Low-temperature fabrication of titanium metal/barium titanate composite capacitors via hydrothermal method and their dielectric properties

Shintaro UENO, Yasunao SAKAMOTO, Kouichi NAKASHIMA and Satoshi WADA

Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4–1–37 Takeda, Kofu 400–8510, Japan

We attempted to fabricate metal/dielectrics composite capacitors exhibiting high effective dielectric constant by a low-temperature wet chemical approach. The green compacts consisting of Ti metal particles, BaTiO3 fillers, and TiO2 precursor nanoparticles were successfully converted into Ti/BaTiO3 composite compacts by the hydrothermal method at 160°C. The effective dielectric constant of these composites tends to increase with the Ti metal content and jumped up to over 10^4 near the percolation threshold. When we used the Ti(core)-BaTiO3(shell) particles as the metal component, the thin BaTiO3 shell layers covering on the Ti particles prevented the direct contact among metal particles and increases the percolation threshold. Since the effective dielectric constant of these composites depends largely on the dielectric properties of the BaTiO3 layers, it is important to control the microstructure of these composites to improve the dielectric properties of such composites.

Key-words: Metal/dielectrics composite, Capacitors, Hydrothermal method, Percolation effect

1. Introduction

To develop a high-performance energy-storage device, we focus on ceramics capacitors because of their higher power density, though the dielectric constant of these capacitors is required to be further enhanced. A series of conductor/insulator composite materials categorized as percolation materials have attracted much attention because these composites exhibit the outstanding dielectric properties. Actually, a large amount of researches on these composites capacitors such as metal/dielectrics, metal/polymer, and carbon/polymer compositions has been undertaken and they are expected to be applied to sensors, tunable filters, and energy-storage devices. In general, the effective dielectric constant of such conductor/insulator composite materials increases with a content of the conductive particles distributed in the insulator layers, and a drastic increase in the effective dielectric constant is up to several orders of magnitude close to a percolation threshold (an insulator to metal transition point). Such an anomalous dielectric behavior is frequently interpreted by the percolation theory. The variation of the effective dielectric constant near the percolation threshold is given by the following equation:

\[ \langle \varepsilon \rangle = \varepsilon_m \frac{f_C - f}{f_C} \]

where \( \langle \varepsilon \rangle \) is the effective dielectric constant, \( \varepsilon_m \) is the dielectric constant of matrix, \( f_C \) is the percolation threshold, \( f \) is the filling factor, and \( q \) is the critical exponent. In this manuscript, we selected metal/dielectric ceramics composite capacitors and attempted to modify their microstructures to improve the dielectric properties. There is a large number of reports for fabrication of metal/dielectric composites with the high effective dielectric constant by a conventional solid-state synthesis method.

Pecharromán, et al. fabricated the Ni/barium titanate (BaTiO3, BT) composite materials with a high, frequency-independent effective dielectric constant (\( \varepsilon_r \approx 80,000 \)) by sintering the mixture of Ni particles and BT particles at higher temperature in a 90%Ar/10%H2 atmosphere. It is also reported that the Mo/mullite composites with the high effective dielectric constant of 500,000 were prepared by sintering in vacuum. Although the solid-state synthesis is convenient to fabricate the metal/dielectrics composites with the higher effective dielectric constant, the kinds of metals available for this method are significantly limited and most of them need to be heated under reduction atmosphere due to the oxidation of metal particles except for Pt, Pd, and Ag. On the other hand, some of the research groups reported on the fabrication of Ti/BT and Ti/SrTiO3 composite ceramics by a hydrothermal electrophoresis deposition under relatively mild conditions. However, since the metal layers also play a role in electrodes in this method, only the metal plates or foils covered by thin dielectric layers have been demonstrated. Additionally, this method needs the special reaction systems. Zhu, et al. reported the Ti foils/BT thin film composites fabricated by a simple hydrothermal method, but the dielectric constant is relatively small (\( \varepsilon_r = 400 \)) due to the geometric limitation.

It has not been reported on the fabrication of the metal/dielectric ceramics composites with metal particles densely distributed in dielectric layers by the wet chemical approach. We propose to fabricate Ti/BT composite compacts by chemically converted from green compacts consisting of Ti particles, BT fillers, and TiO2 under a hydrothermal condition. Since individual metal particles need to be separated by thin dielectric layers, we also employed Ti(core)-BT(shell) particles as the metal component to suppress the percolation.

2. Experimental

2.1 Preparation of Ti-BT core–shell particles

We employed two kinds of metal particles. Ti metal particles were purchased by the company (particle size <45 µm, Wako...
1.0 g of Ti metal powders were put into a Teflon container filled with 7.5 mL of Ba(OH)$_2$·8H$_2$O aqueous solution with a concentration of 50 mM. Then, the hydrothermal treatment was carried out at 230°C for 12 h in an autoclave. The resultant particles were washed with water and methanol and collected by decantation. The collected powders were dried at 80°C.

2.2 Fabrication of Ti/BT composite compacts

The Ti metal particles or the Ti–BT core–shell particles were mixed with rutile-type TiO$_2$ (MPT-851, Ishihara Sangyo Kaisha), BT nanoparticles (BT01; particle size is approximately 100 nm, or BT03; particle size is approximately 300 nm, Sakai Chemical Industry), and acetone by an ultrasonic stirrer (USS-1, Nihonseiki Kaisha Ltd., Japan) until acetone was evaporated. The molar ratio of TiO$_2$/BT was fixed at 1.0, and the mixing ratios of the metal particles in these precursor powders were varied. Then, these mixed powders were pressed into green compacts by a uniaxial press at 625 MPa. The green compact was placed in a Te container filled with 7.5 mL of Ba(OH)$_2$·8H$_2$O (Wako Pure Chemical, 99.9%) aqueous solution with a concentration of 50 mM. Then, the hydrothermal treatment was carried out at 230°C for 12 h in an autoclave. The resultant particles were washed with water and methanol and collected by decantation. The collected powders were dried at 80°C.

2.3 Characterization

The relative density of the compacts was measured by an Archimedes method. Crystal structures of the samples were identified by an X-ray diffraction (XRD, Ultima IV, Rigaku, Cu Kα, 40 kV, 30 mA). Microstructures of the samples were observed by a scanning electron microscope (SEM, JSM-6510, JEOL) and a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM, Tecnai Osiris, FEI). For electrical measurements, gold electrodes were sputtered on the top and bottom surfaces of samples and these samples were cut down. The dielectric properties were measured at frequency ranged from 10 Hz to 100 MHz at room temperature by an impedance analyzer (HP4294A, Agilent). Before the electrical measurements, these samples were dried at 200°C for 1 h in vacuum to remove the adsorbed water.

3. Results and discussion

3.1 Characterization of core–shell particles

The color of the Ti powder after the hydrothermal treatment was changed from metallic gray to metallic deep-blue. It may be due to an interference of light arising from thin oxide layers homogeneously formed on the Ti metal surface. Figure 1 shows SEM images of the Ti metal particles before and after the hydrothermal treatment. While the smooth surface can be seen for Ti metal particles [Fig. 1(a)], nanoparticles formed on the surface of micro-size Ti metal particles after the hydrothermal treatment [Fig. 1(b)]. According to the XRD measurements, the particles obtained by the hydrothermal treatment are composed by Ti metal and BT (data not shown here), suggesting the formation of the Ti(core)–BT(shell) particles. Figure 2 shows HAADF-STEM and energy dispersive X-ray spectroscopy (EDX) mapping images of the Ti–BT core–shell particles. The micron-sized Ti metal particle is covered by nanoparticles and EDX-mapping analysis also suggests the presence of the BT nanoparticle layer on the surface of the Ti metal particle. The BT shell layer is considered to be formed by the local dissolution of Ti metal and the precipitation of BT nanoparticles on the surface through the chemical reaction. 19,21 The size of BT particles covered on the surface is 100–600 nm and the thickness of the BT layer is estimated for about 10–100 nm by the calculation based on the weight change of the powders by the hydrothermal treatment. This estimation is based on the assumption that Ti spherical particles were covered by the homogeneous BT thin layers. In this process, BT nanoparticles formed by a homogeneous nucleation were also confirmed by TEM observation. However, most of these BT nanoparticles were removed by the collection procedure with decantation.
compacts increases because the conversion from TiO₂ to BT green compacts, the relative density of all the Ti composite compacts, which were calculated by an Archimedes method, are summarized in Tables 1-3. In comparison with the green compacts, the relative density of all the Ti/BT composite compacts did not change compared to the green compacts, but all the compacts became more rigid. The XRD patterns of the ground powders of the composites after the hydrothermal treatment are shown in Fig. 3. All the peaks of the composites are indexed by Ti metal and BT, and there is no peak assigned to BT03. Thus, TiO₂ is considered to be completely converted into Ti metal and BT, and there is no peak assigned to BT by the following chemical reaction.\(^{18,22}\)

\[
\text{TiO}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ti(OH)}_4 \text{aq} \quad (2)
\]

\[
\text{Ti(OH)}_4 \text{aq} + \text{Ba(OH)}_2 \rightarrow \text{BaTiO}_3 + 3\text{H}_2\text{O} \quad (3)
\]

The relative density and the Ti metal content of the Ti/BT composite compacts, which were calculated by an Archimedes method, are summarized in Tables 1-3. In comparison with the green compacts, the relative density of all the Ti/BT composite compacts increases because the conversion from TiO₂ to BT is accompanied by a volume increase. It is also found that the relative density of the Ti/BT composites tends to increase with a Ti metal content because metal particles transformed to fill a space by the uniaxial press. Actually, the same tendency can be found in the relative density of the green compacts. The Ti metal content in Tables 1-3 means a volume fraction of metal components to a total volume of the sample including a pore volume. Regardless of the kinds of the metal particles and the fillers, the metal contents are comparable at the same metal-particle mixing ratio.

Fractured cross-sectional SEM images of these composites prepared from the green compacts with the metal-particle mixing ratio of 80 wt % are shown in Fig. 4. The magnified SEM images of the metal particles pointed by arrows in Figs. 4(a), 4(c), and 4(e) are shown in Figs. 4(b), 4(d), and 4(f), respectively. The flat Ti metal surface is exposed for the Ti/BT01 composite even after the hydrothermal treatment [Fig. 4(b)], whereas the BT nanoparticle layers, which prevent the direct contact of metal particles, can be seen in the core-shell/BT01 and the core-shell/BT03 composites [Figs. 4(d) and 4(f)]. The aggregated nanoparticles in Fig. 4 are synthesized BT because the Ti metal particles used in this experiment are micron-size. As there is a wide size-distribution of the BT particles, it can be assumed both nucleation of BT and crystal growth of BT fillers proceeded during the hydrothermal treatment. A part of these BT particles connected with each other by the BT formation, and thereby the compact can become more rigid. This method is useful to fabricate ceramics compacts at lower temperature and hence can be applicable to fabrication of composite compacts including low-thermostability materials.

### 3.3 Dielectric properties of Ti/BT composites

The variations of impedance and phase of the Ti/BT comp-
posites with the metal content are shown in Figs. 5(a)–5(c). In the case of the uncoated Ti metal particles used as the metal component [Fig. 5(a)], the impedance gradually decreases with a Ti metal content and then drastically decreased at a Ti metal content of 47.3 vol% . At this point the electric paths had been formed by connection of the Ti metal particles and the insulator to metal transition occurred. The phase of the Ti/BTO1 composites clearly changes at this Ti metal content, suggesting the current leakage. Thus, we determined the percolation threshold, \( f_c \), is 0.473 for the Ti/BTO1 composites. To suppress the current leakage at a lower metal content, we attempted individual metal particles are covered by the thin dielectric layer. Actually, for the Ti/BT composites using the Ti–BT core–shell particles, the insulator to metal transition occurs at the higher metal contents [Figs. 5 (b) and 5(c)]. In these cases, the metal to insulator transition points determined from the impedance and phase plots are not corresponding and thus we decided the \( f_c \) is determined from the phase plots hereafter. The \( f_c \) increases up to 0.727 and 0.777 for the core–shell/BTO1 and the core–shell/BTO3 composites, respectively. Therefore, the BT shell layers effectively prevented the direct contacts among the metal particles and the resistivity of the composites was enhanced.

The variations of the effective dielectric constant and loss tangent of the Ti/BT composites are shown in Figs. 5(d)–5(f). The effective dielectric constant tends to increase with the metal content and drastic increase can be found near the percolation threshold. By comparing the dielectric constant of the core–shell/BTO1 and the core–shell/BTO3 composites [Figs. 5(e) and 5(f)] at the similar metal content, the effective dielectric constant of the core–shell/BTO3 is higher than that of the core–shell/BTO1 composites. This is because the dielectric constant of the BT layers in the core–shell/BTO1 composites was lower than that in the core–shell/BTO3 composites due to the size effect of the BT fillers,\(^{23,24}\) and the effect of dielectric properties of dielectric layers is considered in the percolation theory as \( \varepsilon_m \) in Eq. (1).

In the heterogeneous systems in which the components have different conductivities, a considerable increase in the effective dielectric constant due to the Maxwell–Wagner effects is observed especially in the lower frequency region.\(^{25}\) In our case, the dielectric constant and loss tangent of the obtained Ti/BT composites depend largely on frequency, and especially at a frequency below 1 kHz, relatively high effective dielectric con-

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**Fig. 4.** SEM images of fractured cross sections of (a) the Ti/BTO1, (c) the core–shell/BTO1 composites, and (e) the core–shell/BTO3 composites prepared from the green compacts with the metal-particle mixing ratio of 80 wt% . (b), (d), and (f) show magnified SEM images of the areas pointed by arrows in (a), (c), and (e), respectively.

**Fig. 5.** The dependence of (a–c) the impedance and the phase and (d–f) the effective dielectric constant and the tangent loss of the Ti/BT composites on the Ti metal content measured at room temperature; (a, d) the Ti/BTO1 composites, (b, e) the core–shell/BTO1 composites, and (c, f) the core–shell/BTO3 composites. The dashed lines indicate the variation of effective dielectric constant at a frequency of 10kHz assumed by the percolation theory.
stant and loss tangent are recorded. The Maxwell–Wagner effects may partially contributed to an increase in the effective dielectric constant at the lower frequency region, but the enhancement in the effective dielectric constant at the sufficiently high frequency region is attributed to the percolation effect.

The dielectric behaviors simulated by the percolation theory [Eq. (1)] based on our experimental data are depicted by dashed lines in Figs. 5(d)–5(f). The values used for these calculations are as follows; $\varepsilon_m = 107$, $q = 1.15$, and $f_c = 0.473$ for the Ti/BTO composites, $\varepsilon_m = 178$, $q = 1.01$, and $f_c = 0.727$ for the core–shell/BTO composites, and $\varepsilon_m = 700$, $q = 0.96$, and $f_c = 0.777$ for the core–shell/BT03 composites. The dashed lines are roughly consistent with the dielectric behavior of the Ti/BT composites, supporting the contribution of the percolation effect.

The Ti/BT composite capacitors could be fabricated by the wet chemical approach without heating procedure exhibited the relatively high effective dielectric constant over $10^3$. However, the dielectric strength of these Ti/BT composite capacitors was still much lower level (60–80 kV/cm for the metal content of around 15 vol% and 15–30 kV/cm for the metal content of around 30 vol%), and thus electric resistance should be enhanced to apply these composites to the energy-storage devices. There are some problems to deteriorate the dielectric strength such as a heterogeneous distribution of the large metal particles, formation of leakage paths through grain boundaries at the BT polycrystalline shells and the BT layers, and the lower crystallinity of the synthesized BT particles. Accordingly, now we are trying to elaborate the microstructures of these composites; for example, dense, high-quality dielectric layers are formed by controlling crystal growth of BT and the metal particles are covered by single-crystalline dielectric shell layers.

4. Conclusion

The percolation materials, Ti/BT composite compacts, were fabricated without high-temperature heating procedure. The green compacts consisting of the Ti metal particles (or Ti–BT core–shell particles), the BT fillers, and the TiO2 nanoparticles were completely converted into Ti/BT composite compacts by the hydrothermal treatment at 160°C. The effective dielectric constant of these composites tends to increase with the Ti metal content and jumped up to over $10^7$ near the percolation threshold. In the case of the composites using the Ti–BT core–shell particles, the BT shell layers covering on the Ti metal particles effectively prevented the direct contact among Ti metal particles and increase the percolation threshold. As the effective dielectric constant of these composites also depends largely on the dielectric properties of the BT layers, it is important to control the microstructure of these composites to improve the dielectric properties of such composites.

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References

1) C. Pecharromán, F. Esteban-Betegón, J. F. Bartolomé, S. López-Esteban and J. S. Moya, Adv. Mater., 13, 1541–1544 (2001).
2) C. Pecharromán and J. S. Moya, Adv. Mater., 12, 294–297 (2000).
3) Z.-M. Dang, Y.-H. Lin and C.-W. Nan, Adv. Mater., 15, 1625–1629 (2003).
4) V. Singh, A. N. Tiwari and A. R. Kulkarni, Mater. Sci. Eng., B, 41, 310–313 (1996).
5) R. Simoes, J. Silva, R. Vaia, V. Sencadas, P. Costa, J. Gomes and S. Lanceros-Méndez, Nanotechnology, 20, 035703 (2009).
6) B. Zhang, C. Xie, J. Hu, H. Wang and Y. Gui, Compos. Sci. Technol., 66, 1558–1563 (2006).
7) M. C. Lonergan, E. J. Severin, B. J. Doleman, S. A. Beaber, R. H. Grubbs and N. S. Lewis, Chem. Mater., 8, 2298–2312 (1996).
8) J. Huang, Y. Cao, M. Hong and P. Du, Appl. Phys. Lett., 92, 022911 (2008).
9) N. Guo, S. A. DiBenedetto, P. Tewari, M. T. Lanagan, M. A. Ratner and T. J. Marks, Chem. Mater., 22, 1567–1578 (2010).
10) A. L. Efros and B. I. Shklovskii, Phys. Status Solidi B, 76, 475–485 (1976).
11) J. S. Moya, S. Lopez-Esteban and C. Pecharromán, Prog. Mater. Sci., 52, 1017–1090 (2007).
12) W.-H. Tuan and Y.-C. Huang, Mater. Chem. Phys., 118, 187–190 (2009).
13) P. Ren, H. Fan, X. Wang and J. Shi, J. Alloys Compd., 509, 6423–6426 (2011).
14) S. George and M. T. Sevastian, Compos. Sci. Technol., 68, 2461–2467 (2008).
15) R. Basca, P. Ravindranathan and J. P. Dougherty, J. Mater. Res., 7, 423–428 (1992).
16) W.-D. Yang and K.-M. Hung, J. Mater. Sci., 37, 1337–1342 (2002).
17) K. Kajiyoshi and K. Yanagasawa, J. Phys.: Condens. Matter, 16, S1351–S1360 (2004).
18) W. Zhu, S. A. Akbar, R. Asiaie and P. K. Dutta, J. Electroceram., 2, 21–31 (1998).
19) R. R. Basca and J. P. Dougherty, J. Mater. Sci. Lett., 14, 600–602 (1995).
20) H.-Y. Chang, S.-Y. Cheng, C.-I. Sheu and Y.-H. Wang, Nanotechnology, 14, 603–608 (2003).
21) P. Bendale, S. Venigalla, J. R. Ambrose, E. D. Verink, Jr. and J. H. Adair, J. Am. Ceram. Soc., 76, 2619–2627 (1993).
22) P. K. Dutta, R. Asiaie, S. A. Akbar and W. Zhu, Chem. Mater., 6, 1542–1548 (1994).
23) G. Arlt, D. Hennings and G. de With, J. Appl. Phys., 58, 1619–1625 (1985).
24) H. I. Hsiang and F.-S. Yen, J. Am. Ceram. Soc., 79, 1053–1060 (1996).
25) N. Bonanos, B. C. H. Steele, E. P. Butler, W. B. Johnson, W. L. Worrell, D. D. McDonald and M. C. H. McKubre, “Impedance Spectroscopy”, Ed. by J. R. MacDonald, Wiley, New York (1987).