

Effects of heat treatment on the dielectric properties of aerosol-deposited Al_2O_3 -polyimide composite thick films for room-temperature fabrication

Hyung-Jun KIM and Song-Min NAM*

Department of Electronic Materials Engineering, Kwangwoon University 447-1, Wolgye-dong, Nowon-gu, Seoul 139-701, Korea

Al_2O_3 -polyimide composite thick films for integrated substrates were successfully fabricated at room temperature by an aerosol deposition method (ADM). When using as-received $\alpha\text{-Al}_2\text{O}_3$ as a starting powder, the Al_2O_3 -polyimide composite thick films exhibited a high dielectric loss and high frequency dependence. The relative permittivity and $\tan \delta$ of the Al_2O_3 -polyimide composite thick films using as-received Al_2O_3 powder were 6.7 and 0.026 at 1 MHz, respectively. However, their dielectric loss was remarkably decreased from 0.026 to 0.007 at 1 MHz after post-annealing at 100°C although their relative permittivity did not change. It was determined that the decreases of dielectric loss mainly depended on the state of the Al_2O_3 . Based on these results, the heat treatment of the Al_2O_3 starting powder was carried out in order to fabricate Al_2O_3 -polyimide composite films with a low dielectric loss at room temperature. As a result, their $\tan \delta$ was also decreased from 0.026 to 0.007 without a long post-annealing. It was confirmed that the preparation of the ceramic Al_2O_3 starting powder was important for the room-temperature fabrication of the aerosol deposited Al_2O_3 -polyimide composite thick films with a low dielectric loss.

Key words: Aerosol deposition method, Al_2O_3 , polyimide, polymer composite, heat treatment, room temperature process, integrated substrates.

Introduction

Today, the integration technologies of electronic components are being rapidly developed to respond to the customer demands of multifunction, high speed and miniaturization.

The integration of components has developed to raise the integration level not only using 2-dimensional integration on substrates but 3-dimensional integration such as system-on-package (SOP) [1, 2]. However, widely used FR-4 substrates are no longer suitable for high frequency devices and 3-dimensional integration because of its high dielectric loss and high coefficient of thermal expansion (CTE) [3-5]. So, ceramics have been used as the high frequency substrates instead of FR-4 due to their high reliability, good dielectric properties, excellent thermal conductivity and low CTE close to that of silicon. However, a low temperature processing of ceramics is necessary to realize this 3-dimensional integration because of the low melting points of the integrated metal or polymer materials in the integrated substrates. For this reason, polymer composites have been studied as candidates but it has been hard to fabricate ceramic-based polymer composite thick films [6-11].

To break through these problems, we fabricated Al_2O_3 -based polyimide composite thick films for integrated substrates using the benefits of the aerosol deposition method (ADM) which can fabricate dense ceramic thick films and heterogeneous junctions of different materials in

the sub-micrometer range at room temperature [12, 13].

In our previous research, the dielectric properties of polyimide thick films produced by ADM were as good as that of bulk polyimide [14]. On the other hand, it has been reported that the dielectric loss of fabricated Al_2O_3 thick films is higher than that of bulk Al_2O_3 , although they can be fabricated at room temperature [13, 15].

In this research, we focused on an improvement in the dielectric properties of Al_2O_3 in order to enhance the Al_2O_3 -polyimide composite thick films prepared by ADM at room temperature. Through post-annealing at low temperature for a long time, an improvement in the dielectric properties of Al_2O_3 -polyimide composite thick films was attempted. Based on these results, heat treatment of the Al_2O_3 starting powder before the deposition was carried out for the room temperature fabrication of the Al_2O_3 -polyimide composite thick films was used.

Experimental Procedure

Ceramic and polymer starting powders were prepared to fabricate the composite thick films. As the polymer starting powder, polyimide powder 200 μm average diameter was used. However, the initial size of the polyimide powder was too large to turn into an aerosol state in the aerosol chamber and polyimide films could not be formed. For this reason, we reduced the particle size of polyimide powder using a planetary ball milling machine and then polyimide powder 1 μm average diameter was prepared. As the ceramic starting powder, $\alpha\text{-Al}_2\text{O}_3$ powder 0.5 μm primitive size and a purity of 99.4% was used. Then a mixture of Al_2O_3 and

*Corresponding author:
Tel : +82-2-940-5764
Fax: +82-2-942-5764
E-mail: smnam@kw.ac.kr

polyimide powders was prepared for fabrications Al_2O_3 -polyimide composite thick films by ball mill. Using this starting powder, the Al_2O_3 -polyimide composite thick films were deposited on Cu and glass substrates at room temperature for 10 minutes. Energy dispersive X-ray spectroscopy (EDS) of the composite thick films was used to confirm the Al_2O_3 and polyimide in the composite thick films. The dielectric measurements were conducted in a metal-insulator-metal (MIM) configuration. For this purpose, several gold electrodes (1 mm in diameter) were deposited on the composite thick films by a shadow mask technique to form MIM capacitors. The dielectric properties of Al_2O_3 -polyimide composite thick films were measured by an impedance analyzer. The composite thick films were heated to improve the dielectric properties to 100 °C for a total of 80 hours in an electrical oven in the atmosphere and the variation of the dielectric loss was measured by the impedance analyzer. On the other hand, heat treatment of the Al_2O_3 starting powder was carried out for the room temperature processing of the composite thick films. For

this purpose, the Al_2O_3 starting powder was heated to 900 °C for 2 hours by an electric furnace in the atmosphere. However, composite thick films could not be fabricated using the heat-treated Al_2O_3 powder. So, the variation of the particle size through the heat treatment was observed by a particle size analyzer (PSA). After that the heat-treated powder was crushed in a ball mill to reduce the degree of agglomeration of the powder after heat treatment of the Al_2O_3 starting powder. Using this starting powder, Al_2O_3 -polyimide thick films were fabricated and their dielectric properties were measured by the impedance analyzer.

Results and Discussion

Fabrication of Al_2O_3 -polyimide composite thick films at room temperature

The Al_2O_3 starting powder 0.5 μm size was prepared and dense Al_2O_3 thick films could be fabricated using it by ADM as shown in Figs. 1(a) and (d). However, polyimide thick films could not be fabricated using the as-received

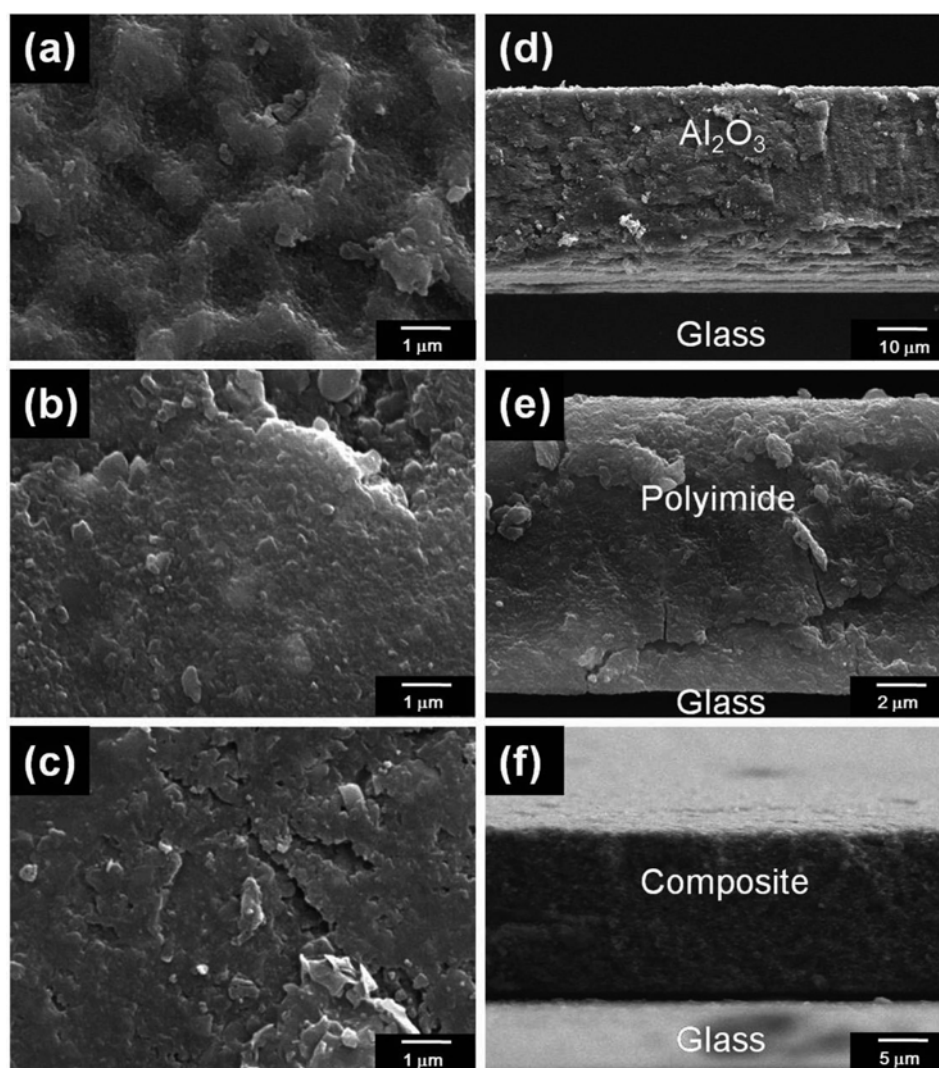


Fig. 1. SEM surface images of (a) Al_2O_3 thick films, (b) polyimide thick films, (c) Al_2O_3 -polyimide composite thick films and SEM cross-sectional images of (d) Al_2O_3 thick films, (e) polyimide thick films, (f) Al_2O_3 -polyimide composite thick films.

polyimide starting powder because its particle size was too large to achieve an aerosol state in the aerosol chamber. So, the particle size of polyimide powder was reduced by a planetary ball milling machine and then polyimide thick films could be fabricated by ADM as shown in Figs. 1(b) and (e). The particle size of polyimide powder after crushing was measured by the PSA. As the result, the polyimide powder was reduced to 1.0 μm in average diameter.

The prepared Al_2O_3 and polyimide starting powder were mixed by a ball mill for the preparation of mixed starting powder. The amount of Al_2O_3 in the mixture was 95 wt%. As a result of the deposition, dense Al_2O_3 -polyimide composite thick films were successfully fabricated on Cu and glass substrates at room temperature as shown in Figs. 1(c) and (f). Particularly, Fig. 1(f) shows a cross-sectional SEM image of a dense Al_2O_3 -polyimide composite thick film after polishing. The composite thick films were dense enough to be polished. In addition, EDS analysis of composite thick films was carried out to confirm the presence of Al_2O_3 and polyimide in the composite thick films. As shown in Fig. 2(a), the existence of the Al_2O_3 in the Al_2O_3 thick films was confirmed from the aluminum and oxygen signals of the Al_2O_3 by the EDS analysis. In the case of the composite thick films, an additional carbon signal from

polyimide was detected as shown in Fig. 2(a).

Next, the dielectric properties of composite thick films for integrated substrates were measured with the Al_2O_3 thick films and polyimide thick films. As shown in Fig. 3, the dielectric properties of Al_2O_3 -polyimide composite thick films showed mixed properties of the Al_2O_3 and the polyimide. Their relative permittivity and $\tan \delta$ were 6.7 and 0.026 at 1 MHz, respectively. In the case of the polyimide thick films, the relative permittivity and $\tan \delta$ were 3.2 and 0.007 at 1 MHz, respectively. It was confirmed that the dielectric properties of polyimide thick films deposited by ADM was as good as that of conventional the bulk polyimide. The relative permittivity and $\tan \delta$ of Al_2O_3 thick films were 9.1 and 0.168 at 1 MHz, respectively. The dielectric loss of Al_2O_3 thick films using the as-received powder was higher than that of bulk Al_2O_3 , although they could be fabricated at room temperature.

Improvement in dielectric properties through post-annealing

The dielectric properties of fabricated Al_2O_3 -polyimide composite thick films using as-received Al_2O_3 starting powder were not sufficient to be applied to high frequency dielectric substrates, although they could be fabricated by ADM at room temperature. The dielectric loss of composite

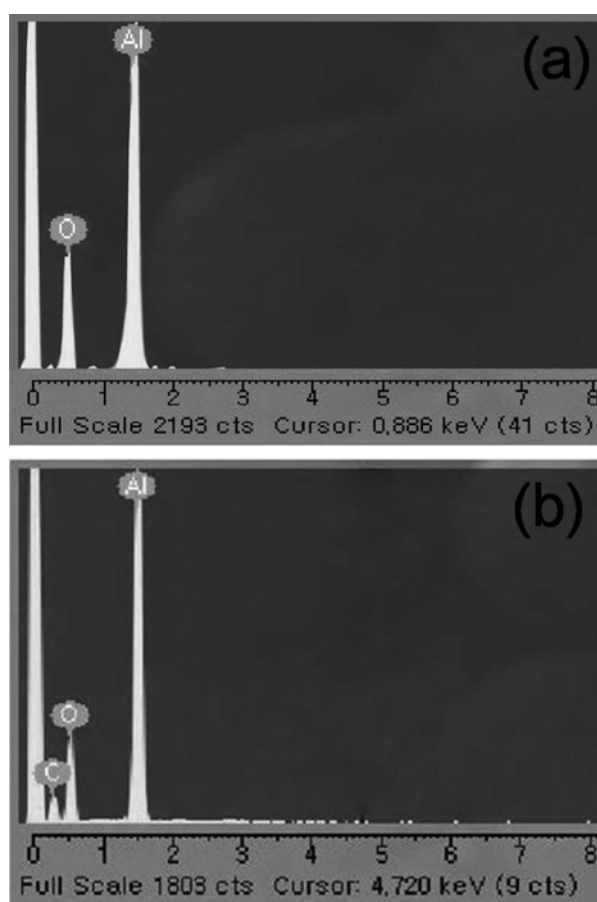


Fig. 2. EDS analysis of (a) Al_2O_3 thick films and (b) Al_2O_3 -polyimide composite thick films.

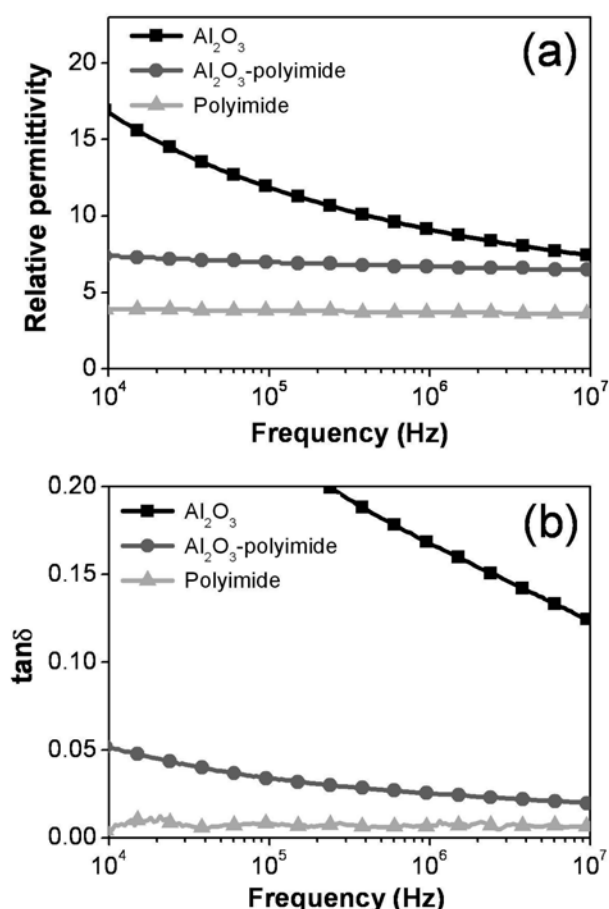


Fig. 3. Relative permittivity and $\tan \delta$ as a function of frequency for thick films deposited by ADM.

thick films was similar to that of the conventional FR-4 substrates and this needed to be improved for high frequency applications. To improve the dielectric properties of the composite thick films, post-annealing was performed after the deposition. Deposited thick films were heated at 100 °C, because the melting point of the polyimide powder used was 160-170 °C. The Al_2O_3 -polyimide composite thick films and Al_2O_3 thick films were heated and properties measured for a total of 80 hours in an electrical oven in the atmosphere.

Fig. 4 shows the dependence of post-annealing time on dielectric loss of the Al_2O_3 -polyimide composite thick films and the Al_2O_3 thick films. The dielectric loss of Al_2O_3 -polyimide composite thick films were enhanced for the first 15 hours, and then it tended to become saturated after 15 hours. The same post-annealing was carried out to establish the cause of the improvement of the dielectric loss. As the result, we confirmed the same aspect with an improvement of composite thick films. The enhancement in dielectric loss of composite thick films caused by Al_2O_3 is shown in Fig. 4. However, we confirmed that a relatively long heat treatment time was necessary to improve the dielectric properties.

Improvement in dielectric properties through the heat treatment of the Al_2O_3 starting powder

In the case of the deposition using the as-received Al_2O_3 powder, the dielectric properties of Al_2O_3 thick films showed a strong frequency dependence in the low-frequency region and the dielectric loss was high over all. Likewise, the dielectric properties of the Al_2O_3 -polyimide composite thick films using the as-received Al_2O_3 powder also showed the same aspect.

In general, the frequency dependence at low-frequency is caused by moisture or impurities which can generate space charges or impurities, so the heat treatment of the Al_2O_3 starting powder was performed to remove these before the deposition. To achieve this, Al_2O_3 powder was heated at 900 °C for 2 hours by an electric furnace in the atmosphere [15]. However, Al_2O_3 thick films could not be fabricated using the heat-treated Al_2O_3 powder because

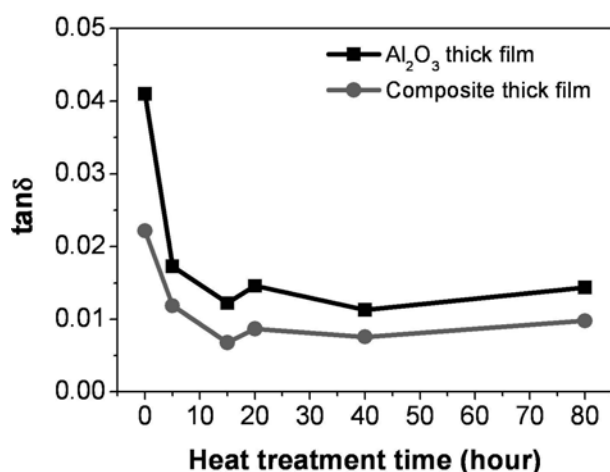


Fig. 4. Variation of loss tangent with post-annealing time (100 °C).

the agglomeration of particles was increased after the heat treatment at 900 °C, although there was no change in the size of the individual particles. Fig. 5(b) shows the failed deposition using the starting powder after heat treatment at 900 °C.

It was estimated that these failed depositions resulted from etching caused by the high kinetic energy of the large agglomerated particles. So, the heat-treated Al_2O_3 powder was crushed to decrease the degree of agglomeration of particles in a ball mill with zirconium oxide beads for

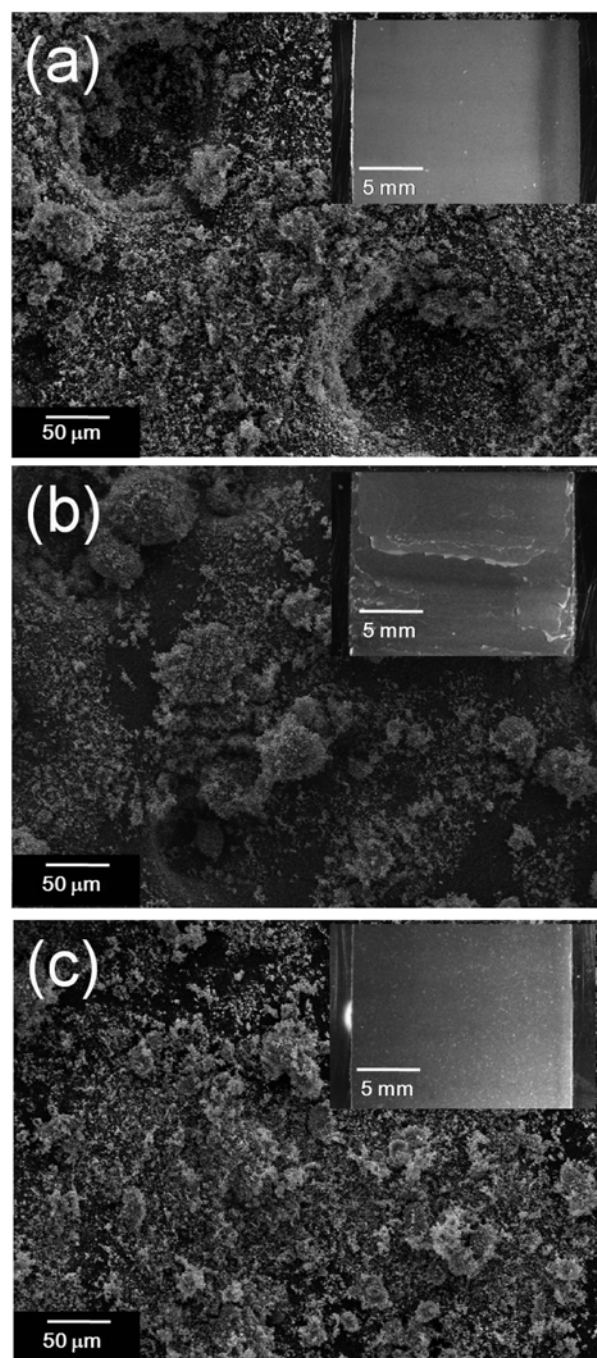


Fig. 5. SEM images of (a) as-received Al_2O_3 powder, (b) Al_2O_3 powder heat-treated at 900 °C, (c) Al_2O_3 powder crushed by a ball mill after the heat treatment and optical images of their deposited films.

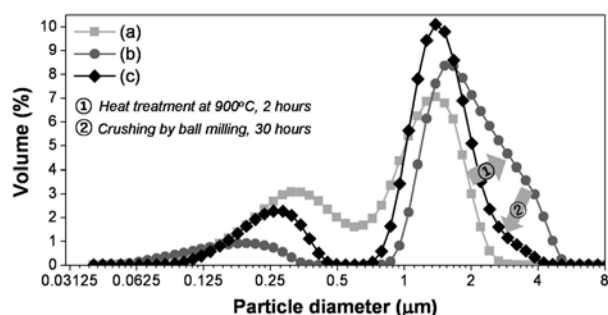


Fig. 6. PSA results of (a) as-received Al_2O_3 powder, (b) Al_2O_3 powder heat-treated at 900 °C and (c) Al_2O_3 powder crushed by a ball mill after the heat treatment.

30 hours, and then we could obtain a suitable heat-treated Al_2O_3 starting powder for the deposition of thick films by ADM as shown in Fig. 5(c).

In addition, these increases or decreases of the agglomerated particles was quantitatively measured by PSA. Fig. 6 shows the PSA results of the variation through heat treatment and crushing. The agglomerated particles over 3 μm in size were increased after the heat treatment at 900 °C and they were decreased again by the crushing of the heat-treated powder as shown in Fig. 6. As a result, Al_2O_3 thick films could be successfully fabricated on Cu and glass substrates using the heat-treated Al_2O_3 starting powder as shown in Fig. 5(c). In addition, the frequency dependence of dielectric properties of Al_2O_3 thick films was markedly decreased in the low-frequency and the dielectric loss was enhanced on the whole as shown in Fig. 7(b).

The amount of Al_2O_3 in the starting power was increased to raise the Al_2O_3 content in the composite thick films from 95 wt.% to 97 wt.% after the confirmation of the improvement in the dielectric properties of the heat-treated Al_2O_3 .

Fig. 7 shows the improvement in the dielectric properties through the heat treatment of the Al_2O_3 starting powder. The $\tan \delta$ of them was decreased from 0.025 ($Q = 38$) to 0.007 ($Q = 150$) at 1 MHz through the heat treatment of the Al_2O_3 starting powder at 900 °C for 2 hours without any heat treatment after the deposition.

In this research, ceramic-based polymer composite thick films could be fabricated at room temperature for integrated substrates with the advantage of plasticity. We confirmed the preparation of the starting powder is very important to achieve superior dielectric properties of deposited thick films by ADM. Through the optimization of the heat treatment and using various polymers or ceramics, ceramic-based polymer composite thick films fabricated by ADM are expected to application for integrated substrates in the near future.

Conclusions

We fabricated Al_2O_3 -polyimide composite thick films for integrated substrates by ADM at room temperature and the effects of heat treatment on their dielectric properties were investigated. As a result, we can draw the following

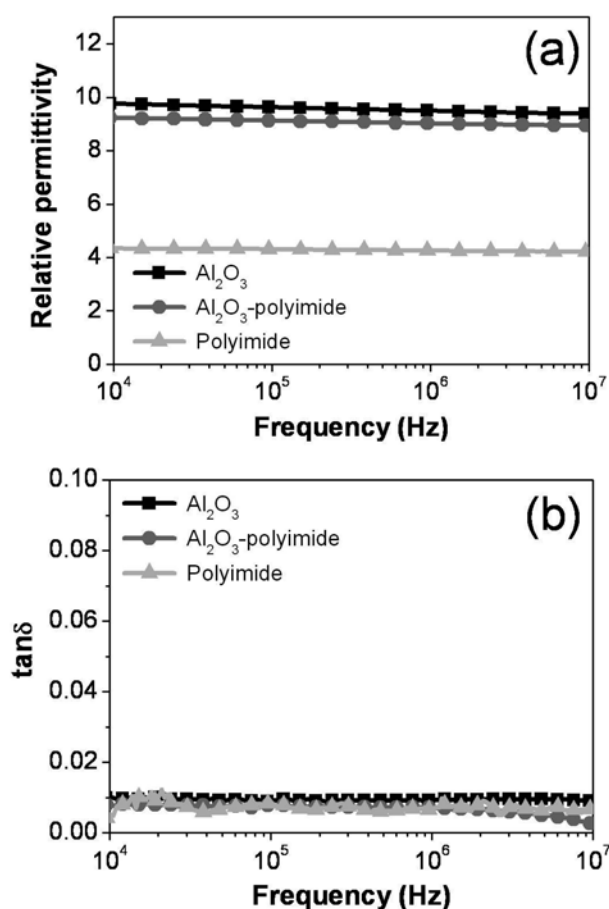


Fig. 7. Relative permittivity and $\tan \delta$ as a function of frequency for deposited thick films using the Al_2O_3 powder heat-treated at 900 °C.

conclusions. Dense Al_2O_3 -based polyimide composite thick films with a thickness in the micrometer range were successfully fabricated at room temperature by ADM. It was confirmed that the dielectric properties of the Al_2O_3 -polyimide composite thick films were enhanced through post-annealing after the deposition. Moreover, an improvement in the dielectric properties of Al_2O_3 -polyimide composite thick films fabricated at room temperature could also be achieved through the heat treatment of the Al_2O_3 starting powder without any heat treatment after the deposition. It is now known that the heat treatment of the ceramic Al_2O_3 starting powder is critically important for the room-temperature fabrication of aerosol deposited Al_2O_3 -polyimide composite thick films with a low dielectric loss.

Acknowledgements

This research was supported by a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Commerce, Knowledge and Economy, Republic of Korea.

Reference

1. R.R. Tummala, P.M. Raj, S. Atmur, S. Banerji, F. Liu, S.

- Bhattachatya, V. Sundaram, K.I. Shinotani and G. White, *J. Electroceram.*, 13 (2004) 417-422.
2. R.R. Tummala, M. Swaminathan, M.M. Tentzeris, J. Laskar, G.K. Chang, S. Sitaraman, D. Keezer, Da. Guidotti, Z. Huang, K. Lim, L. Wan, S.K. Bhattacharya, V. Sundaram, F. Liu and P. Raj. Markondeya, *IEEE Trans. Adv. Packag.*, 27 (2004) 250-267.
3. R.S. Tomar and P. Bhartia, *IEEE Trans. Microw. Theory Tech.*, Vol. MTT-35 (2007) 453-457.
4. Y. Rao, J. Yue and C.P. Wong, *Active and Passive Elec. Comp.*, 2002, 25 (2002) 123-129.
5. H. Windlass, P.M. Raj, D. Balaraman, S.K. Bhattacharya and R.R. Tummala, *IEEE Trans. Adv. Packag.*, 26[2] (2003).
6. D.H. Kuo, C.C. Chang, T.Y. Su, W.K. Wang and B.Y. Lin, *J. Eur. Ceram. Soc.*, 21 (2001) 1171-1177.
7. R. Popielarz, C.K. Chiang, R. Nozaki and J. Obrzut, *Macromolecules*, 34 (2001) 5910-5915.
8. S.K. Bhattacharya and R.R. Tummala, *Microelectron. J.*, 32 (2001) 11-19.
9. Y. Rao, S. Ogitali, P. Kohl and C.P. Wong, *J. Appl. Polym. Sci.*, 83 (2001) 1084-1090.
10. R. Kota, A.F. Ali, B.I. Lee and M.M. Sychov, *Microelectron. Eng.*, 84 (2007) 2853-2858.
11. F. Xiang, H. Wang and X. Yao, *J. Eur. Ceram. Soc.*, 27 (2007) 3093-3097.
12. J. Akedo, *Mater. Sci. Forum*, 43 (2004) 449-452.
13. S.M. Nam, N. Mori, H. Kakemoto, S. Wada, J. Akedo and T. Tsurumi, *Jpn. J. Appl. Phys.*, 43 (2004) 5414-5418.
14. H.J. Kim, Y.J. Yoon, J.H. Kim and S.M. Nam, *Mat. Sci. Eng. B*, 161[1-3] (2009) 104-108.
15. J.C. Park, Y.J. Yoon, H.T. Kim, E.H. Koo, S.M. Nam, J.H. Kim and K.B. Shim, *J. Kor. Ceram. Soc.*, 45 (2008) 411-417.