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Dielectric behavior of Nb_2O_5-doped TiO_2/epoxy thick films

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Abstract

TiO_2/epoxy composite thick films containing the TiO_2 powders doped with 4 and 10 vol% Nb_2O_5 heat treated under vacuum at 1050 and 1150 °C, were prepared by the screen printing and curing steps. The Nb_2O_5-doped TiO_2 ceramic bulks demonstrated a higher effective dielectric constant at different densification environments, as compared with pure TiO_2. The dielectric properties of the TiO_2/epoxy thick films were improved if the heat-treated 4 vol% Nb_2O_5-doped TiO_2 powder was incorporated instead of the un-doped and heat-treated 10 vol% Nb_2O_5-doped TiO_2 powders. The disadvantage of the doped TiO_2 having higher dielectric loss tangent could be minimized after its powder was properly treated and mixed with epoxy to form the TiO_2/epoxy composite. A best result with the dielectric constant of 23 and the loss tangent of 0.046 was obtained for the 40 vol% TiO_2/epoxy composite thick films, where the TiO_2 powder was doped with 4 vol% Nb_2O_5 followed by calcination at 1000 °C in air and heat treatment at 1150 °C under vacuum.

Keywords: B. Composites; C. Dielectric properties; D. TiO_2; E. Capacitors

1. Introduction

Most multichip modules (MCMs) require decoupling capacitors with a dielectric constant (ε_r) of 25–l70 to suppress the power distribution noise [1,2]. Nowadays, the integration of capacitors with other passive components on a substrate especially on a printed wiring board (PWB) are being considered for use in MCM applications to reduce substrate size and to improve functionality and manufacturing cost. Composite materials consisting of ferroelectric ceramics and polymers have aroused much attention for advanced capacitors because their properties can be adjusted by changing the fractions of the constituents. Epoxy is a suitable polymer for its compatibility with PWBs.

In our previous studies in the ferroelectric ceramic/epoxy thick films, self-synthesized $BaTiO_3$ and commercial $BaTiO_3$ and PMN ($Pb(Mg_{1/3}Nb_{2/3})O_3$) were incorporated into epoxy. ε_r and $\tan\delta$ for the sintered ferroelectric ceramics at 25 °C were 25,000 and 0.3, 8500 and 0.03, and 18,000 and 0.13 for self-synthesized $BaTiO_3$ and commercial $BaTiO_3$ and PMN, respectively. The self-synthesized $BaTiO_3$/epoxy had a highest r of 44 at 40 vol% ceramic content, while 28 and 25 for commercial $BaTiO_3$/epoxy and PMN/epoxy. Nevertheless, all of the $BaTiO_3$/epoxy thick films had the close $\tan\delta$ of 0.02–0.03 no matter their sintered ceramics had a high or low $\tan\delta$.

Titanium dioxide (TiO_2) crystal has the values of 170 and 90 at 25 °C in the C and a directions, respectively, while polycrystalline TiO_2 has an intermediate value. Barrier-layer ceramic capacitors have been known for their high effective and high $\tan\delta$. Barrier-layer TiO_2 capacitors with of 50000 and $\tan\delta$ of 4% have been developed 20 years ago [3]. Based upon the results of the barrier-layer TiO_2 and our previous ceramic/epoxy thick films, the research of adding the treated TiO_2 powder into epoxy for flexible capacitors is encouraged.

In this study, 40 vol% TiO_2/epoxy thick films were fabricated by screen printing. The TiO_2 powders were doped with 4 and 10 vol% Nb_2O_5 by a calcinations step.

Some calcined powders were heat treated at 1050 and 1150 °C under vacuum. The variation of dielectric properties

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of these thick films with test temperature and frequency was measured.

2. Experimental procedure

Nb_2O_5-doped TiO_2 ceramic powders were prepared by a calcinations step at 1000 °C for 1 h, where the amounts of Nb_2O_5 were 0, 4, and 10 vol%. After ball milling, drying, and sieving, the calcined TiO_2 powders was ready for the following studies.

To study the dielectric property of un-doped and doped TiO_2 bulks, the TiO_2 powders were pressed into pellets and sintered at 1300 °C for 1 h in air (the air-sintered specimen) and under vacuum followed by a re-oxidation reaction in air (the re-oxidized specimen). Before incorporating the TiO_2 powders into epoxy, different heat treatments were conducted on the calcined powder to modify their property. The calcined powders were heat treated at 1050 and 1150 °C under vacuum (2×10^{-2} Torr) for 1 h to form the 1050 and 1150 °C-vacuum-treated powders, respectively. The heat-treated powders were ready for ceramic/epoxy thick films after milling, drying, and sieving. The calcined and pre-treated powders were mixed with a solution of epoxy (bisphenol F), curing agent (dicyandiamide) and catalyst (2-methylimidazole) to form the screen-printing ink containing 40 vol% ceramic powder and 60 vol% epoxy. The thick films were prepared on copper foils by screen-printing and ready for property measurements after pre-cured at 140 °C for 1 h and post-cued at 180 °C for 1/2 h. Three types of ceramic/epoxy composite thick films were formed, the calcined TiO_2/epoxy, the 1050 °C-vacuum-treated TiO_2/epoxy, and the 1150 °C-vacuum-treated TiO_2/epoxy. Surface morphology of the films was examined by a scanning electron microscope (SEM, Hitachi model S-3500H). The variations of dielectric properties with test temperature and frequency

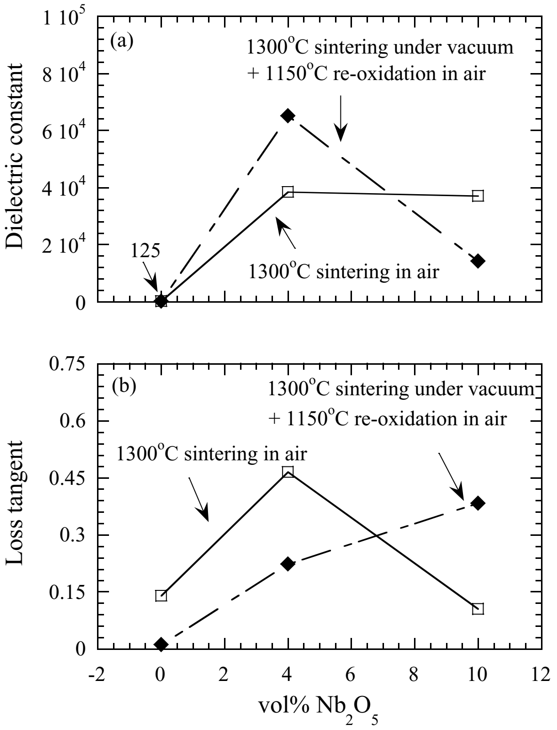

Fig. 1. (a) Dielectric constant and (b) loss tangent of TiO_2 pellets as a function of the volume fraction of the added Nb_2O_5. The pellets were sintered at 1300 °C for 1 h in air and vacuum sintered at 1300 °C for 1 h followed by 1150 °C re-oxidation in air. The tests were measured at 25 °C and 100 kHz.

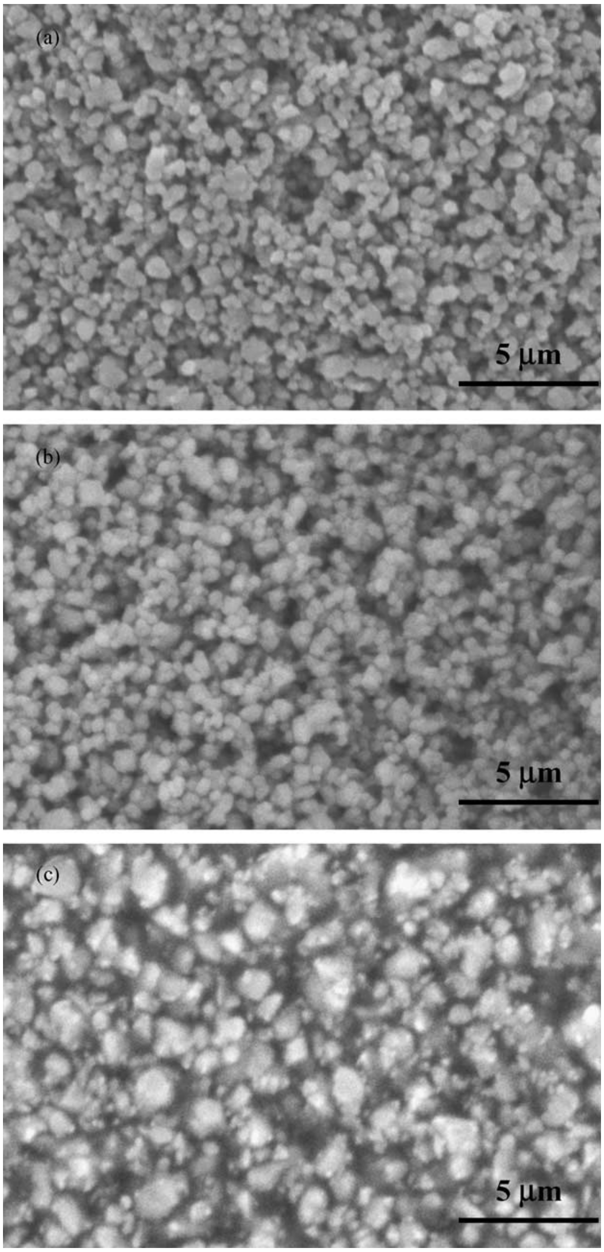

Fig. 2. SEM surface morphology of the 40 vol% TiO_2/epoxy composite thick turns, where the T1O$_2$ powders containing 4 vol% Nb_2O_5 underwent different modifications. The doped TiO_2 powders were (a) calcined at l000 °C in air or (b) heat treated at 1050 °C and (c) heat treated at 1150 °C under vacuum after 1000 °C sintering in air.

for the 40% TiO_2/epoxy thick films were measured by employing HP 4284A LCR meter (Hewlett-Packard, USA) in the frequency range of 20 Hz–1 MHz at an average voltage of 1 V.

3. Results and discussion

3.1. *Dielectric properties of un-doped and Nb_2O_5-doped TiO_2 pellets*

Dielectric constants of TiO_2 pellets sintered at 1300 °C for 1 h in air and under vacuum followed by a re-oxidation reaction at 1150 °C in air were measured as a function of the volume fraction of the added Nb_2O_5, as shown in Fig. 1. The un-doped TiO_2 pellets had a close value of 125 for both the air-sintered and re-oxidized specimens. The addition of Nb_2O_5 to TiO_2 greatly increased the r value. For the air-sintered pellets, the values were 38,000 and 37,000 for pellets with the addition of 4 and 10% Nb_2O_5, respectively. For the re-oxidized pellets, the values were 65,000 and 14,000 at 4 and 10% Nb_2O_5 additions, respectively. Obviously, the Nb_2O_5-doped TiO_2 has the capability to create the defected structure and to enhance the electric polarization even for specimens sintered in air and for re-oxidized pellets. For the incorporation of Nb_2O_5 as a solute in TiO_2, both ionic and electronic compensation can occur. However, the reduction reaction is dominated and the electronic conduction prevails when Nb_2O_5-doped TiO_2 is sintered at high temperatures [4]. Therefore, the high effective dielectric constants of the doped TiO_2 pellets can be attributed to the substitutional defects of Nb^+ and the electronic defects. The enhanced polarization and the electronic defects for the Nb_2O_5-doped TiO_2 also increased the dielectric loss, which was displayed by the results of dielectric loss tangent as shown in Fig. lb.

3.2. *SEM micrographs of the doped TiO_2/epoxy composite thick films*

Fig. 2 demonstrates the SEM morphology of the 40 vol% TiO_2/epoxy composite thick films, incorporating with three kinds of 4 vol% Nb_2O_5-doped TiO_2 powders: the calcined powder (Fig. 2a), the 1050 °C-vacuum-treated powder (Fig. 2b), and the 1150 °C-vacuum-treated powder (Fig. 2c). The 1050 °C-vacuum-treated powder embedded in epoxy did not have apparently sintering at 1050 °C under vacuum for 1 h and had similar particle size to the 1000 °C-calcined TiO_2 powder. The 1150 °C-vacuum-treated powder had a larger particle size, indicating sintering had undergone at the higher temperature of 1150 °C.

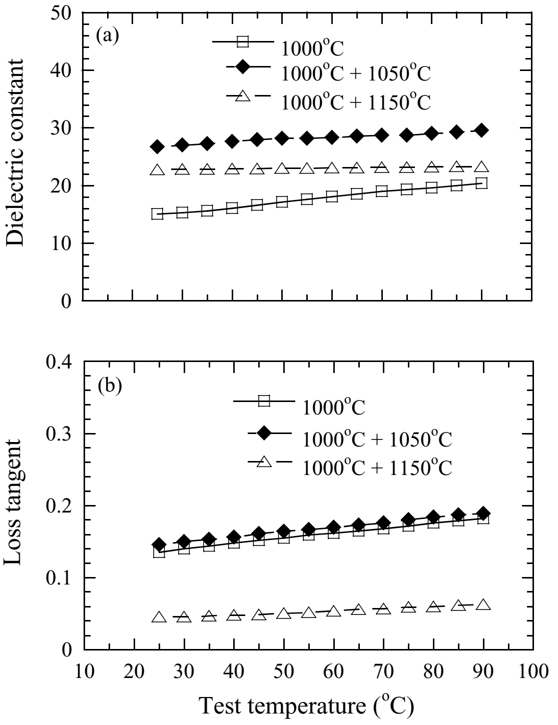

Fig. 3. Variations of (a) dielectric constant and (b) dielectric loss tangent of the 40 vol% TiO_2/epoxy composite thick films with test temperature, where the TiO_2 powders containing 4 vol% Nb_2O_5 underwent different modifications. The doped TiO_2 powders were calcined at 1000 °C in air, and heat treated at 1050 and 1150 °C under vacuum after l000 °C sintering in air. The tests were measured at l00 kHz and an average voltage of 1 V.

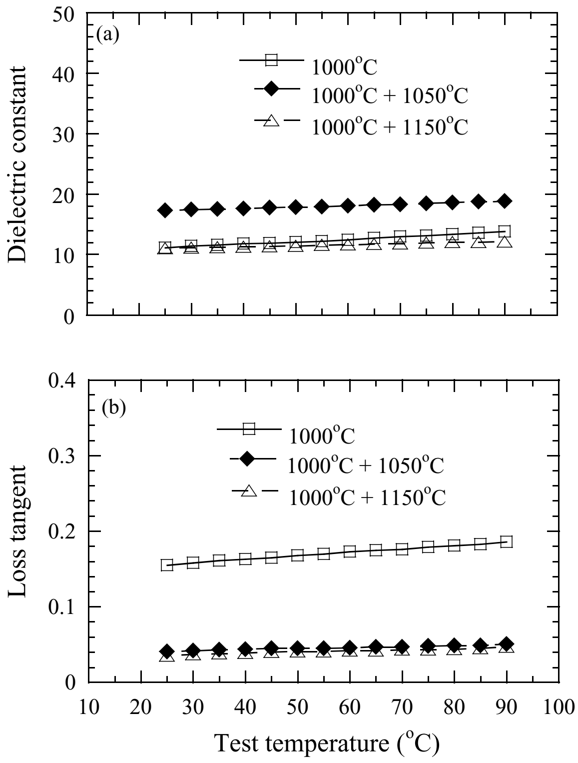

Fig. 4. Variations of (a) dielectric constant and (b) dielectric loss tangent of the 40 vol% TiO_2/epoxy composite thick films with test temperature, where the TiO_2 powders containing 10 vol% Nb_2O_5 undergone different modifications. The doped TiO_2 powders were calcined at 1000 °C in air, and heat treated at 1050 and 1150 °C under vacuum after 1000 °C sintering in air. The tests were measured at 100 kHz and an average voltage of 1 V.

3.3. Dielectric properties ofNb_2O_5-doped TiO_2 pellets at different test temperatures

The high ε_r value of 65,000 for the re-oxidized pellets was strongly related to the vacuum sintering (Fig. 1). From the previous research results, the ceramic powders of doped $BaTiO_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3$ with higher dielectric loss formed ceramic/epoxy composite films with low dielectric loss after dispersed in epoxy [5]. Based upon the above two results, the vacuum sintering was recommended to modify the dielectric properties of the doped TiO_2 powders for incorporating into epoxy for ceramic/polymer composite thick films. Fig. 3 demonstrates the variations of dielectric constant and loss tangent with test frequency for the doped TiO_2/epoxy composite thick films fabricated with different types of 4 vol% Nb_2O_5-doped TiO_2 powders, which include the calcined powder, 1050 °C-vacuum-treated powder, and 1150 °C-vacuum-treated powder. Dielectric properties increased slightly with test temperature for the calcined TiO_2/epoxy and the 1050 °C-vacuum-treated TiO_2/epoxy, but remained steady for the 1150 °C-calcined TiO_2/epoxy. The 1150 °C-vacuum-treated TiO_2/epoxy had ε_r of 23 and $\tan\delta$ of 0.046 at 25 °C and test frequency of 100 kHz. High ε_r of 27 and high $\tan\delta$ of 0.15 were observed for the 1050 °C-vacuum-treated TiO_2/epoxy, while low ε_r of 15 and high $\tan\delta$ of 0.13 for the calcined TiO_2/epoxy. Although the dielectric performance of the TiO_2/epoxy cannot surpass that of our self-synthesized $BaTiO_3$/epoxy, the result of the 1150 °C-vacuum-treated TiO_2/epoxy shown in Fig. 3 is comparable to that of ferroelectric ceramic/epoxy made by commercial $BaTiO_3$ and PMN powders [5].

Fig. 4 demonstrates the variations of dielectric constant and loss tangent with test frequency for the doped TiO_2/epoxy composite thick films fabricated with different types of 10 vol% Nb_2O_5-doped TiO_2 powders, which include the calcined powder, 1050 °C-vacuum-treated powder, and 1150 °C-vacuum-treated powder. Dielectric properties of the TiO_2/epoxy thick films fabricated with the 10 vol% Nb_2O_5-doped TiO_2 powder containing remained constant at different test temperatures ranging from 25 to 90 °C. The 1050 °C-vacuum-treated TiO_2/epoxy thick film had the best properties of high of 17 and low $\tan\delta$ of 0.040 at 25 °C and 100 kHz. The and $\tan\delta$ values were 11 and 0.155 for the calcined TiO_2/epoxy, and 11 and 0.035 for the 1150 °C-vacuum-treated TiO_2/epoxy. The lower dielectric constants of the TiO_2/epoxy thick films fabricated with the 10 vol% Nb_2O_5-doped TiO_2 powder (Fig. 4), as compared with those of composite thick films containing the 4 vol% Nb_2O_5-doped TiO_2 powder (Fig. 3), can be explained by the bulk dielectric properties of the doped TiO_2 pellets, as shown in Fig. 1. The higher r value of the TiO_2/epoxy thick

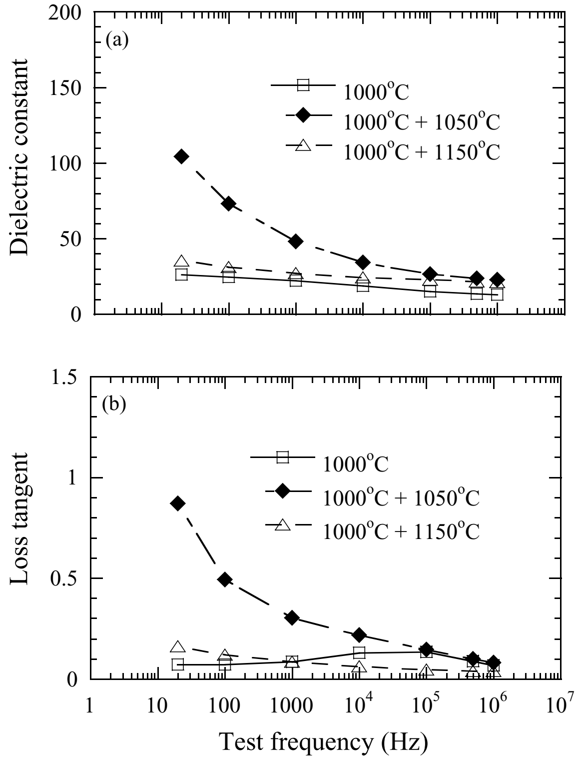

Fig. 5. Frequency dependence of (a) dielectric constant and (b) dielectric loss tangent of the 40 vol% TiO_2/epoxy composite thick films on test temperature, where the TiO_2 powders containing 4 vol% Nb_2O_5 underwent different modifications. The doped TiO_2 powders were calcined at 1000 °C in air, and heat treated at 1050 and 1150 °C under vacuum after 1000 °C sintering in air.

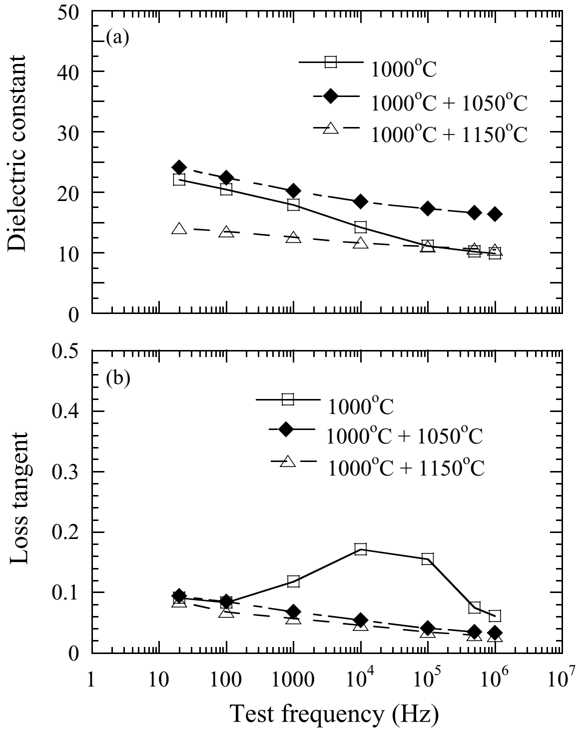

Fig. 6. Frequency dependence of (a) dielectric constant and (b) dielectric loss tangent of the 40 vol% TiO_2/epoxy composite thick films on test temperature, where the TiO_2 powders containing 10 vol% Nb_2O_5 underwent different modifications. The doped TiO_2 powders were calcined at 1000 °C in air, and heat treated at 1050 and 1150 °C under vacuum after 1000 °C sintering in air.

films can be obtained by incorporating the TiO_2 powder with higher ε_r values.

3.4. Dielectric properties of Nb_2O_5-doped TiO_2 pellets at different test frequencies

The frequency dependence of dielectric properties for the composite thick films fabricated with different types of 4 vol% Nb_2O_5-doped TiO_2 powders is shown in Fig. 5. The dielectric properties of the 1050 °C-vacuum-treated TiO_2/epoxy thick film had a strong dependence on the test frequency, while remained slightly changed for the calcined and 1150 °C-vacuum-treated TiO_2/epoxy thick films. The low frequency response indicates the existence of the dipole-switched ionic defects in an amount to develop a larger dipolar polarization. On the other hand, the dielectric properties of all the composite thick films fabricated with different types of 10 vol% Nb_2O_5-doped TiO_2 powders changed slightly with the test frequency, as shown in Fig. 6. Obviously, the formed composite films fabricated with different types of 10 vol% Nb_2O_5-doped TiO_2 powders had less ionic dipoles available to form the switchable dipoles under an alternating electric field.

4. Conclusions

TiO_2/epoxy composite thick films containing the doped and heat-treated TiO_2 powders were successfully prepared by screen printing and curing. Nb_2O_5 was incorporated into TiO_2 and the doped TiO_2 powder was vacuum treated for the purpose of modifying the dielectric properties of the TiO_2 powder. The motivation of modifying the Nb_2O_5-doped TiO_2 powder by vacuum heat treatment was originated from the study of the sintered bulks. The 4 vol% Nb_2O_5-doped TiO_2 pellets displayed a high effective dielectric constant of 65,000 and loss tangent of 0.224 if vacuum sintering was executed. The TiO_2/epoxy thick films containing the 4 vol% Nb_2O_5-doped TiO_2 powder as a second phase presented better dielectric properties. The effects of test temperature and frequency were strongly dependent upon the amount of the dopant and the preparation of the TiO_2 powder. Basically, the Nb_2O_5-doped TiO_2/epoxy thick films had a higher dielectric constant if the 1050 °C-vacuum-treated TiO_2 powder was used, while a lower loss tangent for the 1150 °C-vacuum-treated TiO_2 powder. The best result with the dielectric constant of 23 and the loss tangent of 0.046 measured at 25 °C and 100 kHz was obtained for the 40 vol% TiO_2/epoxy composite thick films, where the TiO_2 powder was doped with 4 vol% Nb_2O_5 and subjected to heat treatment at 1150 °C under vacuum to form the 1150 °C-vacuum-treated TiO_2 powder.

References

[1] P. Chahal, R.R. Tummala, IEEE Transaction on Components, Packaging, and Manufacturing Technology B 21 (2) (1998) 184–193.
[2] S. Bhattacharya, R.R. Tummala, P. Chahal, G. White, in: Proceedings of the International Symposium on Advanced Packaging Materials, 1997, pp. 68–70.
[3] M.F. Yan, W.W. Rhodes, Ultrahigh dielectric capacitance in TiO_2 ceramics, in: M.F. Yan, A.H. Heuer (Eds.), Additives and Interfaces in Electronic Ceramics, The American Ceramic Society, 1983.
[4] Y.M. Chiang, D. Birnie III, W.D. Kingery, Physical Ceramics, John Wiley & Sons, Inc., New York, 1997, pp. 129–130.
[5] D.H. Kuo, C.C. Chang, T.Y. Su, W.K. Wang, B.Y. Lin, Mater. Chem. Phys. 85 (2004) 201–206.