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The dielectric properties of epoxy/AlN composites

Chia-Ching Wu [a], Ying-Chung Chen [a,*], Cheng-Fu Yang [b,1], Chean-Cheng Su [b,1], Chien-Chen Diao [c,2]

[a] Department of Electrical Engineering, National Sun Yat-sen University, Kaohsiung, Taiwan, ROC
[b] Department of Chemical and Materials Engineering, National University of Kaohsiung, Kaohsiung, Taiwan, ROC
[c] Department of Electronic Engineering, Kao Yuan University, Kaohsiung, Taiwan, ROC

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Abstract

In this paper, AlN ceramic powder is chosen to be mixed with epoxy to form epoxy/AlN composites, the effects of the content of AlN filler on the physical and dielectric properties of epoxy/AlN composites are developed. From the SEM observation, the particles of self-synthesized AlN powder, obtained by using combustion method, is less uniformity and the average particle size is about 3.12 μm. Only the AlN phase can be detected in the XRD patterns of the epoxy/AlN composites. The more AlN powder is mixed with epoxy, the higher crystal intensity of AlN phase will exist in the XRD patterns. As the content of AlN powder in the epoxy/AlN composites increases from 5 to 40 wt.%, the dielectric constant increases from 6.52 to 7.28 (measured at 1 MHz). The loss tangent of epoxy/AlN composites is slightly increased as the measured frequency increases. Moreover, the epoxy/AlN composites in this investigation show less pores as compared to other literatures. The results indicate that the fabrication process has an apparent effect on the decrease of porosities, and the composites with a low porosity will lead to a low loss tangent.

Keywords: Mixing; Dielectric properties; Composites; X-ray method

1. Introduction

Recently, the evolutions of wireless communication systems are growing rapidly to satisfy the personal communication requirements. Compact, small size, low cost, and multi-function are the major developing trends among these modern wireless communication devices. The electronic systems are composed of active components such as ICs and passive components like resistors (*R*), inductors (*L*), and capacitors (*C*). The ratio of the passive elements to active components in mobile cellular phone is over 20,[1] therefore, the passive components take up large area of substrate and lower electric performance due to more solder joints. To solve these problems, embedded passive technology, which is to incorporate passive components into one of inner layers of multi-layer substrate, has been actively investigated.

The electromagnetic band-gap (EBG) substrates are organic materials compositing periodical cells of metallic or dielectric elements. The electromagnetic band-gap characteristics are dependent on the material structure such as dimensions, periodicity, and permittivity.[2,3] Many different structures of EBG substrate were researched. Compared to other EBG structure, the high-*k* ceramics embedded into a low-*k* host to fabricate an EBG structure has a preferable feature of compactness.[4–7]

Hence, studying the dielectric materials with stable characteristics and high frequency performance becomes more and more important. The use of ceramic materials with high permittivity can effectively reduce the sizes of high frequency devices. The epoxy resin is a suitable polymer for its inertness to the electroless plating solution and its compatibility with printed wiring boards (PWBs). For this reason, epoxy/ceramic composites have been of great interest as embedded devices and EBG substrate materials, because the epoxy/ceramic composites not only reveal process mixing ability of polymers with high dielectric constant ceramics but have good compatibility with printed circuit boards (PCBs).[8–10] In this investigation, self-synthesized aluminum nitride (AlN) ceramic powder was chosen as the dielectric ceramic filler, and the filler content was varied in the epoxy/AlN composites. The dielectric constant (ε_r) and loss tangent ($\tan\delta$) of the epoxy/ceramic composites as a function of ceramic filler content and measured frequency were discussed.

* Corresponding author. Fax: +886 7 5254015.
E-mail address: ycc@mail.ee.nsysu.edu.tw (Y.-C. Chen).
[1] Present address: 700, Kaohsiung University Rd., Nan Tzu Dist., Kaohsiung, Taiwan, ROC.
[2] Present address: 1821, Jhongshan Rd., Lujhu Township, Kaohsiung, Taiwan, ROC.

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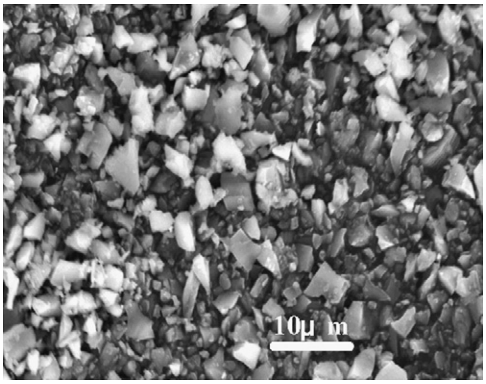

Fig. 1. The SEM micrograph of self-synthesized AlN powder.

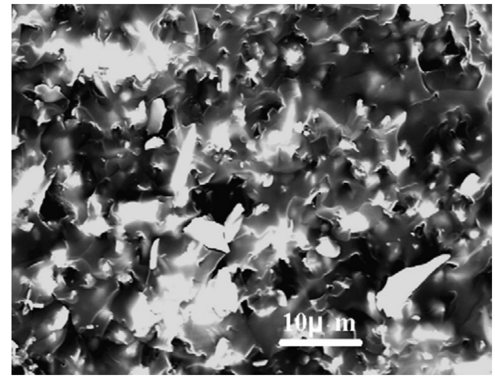

Fig. 3. The cross-sectional morphology of epoxy/AlN composite with 40 wt.% AlN powder.

2. Experimental detail

In this investigation, the AlN powder was chosen as ceramic filler in the composite. The starting powders of Al and NH_4Cl (0.3–1 wt.%) were mixed to form AlN powders using combustion synthesis method in a N_2 atmosphere.[11] Subsequently, the self-synthesized AlN powder was mixed with a solution of epoxy resin (*O*-Cresol Novolac) and curing agent (Phenol-Novolac) to form the composite materials. The epoxy/ceramic composites with 5–40 wt.% AlN powders were prepared. Prior to mixing with the AlN powder, the epoxy and curing agent were heated at 150 °C to form sticky state. Then the epoxy/AlN composites were formed and cooled at room temperature. The microstructures of epoxy/ceramic composites were observed via the scanning electron microscopy (SEM). Energy dispersive X-ray spectrometer (EDS) was used to analyze the composition of epoxy/AlN composites. The crystal structures of epoxy/AlN composites were determined by X-ray diffraction (XRD) employing Cu Kα radiation. The dielectric constant (ε_r) and loss tangent (tan δ) of epoxy/AlN composites were measured by HP4294 LCR meter at room temperature in the frequency range of 100 Hz to 1 MHz.

3. Results and discussion

The SEM micrograph of self-synthesized AlN powder is shown in Fig. 1. The AlN powder reveals a less uniformity of particle size distribution, and the average particle size of self-synthesized AlN powder is about 3.12 μm. Fig. 2 shows the surface morphologies of epoxy/AlN composites with the AlN contents of 10, 20, 30, and 40 wt.%, respectively. The cross-sectional microstructure observation of epoxy/AlN composite with 40 wt.% AlN powder is shown in Fig. 3. In Figs. 2 and 3, the black region is the epoxy and the white and gray particles are the AlN powder, respectively. From the observations of bulk samples, it is found that the AlN particles appear more apparent as the content of AlN in epoxy/AlN composites increases. As observed shown in Figs. 2 and 3, the AlN powder shows a uniform dispersing in epoxy. Besides, the epoxy/AlN composites in this investigation show less pores as compared to other report.[12] These results demonstrate that the epoxy/AlN composites are fitted to the requirements for the further application in embedded passive technology and EBG substrates.

Energy dispersive X-ray spectrometer (EDS) is used to analyze the elements of epoxy/AlN composites. Fig. 4 clearly shows that the C, O, Al, and N elements are contained in epoxy/AlN composites. The carbon and oxygen atoms are contributed by epoxy, and the aluminum and nitrogen atoms are from AlN, respectively. The less nitrogen element is found on the surfaces of epoxy/AlN composites with low contents of AlN ceramics. Fig. 5 shows the XRD patterns of epoxy/AlN composites as a function of the weight ratio of AlN powder. It reveals that only the crystal phase of AlN ceramic exists in the XRD patterns of epoxy/AlN composites, and the crystal intensities of AlN phases increase with the increase of AlN content.[13] The relative intensities of epoxy/AlN composites in the low angle range (20–30°) decrease as the content of AlN increases. Because the epoxy is an amorphous structure, for that as the content of AlN powder increases in the epoxy/AlN composites, the AlN phase will dominate the crystal properties of epoxy/AlN composites.

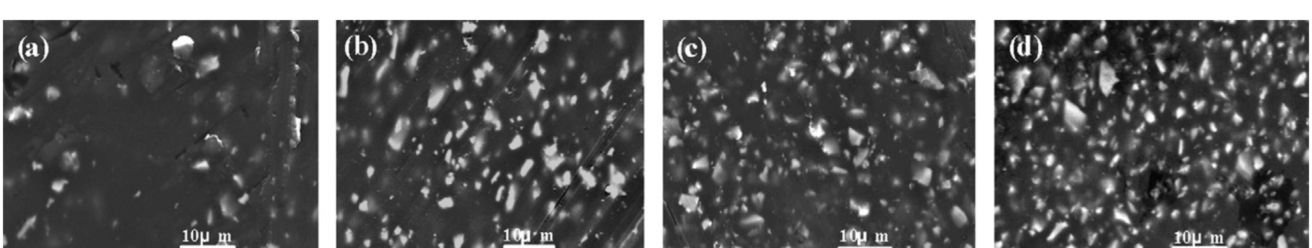

Fig. 2. The surface morphologies of epoxy/AlN composites with different wt.% of AlN powder: (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%, and (d) 40 wt.%.

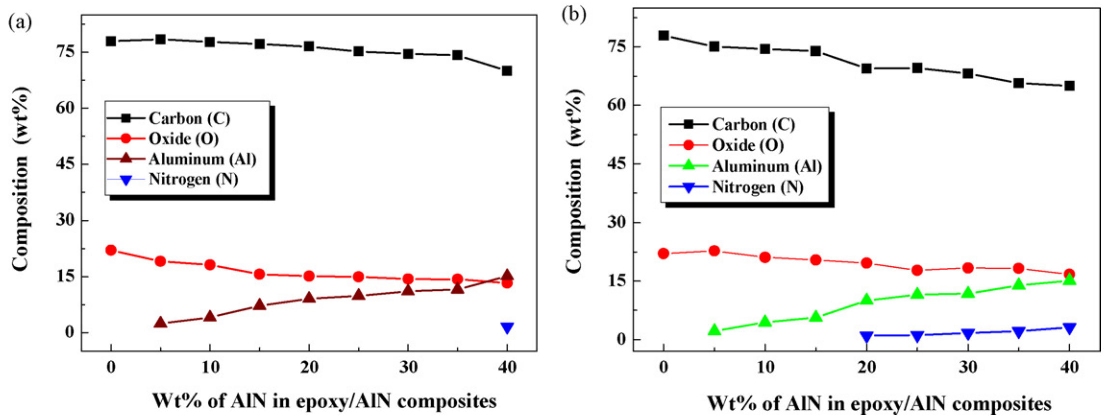

Fig. 4. The EDS analyses for epoxy/AlN composites with different compositions: (a) surface, and (b) cross-section.

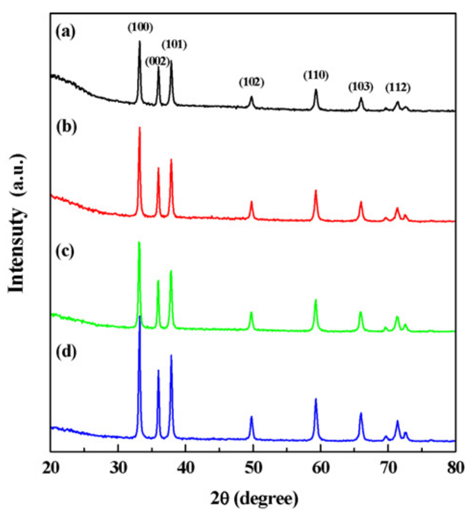

Fig. 5. XRD patterns of various AlN/epoxy composites as a function of AlN content: (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%, and (d) 40 wt.%.

From the dielectric constant–frequency (ε_r–f) curves, as shown in Fig. 6, it is found that the dielectric constant slightly decreases as the measured frequency increases. At a measured frequency, the dielectric constant of epoxy/AlN composites increases as the content of AlN powder increases. The theoretical prediction of the dependence of dielectric constant on the ceramic ratio is based on assuming a composite with a high permittivity ceramic powder uniformly dispersed in a low permittivity polymer,[14] as shown in Fig. 2, and the logarithmic mixing rule can be used to predict and calculate the dielectric constant of epoxy/AlN composites. The mixing rule is as follow:

$$\left(\frac{W_1}{D_1}+\frac{W_2}{D_2}\right)\log\varepsilon=\frac{W_1}{D_1}\log\varepsilon_1+\frac{W_2}{D_2}\log\varepsilon_2 \quad (1)$$

where W_1/D_1 and W_2/D_2 represent for the volume fraction of epoxy and dispersed dielectric materials, and ε_1 and ε_2 represent dielectric constants of epoxy and dispersed dielectric materials, respectively, and the $W_1/D_1 + W_2/D_2 = 1$. The measured and predicted relative dielectric constants (ε_r) at 1 MHz of epoxy/AlN composites are shown in Fig. 7. The hardened epoxy has a dielectric constant of 6.47. From Fig. 7, the dielectric constants of epoxy/AlN composites with different wt.% (5–40 wt.%) AlN content are in the range of 6.52–7.28. It is found that the higher dielectric constant of epoxy/AlN composites can be obtained as the content of AlN powder increases, which matches the predicted values. The logarithmic mixing rule is an inference equation that including parallel connection and series connection model. From the self-AlN ceramic powder shown in Fig. 1, the AlN ceramic includes the finer and coarser particle size. For that, the parallel connection model maybe not completely matched the real situation of epoxy/AlN composites. Therefore, it will be existed the difference between the measured and predicted dielectric constants. From the measured and predicted

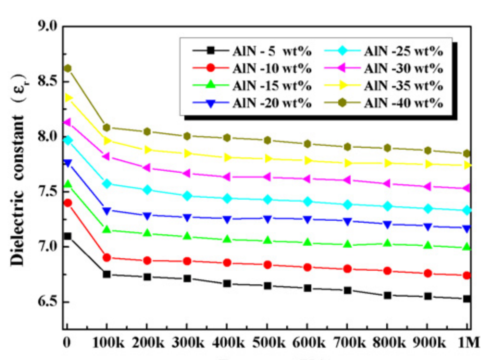

Fig. 6. The dielectric constants of different epoxy/AlN composites as functions of AlN content and measurement frequency.

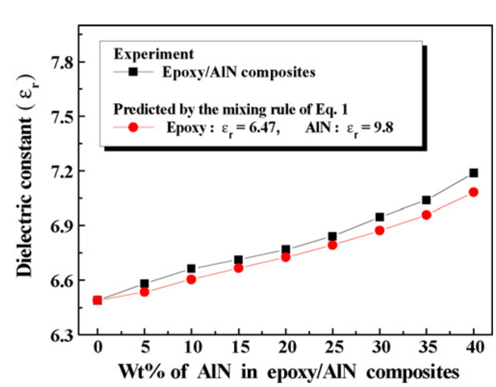

Fig. 7. The experimental and predicted dielectric constants at 1 MHz of epoxy/AlN composites with various AlN contents.

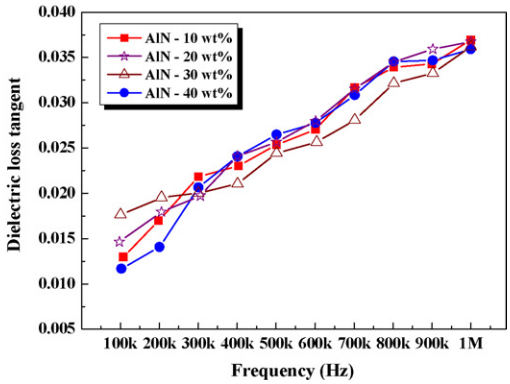

Fig. 8. The loss tangents at 1 MHz of epoxy/AlN composites with various AlN contents.

values, it is found that the measured dielectric constant is about 7.19 and the predicted value is about 7.01 at 40 wt.% AlN content, and the inaccuracy value of $\varepsilon_r = 0.18$ between the measured and predicted dielectric constants is acceptable.

The loss tangents ($\tan \delta$) of epoxy/AlN composites measured at 1 MHz are shown in Fig. 8. As shown in Fig. 1, the self-synthesized AlN powder reveals the lower uniformity including the finer and coarser particle sizes. The finer AlN particles can fill the interstitial sites of coarser AlN particles, and that will result in a denser powder packing. Because the AlN powder is well dispersed in epoxy, and then the epoxy/AlN composites will reveal a lower loss tangent.[12,15] The loss tangent slightly increases with the increase of measured frequency, as shown in Fig. 8, which might be attributed to the existent porosities in the epoxy/AlN composites.[12]

4. Conclusions

(1) Even 40 wt.% AlN powder is added, the AlN powder is still uniformly dispersed in the epoxy. The epoxy/AlN composites in this investigation reveal less pores as compared to other literatures.
(2) From the XRD analysis, the crystal phases of epoxy/AlN composites show identical to those of AlN powder, and the crystal intensities of AlN peaks increase with the increase of content of AlN powder in epoxy. Moreover, the intensity in the low angle range (20–30°) is decreased as the content of AlN powder increases.
(3) As the content of AlN powder in the epoxy/AlN composites increases form 0 to 40 wt.% and measured at 1 MHz, the dielectric constant increases from 6.52 to 7.28.
(4) The low loss tangent is related to the porosity in the epoxy/AlN composites and increases slightly with the increase of measured frequency.

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References

1. Rector, J., Economic and technical viability of integral passives. In *Proceedings of the 48th electric components and technology conference*, 1998, pp. 218–224.
2. Coccioli, R., Yang, F. R., Ma, K. P. and Itoh, T., Aperture-coupled patch antenna on UC-PBG substrate. *IEEE Trans. Microw. Theory Tech.*, 1999, **47**, 2123–2130.
3. Cheype, C., Serier, C., Thevenot, M., Monediere, T., Reineix, A. and Jecko, B., An electromagnetic bandgap resonator antenna. *IEEE Trans. Antennas Propagation*, 2002, **50**, 1285–1290.
4. Chappell, W. J. and Gong, X., Wide bandgap composite EBG substrates. *IEEE Trans. Antennas Propagation*, 2003, **51**, 2744–2750.
5. Yang, F. and Samii, Y. R., Microstrip antennas integrated with electromagnetic band-gap (EBG) structures: a low mutual coupling design for array applications. *IEEE Trans. Antennas Propagation*, 2003, **51**, 2936–2946.
6. Lee, Y., Yeo, J., Ko, K., Lee, Y., Park, W. and Mittra, R., A novel design technique for control of defect frequencies of an electromagnetic bandgap (EBG) superstrate for dual-band directivity enhancement. *Microw. Opt. Technol. Lett.*, 2004, **42**, 25–31.
7. Lee, Y. J., Yeo, J., Mittra, R. and Park, W. S., Application of electromagnetic bandgap (EBG) superstrates with controllable defects for a class of patch antennas as spatial angular filters. *IEEE Trans. Antennas Propagation*, 2005, **53**, 224–235.
8. Bhattacharya, S. K. and Tummala, R. R., Next generation integral passives: materials, processes, and integration of resistors and capacitors on PWB substrates. *J. Mater. Sci. Mater. Electron.*, 2000, **11**, 253–268.
9. Bhattacharya, S. K. and Tummala, R. R., Integral passives for next generation of electronic packaging: application of epoxy/ceramic nanocomposites as integral capacitors. *Microelectron. J.*, 2001, **32**, 11–19.
10. Rao, Y., Ogitani, S., Kohl, P. and Wong, C. P., Novel polymer–ceramic nanocomposite based on high dielectric constant epoxy formula for embedded capacitor application. *J. Appl. Polym. Sci.*, 2002, **83**, 1084–1090.
11. Lin, C. N., Hsieh, C. Y., Liu, S. L. and Chung, S. L., Properties and applications of a combustion synthesized AlN powder. *Bull. Chin. Ceram. Soc.*, 2003, **21**, 56–60.
12. Kuo, D. H., Chang, C. C., Su, T. Y., Wang, W. K. and Lin, B. Y., Dielectric behaviors of multi-doped $BaTiO_3$/epoxy composites. *J. Eur. Ceram. Soc.*, 2001, **21**, 1171–1177.
13. Xiong, Y., Fu, Z. Y., Wang, H., Wang, Y. C. and Zhang, Q. J., Microstructure and IR transmittance of spark plasma sintering translucent AlN ceramics with CaF_2 additive. *Mater. Sci. Eng. B*, 2005, **123**, 57–62.
14. Jayasundere, N. and Smith, B. V., Dielectric constant for binary piezoelectric 0–3 composites. *J. Appl. Phys.*, 1993, **73**, 2462–2466.
15. Cho, S. D., Lee, J. Y., Hyun, J. G. and Paik, K. W., Study on epoxy/$BaTiO_3$ composite embedded capacitor films (ECFs) for organic substrate applications. *Mater. Sci. Eng. B*, 2004, **110**, 233–239.