substrates. Once the $BaTiO_3$ particles were attracted and attached to the ITO (or Pt/ITO) domains, further particles would be driven by the electrohydrodynamic process to form aggregations as the EPD time progressed, and colloidal assembly micropatterns would be attained in the appropriate time. Moreover, it was found that the flocculated $BaTiO_3$ nanoparticles would be mainly maintained after being rinsed with splash water, demonstrating that the as-deposited $BaTiO_3$ nanoparticles had a good adhesion to the substrate. In a word, the above mentioned phenomena could be simply explained in virtue of a theory made by Koelmans et al. [17, 18], i.e., the $BaTiO_3$ colloidal particle transport toward the electrode was mainly determined by the applied electric field; while the adhesion of the $BaTiO_3$ deposit basically depended on the reaction occurred at the electrode surface in which e.g. H^+ might be produced and the suspension near the electrode was flocculated.

4 Conclusions

A combination of photolithography and EPD was employed for fabricating micropatterns of $BaTiO_3$ nanaoparticles. Results demonstrate that $BaTiO_3$ micropatterns with different shapes and sizes have been electrophoretically deposited successfully on the different substrates. This method is a direct demonstration of large-scale assembly of nanoparticles on a moldless substrate by virtue of the EPD process. It is so simple and feasible, implying that extensive applications will be found in the particle alignment processing not only in the assembly of $BaTiO_3$ particles

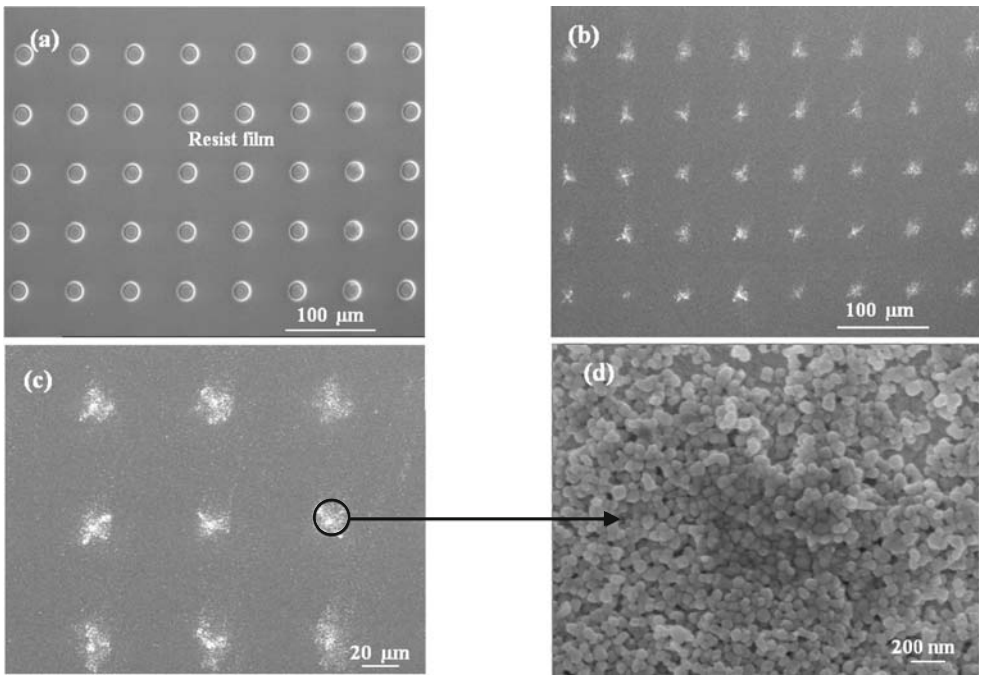

Fig. 7 FE-SEM photographs of the prepared circular microelectrode (**a**) and the as-deposited $BaTiO_3$ micropatterns on the ITO glass slide at different magnifications (**b**), (**c**), and (**d**)

but also in the micropatterning of other inorganic, polymeric, organic/inorganic composite particles on a non-modified conductive substrate.

Acknowledgements The authors are indebted to the Japanese Society of the Promotion of Science and "Top Hundred Talents Program" of Chinese Academy of Sciences for financial support of this work. J. Q. Wang is also grateful to the JSPS for a fellowship (JSPS: P05418).

References

1. J.I. Hamagami, K. Hasegawa, K. Kanamura, Key Eng. Mater. **301**, 243 (2006)
2. M. Trau, S. Sankaran, D.A. Saville, I.A. Aksay, Nature **374**, 437 (1995). doi:10.1038/374437a0
3. Y. J. Wu, J. Li, M. Kuwabara, J. Electroceram., (2008) doi:10.1007/s10832-007-9106-6
4. Y.J. Wu, J. Li, M. Kuwabara, Key Eng. Mater. **301**, 247 (2006)
5. W.M. Choi, O.O. Park, Nanotechnology **17**, 325 (2006). doi:10.1088/0957-4484/17/1/056
6. W.H. Ma, C. Harnagea, D. Hesse, U. Gösele, Appl. Phys. Lett. **83**, 3770 (2003). doi:10.1063/1.1625106
7. P. Sarkar, D. De, R. Rho, J. Mater. Sci. **39**, 819 (2004). doi:10.1023/B:JMSC.0000012909.46419.0e
8. C.R. Martin, I.A. Aksay, J. Electroceram. **12**, 53 (2004). doi:10.1023/B:JECR.0000034001.15359.98
9. E. Kumacheva, R.K. Golding, M. Allard, E.H. Sargent, Adv. Mater. **14**, 221 (2002)doi:10.1002/1521-4095(20020205)14:3<221::AID-ADMA221>3.0.CO;2-V
10. X.G. Xiong, P. Makaram, A. Busnaina, K. Bakhtari, S. Somu, N. McGruer, Appl. Phys. Lett. **89**, 193108 (2006). doi:10.1063/1.2385067
11. A. Winkleman, B.D. Gates, L.S. Mccarty, G.M. Whitesides, Adv. Mater. **17**, 1507 (2005). doi:10.1002/adma.200401958
12. E. Gultepe, D. Nagesha, L. Menon, Appl. Phys. Lett. **90**, 163119 (2007). doi:10.1063/1.2730575
13. A.R. Boccaccini, J. Cho, J.A. Roether, B.J.C. Thomas, E.J. Minay, M.S.P. Shaffer, Carbon **44**, 3149 (2006). doi:10.1016/j.carbon.2006.06.021
14. I. Corni, M.P. Ryan, A.R. Boccaccini, J. Eur. Ceram. Soc. **28**, 1353 (2008)
15. J. Li, Y.J. Wu, T. Yamamoto, M. Kuwabara, Sci. Technol. Adv. Mater. **5**, 393 (2004). doi:10.1016/j.stam.2004.02.002
16. J.P. Zhang, B.I. Lee, J. Am. Ceram. Soc. **83**, 2417 (2000)
17. H. Koelmans, J.T.G. Overbeek, Discuss. Faraday Soc. **18**, 52 (1954). doi:10.1039/df9541800052
18. M. Böhmer, Langmuir **12**, 5747 (1996). doi:10.1021/la960183w