TRANSACTIONS ON ELECTRICAL AND ELECTRONIC MATERIALS VOL. 10, NO. 4, AUGUST 25, 2009

Dielectric Properties of Polymer-ceramic Composites for Embedded Capacitors

Jung-Rag Yoon*, Jeong-Woo Han, and Kyung-Min Lee
R&D Center, Samwha Capacitor Co., Ltd., Yongin 449-884, Republic of Korea

Heun-Young Lee
Department of Electrical Engineering, Myoung Ji University, Yongin 449-880, Republic of Korea

(Received April 9 2009, Revised July 22 2009, Accepted August 14 2009)

Ceramic-polymer composites have been investigated for their suitability as embedded capacitor materials because they combine the processing ability of polymers with the desired dielectric properties of ceramics. This paper discusses the dielectric properties of the ceramic ($BaTiO_3$)-polymer (Epoxy) composition as a function of ceramic particle size at a ceramic loading of 40 vol%. The dielectric constant of these ceramic-polymer composites increases as the powder size decreases. Results show that ceramic-polymer composites have a high dielectric constant associated with the $BaTiO_3$ powder with a 200 nm particle size, high insulation resistance, high breakdown voltage (> 22 KV/mm), and low dielectric loss (0.018-0.024) at 1 MHz.

Keywords: Embedded capacitor, Dielectric constant, Breakdown voltage, Ceramic-polymer film

1. INTRODUCTION

Microelectronic systems are composed of many active and passive components in order them to have an effective performance in their intended electrical functions. The passive components are the main determinants of the highest performance, smallest size, and greatest reliability that are achievable in microelectronic systems. In order to achieve the required electrical functions, there have been intensive studies concerned with embedding passive components in microelectronics packages. The embedding of these components in the form of thin films aids further miniaturization and allows the number of solder joints to be reduced. Amongst various kinds of passive components, embedded capacitors have been in focus as providing the greatest potential benefit in achieving higher capacitance and lower parasitic inductance. In Fig. 1, a cross sectional view of an embedded film capacitor summarizes the advantages of embedding thin film capacitors in a microelectronics package[1]. Polymer-ceramic composites have been pursued as the most promising dielectric materials for embedded capacitors in the organic package [2-4]. The polymer-ceramic films are made by mixing ceramic powders with polymers. The advantages of polymer-ceramic films are organic package compatibility, high dielectric constant and localized capacitor formability. The dielectric constant of the polymer-ceramic films can be increased by increasing the loading of the ceramic. However, increasing the ceramic loading invariably results in poor adhesion of the films and lower strength, as show by C.P.Wong et al[5].

Typically, the ceramic loading should be much lower than 50 vol% in order to successfully pass the high temperature thermal stress reliability test. In this paper, we present a study on the optimization of ceramic-polymer films at a ceramic loading 40 vol% in order to improve the embedded capacitance tolerance and electrical properties. The effects of particle size in the $BaTiO_3$ powder on ceramic-polymer films the dielectric and electrical properties of the ceramic-polymer films were also characterized.

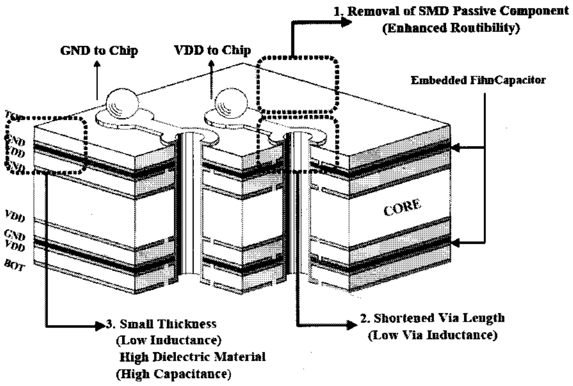


Fig. 1. Cross-section view of the embedded film capacitor and its advantages.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

A. Polymers

A commercial halogen free epoxy resin modified by phosphate epoxy, KDP-550MC65 (EEW : 650, Kukdo Chemicals Inc.,Korea), was used as the polymer matrix. As a curing agent and catalyst, Me-THPA(Kukdo Chemicals Inc.,Korea) and benzyltriethylammonium(BTEAC) was used.

Phospate ether (Disper BYK-110, BYK Cemie, and USA) was used as a dispersant to well-disperse $BaTiO_3$ powders in the epoxy. In addition a leveling agent (BYK-310, BYK Cemie, USA) was used to decrease the surface tension of the epoxy resin. A mixture of methylethly-ketone (MEK) and toluene was used as a solvent.

---

*Author to whom corresponding should be addressed: electronic mail: yoonjungrag@samwha.com

B. $BaTiO_3$ powder

Hydrothermally synthesized powders BT-02, BT-03, BT-04, and BT-05 (products of Sakai Chemical Industry Co., Ltd.) were used in the present investigation. According to the manufacturer, these powders have a median particle size of 200, 300, 400 and 500 nm The Ba/Ti atomic ratio of the two powders was approximately 0.998 and 1.000 respectively.

C. Sample preparation

Figure 2 shows the experimental procedure for the fabrication of the ceramic-polymer composite films. A thin film of this ceramic-polymer mixed composite was then cast by a doctor-blade on a copper substrate and dried at approximately 100℃ for 10 min in an oven to remove residual organic solvent. After solvent drying, films were laminated on a copper surface, with an applied pressure of 50 kgf/cm^2 at 150℃ and then the composite film was cured at 200℃ for 2 hr. The $BaTiO_3$ powders were characterized by X-ray diffraction (XRD) technique using CuKα radiation and the surface morphology of the film composites was studied with a scanning electron microscope. Dielectric properties of the ceramic composite films were measured at room temperature using an impedance/gain-phase analyzer (Model 4192A, HP) and the insulation resistance was measured using a high resistance meter (Model 4339B, HP). Dielectric constants of the ceramic composite films were calculated from the measured film thickness and capacitance.

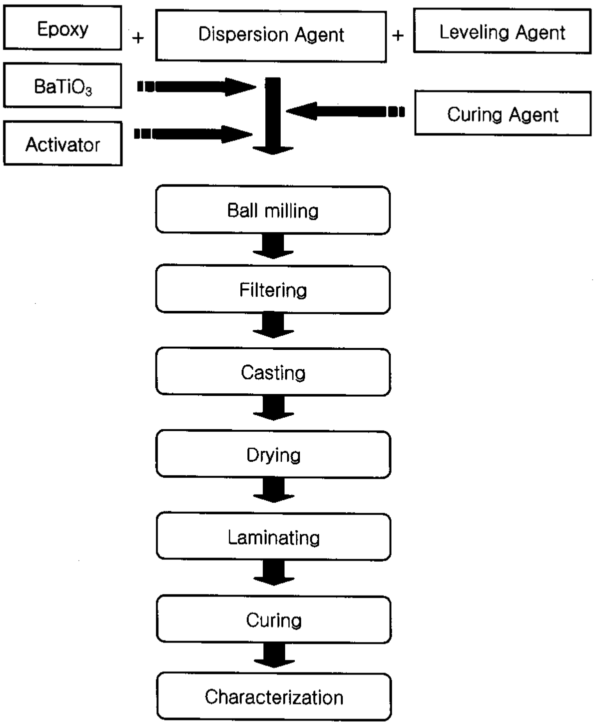


Fig. 2. Flow chart of the experimental procedure.

3. RESULTS AND DISCUSSION

Figure 3(a), (b), (c), and (d) show the SEM images of the morphologies of $BaTiO_3$ powders with 200, 300, 400 and 500 nm mean particle sizes, respectively. The BET surface area of the powders was 2.3 to 5.6 m^2/g.

Figure 4 shows the typical XRD patterns in $BaTiO_3$ with particle sizes of 200, 300, 400 and 500 nm. In general, the differences in tetragonal and cubic phases were confirmed by the separation of the (002) and (200) XRD peaks. The crystal phase of $BaTiO_3$ powers was tetragonal, as is seen from the separation in (002) and (200) peaks. Figure 5 shows the variation of the dielectric constant in polymer-ceramic composites as a function of the $BaTiO_3$ particle size.

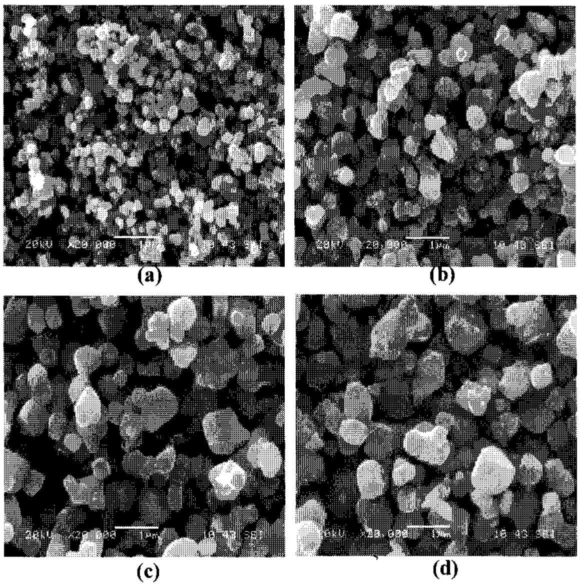


Fig. 3. SEM images of $BaTiO_3$ powders. (a) BT-02, (b) BT-03, (c) BT-04, and (d) BT-05.

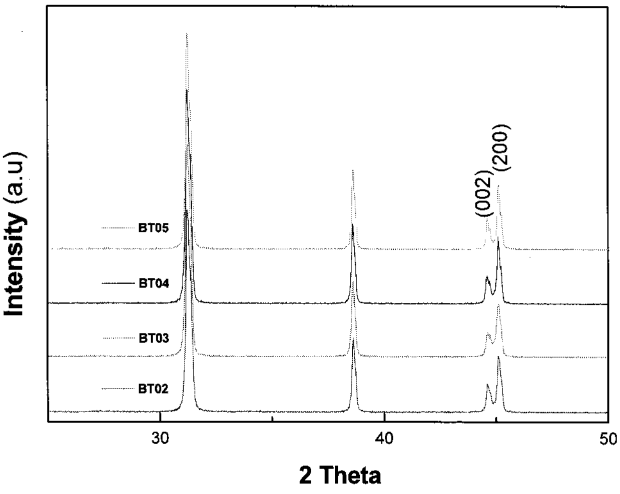


Fig. 4. XRD patterns of $BaTiO_3$ powders. (a) BT-02, (b) BT-03, (c) BT-04, and (d) BT-05.

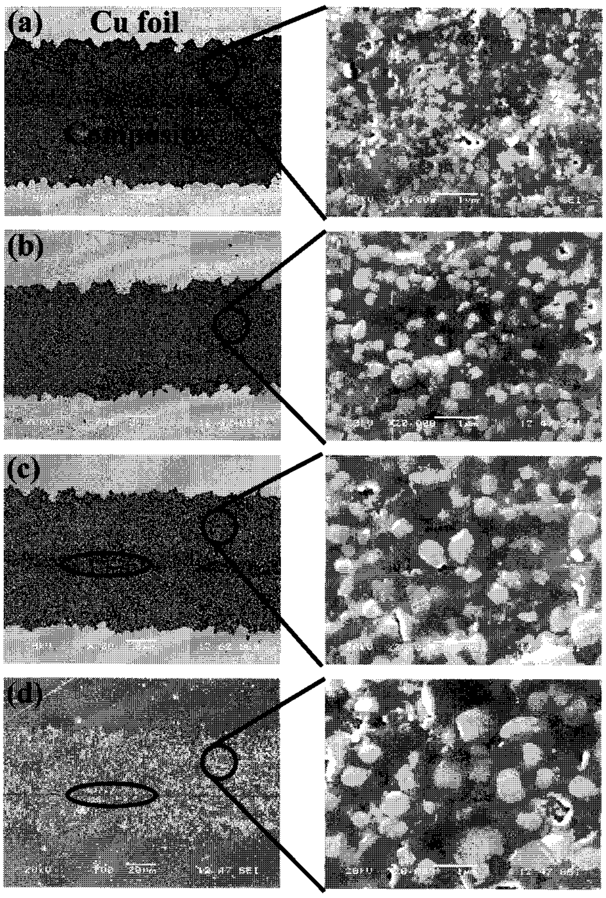


Fig. 5. Surface image of polymer-ceramic composites as a function of the $BaTiO_3$ particle size. (a)BT-02, (b) BT-03, (c) BT-04, and (d) BT-05

Figure 5 shows images of the surface of polymer-ceramic composites for a range of $BaTiO_3$ particle sizes. It appeared that the resin intruded and filled every space between the particles. It is confirmed from Fig. 5(a) that in the composites prepared using the 200 nm powders, the $BaTiO_3$ particles were agglomerated, because the particle size was small. Also it is confirmed from Fig. 5(c), 5(d) that in the composites prepared using the 400 nm and 500 nm powders, the polymer layer exists in the upper part of the film, two materials were arranged in a series structure which caused dielectric constant to decrease[9].

Figure 6 shows the dielectric constants of the $BaTiO_3$/ epoxy composites as a function of the $BaTiO_3$ particle size. When $BaTiO_3$ particle sizes were smaller than 400 nm, the dielectric constant decreases almost linearly with increasing particle size. The reason for this trend is that finer particles with higher surface area may provide better particle to particle contact, so increasing the packing density. In closely packed powders the enhanced polarization arising from the dipole-dipole interaction may also be enhanced. The electrical flux lines between the two electrodes will be directed towards the lowest impedance path across the sample. The agglomeration of the particles would thus cause lower impedance, due to the lower ratio of polymer to ceramic across the lowest impedance path. This effect would allow the passage of a larger electrical flux for the agglomerated particles than for the non-agglomerated particles.

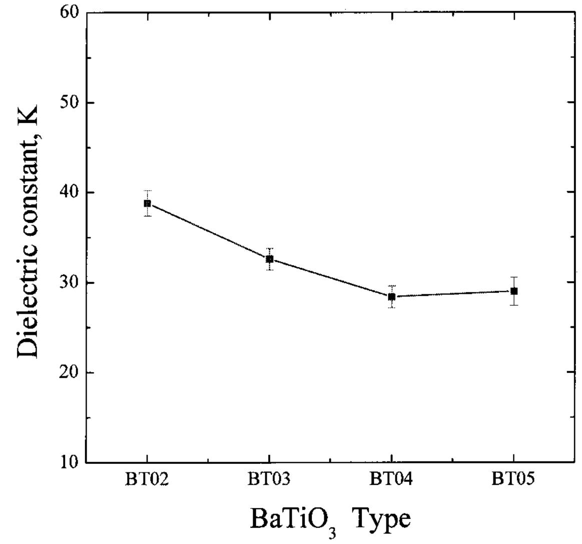


Fig. 6. The dielectric constants of the $BaTiO_3$/epoxy composites as a function of the $BaTiO_3$ particle size.

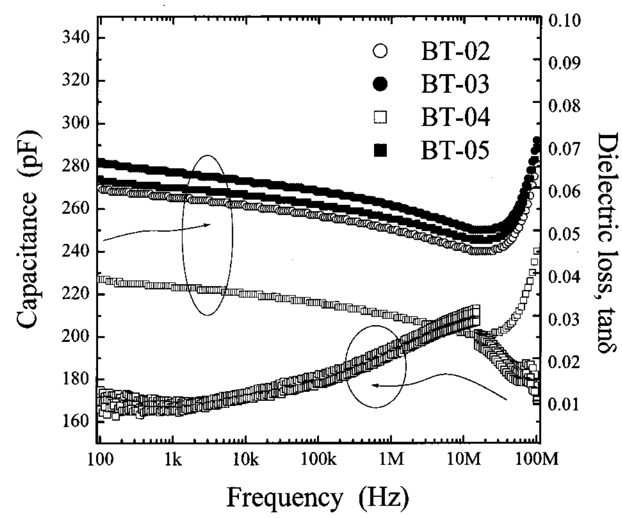


Fig. 7. Frequency properties of polymer-ceramic composites as a function of the $BaTiO_3$ particle size.

Figure 7 shows the capacitance and dielectric loss of the polymer-ceramic composites measured over the frequency range 100 Hz ~ 100 MHz, as a function of the $BaTiO_3$ particle size. It was found that with increasing frequency over the relatively narrow range of 10 Hz ~ 10 MHz, the capacitance decreased slightly and the dielectric loss increased. All of the dielectric loss values were found to be in the narrow range of 0.018 ~ 0.024 at 1 MHz.

Figure 8 shows the variation of the insulation resistance in polymer-ceramic composites as a function of the $BaTiO_3$ particle size. The insulation resistance is very high, about $1x10^{12}$ ohm at the applied voltage of 100 V for a 15 um thick polymer-ceramic composites film. The insulation resistance in polymer-ceramic composites decreased with increasing $BaTiO_3$ particle size. As the particle size decreases, the finer particles can fill the interstices between the coarser particles, resulting in a further increase in powder packing density[8].

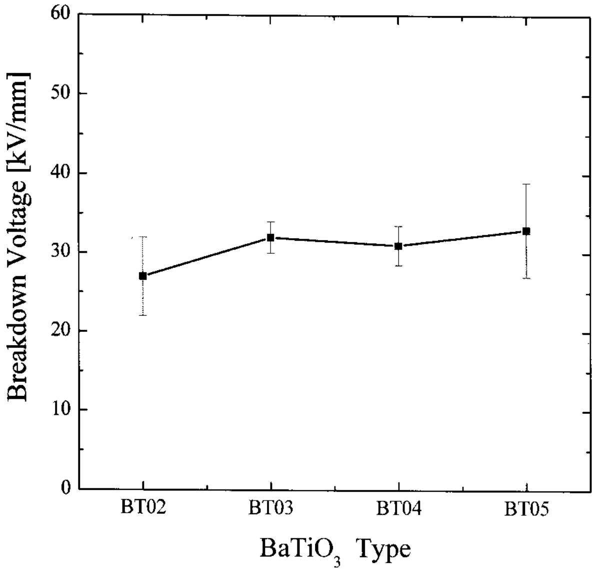


Fig. 8. Insulation resistance in polymer-ceramic composites as a function of the $BaTiO_3$ particle size.

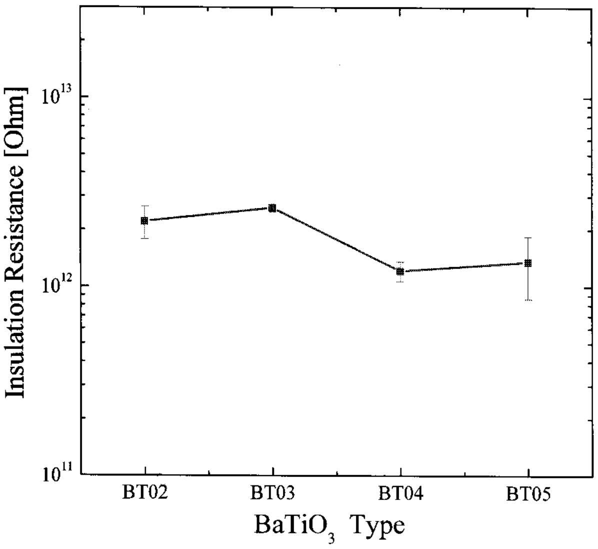
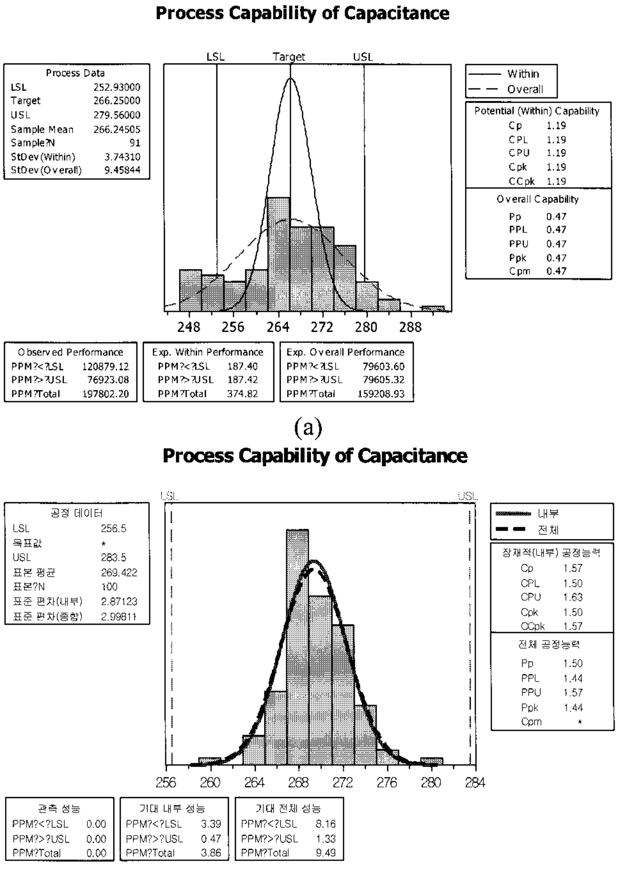


Fig. 9. Breakdown voltage in polymer-ceramic composites as a function of the $BaTiO_3$ particle size.

Figure 9 shows the variation of the breakdown voltage in polymer-ceramic composites as a function of the $BaTiO_3$ particle size. The breakdown voltage for all particle sizes was higher than 22 kV/mm, which is enough for the polymer-ceramic composite to serve as an insulation material embedded capacitor[3].

Figure 10 shows the capacitance tolerance and process capability of $BaTiO_3$/epoxy composites prepared using the 200 nm and 300 nm powders. These composites were found to have the most stable electric properties and microstructures out of out of the 4 composites studied.

The capacitance tolerance of the composites prepared using the 200 nm powders was about 10% and the process capability index was 1.18. While the capacitance tolerance of composites prepared using the 300 nm powders was 5%, the process capability index was 1.57.



(a)

(b)

Fig. 10. Process capability of Capacitance of polymer-ceramic composites using the (a) BT-02 (b) BT-03.

It is confirmed that the process capability of BT-03 is more excellent than that of BT-02. This result shows that there exists the possibility that the process ability improves polymer-ceramic composite film, as the ceramic is well-dispersed in the polymer matrix.

4. CONCLUSIONS

The dielectric properties of embedded capacitors fabricated from different sized particle ceramic-polymer composites containing a 40 vol% ceramic loading, have been measured The particle size of hydrothermally produced $BaTiO_3$ was 100 nm to 500 nm with a tetragonal structure.

Finer particles with a higher ratio of surface area to volume may have better particle-to-particle contact for improving the dielectric constant, dielectric loss, and insulation resistance. As a results, the ceramic-polymer composites having the smallest diameter of $BaTiO_3$ particles (200 nm), have the highest values of dielectric constant (>38) high insulation resistance, (> 1 $\times 10^{12}$ ohm) breakdown voltage (> 22 KV/mm), and the lowest dielectric loss (0.018-0.024) at 1 MHz.

Agglomerated powder enhanced the electric properties, but it has a bad influence on capacitance tolerance. Thus, ceramic powder must be well-dispersed in the polymer matrix for improvement in processing capability.

REFERENCES

[1] H. S. Kim, Doctoral Thesis, Korea Advanced Institute of Science and Technology, 2005.

[2] S. Y. Lee, J.-G. Hyun, H. S. Kim, and K.-W. Paik, IEEE Trans. Adv. Package. **30,** 428 (2007).

[3] J. Xu, K.-S. Moon, P. Pramanik, S. Bhattacharya, and C. P. Wong, IEEE Trans. Adv. Package. **30,** 248 (2007).

[4] R. N. Das, Frank D. Egitto, Jhon M. Lauffer, and Voya R. Markovich, IEEE Trans. Elec. Package. Man. **31,** 97 (2008).

[5] Y. Rao, S. Ogitani, P. Kohl, and C. P. Wong, J. Appl. Poly. Sci., **83,** 1084 (2002).

[6] K.-C. Ahn, H.-W. Kim, J.-K. Ahn, and S.-G. Yoon, J. of KIEEME(in Korean) **20,** 342 (2007).

[7] J. Robertson and B. R. Varlow, IEEE Trans. Dielectr. Electr. Insul. **12,** 779 (2005).

[8] S.-D. Cho, J.-Y. Lee, and K.-W. Paik, J. Microelectron. Packing Soc. **9,** 11 (2003).

[9] S. P. Mitoff, General Electric research and Development Center, Schenectady, New York. 2003.