Journal of Ceramic Processing Research. Vol. 16, No. 4, pp. 445~449 (2015)

JOURNAL OF
Ceramic
Processing Research

Fabrication of Percolative $BaTiO_3$/Al Composite Films Prepared by Aerosol Deposition

Won-Seock Woo[a], Esther Baek[a], Hong-Ki Kim[a], Seung-Hwan Lee[a], Jeong Hyun Lee[a], Ki Hong Choi[b], Jae-Sik Kim[a], Sung-Gap Lee[c] and Young-Hie Lee[a,]*

[a]*Dept. of Electronic materials engineering, Kwangwoon University*
[b]*Dept. of Electrical and Biological physics, Kwangwoon University*
[c]*Dept. of Ceramic Engineering, Eng. Res. Insti., Gyeongsang National University*

The percolative Al-filled $BaTiO_3$ composite films of 5 μm thickness were fabricated by aerosol deposition process at room temperature. The aluminum particles were mixed in the $BaTiO_3$ matrix with 0, 16, 21, 31, 38, 42, 47, 63, and 79 vol%. The 47 vol% Al-filled $BaTiO_3$ composite films had high relative dielectric constant of 1028.8 at 1000 Hz owing to the percolation effect. The percolation threshold was observed as ranging from 40 to 55 vol%, for these results, Al-filled $BaTiO_3$ composite film occurred the phase transition and increased the dielectric constant sharply over the 47 vol% Al constant. The leakage current density of 47 vol% Al-filled $BaTiO_3$ composite films was 5.66 A/cm^{-2} at a high electric field of 20 kV/cm. In addition, fabricated $BaTiO_3$-Al composite films were evaluated their structural and electrical characteristics.

Key words: Aerosol deposition, Percolation, $BaTiO_3$, Aluminum.

Introduction

Recently, wireless network system such as smart phone and tablet PC have been used, and the main techniques involved in the development of these networks is regarded as the miniaturization of many functions electronic devices [1]. As an alternative solution for the downsizing of these products and highly integrated system with multiple functionalities, a System on Package (SOP) concept has proposed [2]. The SOP concept is a technique of the passive elements (L: inductor, C: capacitor, R: resistance) embed in the substrates, and the active elements laminated on the substrate as a package. Capacitor takes up much space in the passive elements, if the capacitor embedded in the substrates, embedding area of the electronic devices can give huge effect in reducing [2, 3].

A percolation theory used to increase the capacity of the capacitor in material aspects [4]. The percolation exists a method such as polymer/metal, ceramic/metal. Using the ceramic as a matrix have an advantage in order to get high capacity density, however, the ceramic / metal composite films have a problem the high sintering temperature of ceramic during fabrication process and the high sintering temperature cause the an easily oxidation of metal and metal diffusion. To solve these problems, we developed the possible fabrication process at room temperature using an aerosol deposition (AD) process. AD is possible high-speed coating and coating layer form without crack caused by inexpensive process at low vaccum, which can use various substrate of metal, ceramic [5-10]. In this study, in order to increase the capacitance density, Al and $BaTiO_3$ powder prepared with different ratios, and Al-filled $BaTiO_3$ composite films on Cu substrates fabricated by using the AD process. In addition, fabricated Al-filled $BaTiO_3$ composite films were evaluated their structural and electrical characteristics.

Experiments

As starting powder, $BaTiO_3$ powder (BT-045J, Samsung Fine Chemical Co., Ltd.) and Al powder were prepared. The average particle sizes are 0.45 and 5 μm, respectively. The prepared BT and Al powder were mixed with various weight percent (10, 20, 30, 40, 60, 70, and 80%). By using mixed $BaTiO_3$/Al powder, Al-filled $BaTiO_3$ composited films were fabricated by aerosol deposition (AD) process with thickness of 5 μm on Cu substrates at room temperature. AD process is based on shock loading solidification due to the impact of ceramic particles. During the AD process, fine ceramic particles are accelerated by gas flow in the nozzle up to a velocity of several hundred meters per second and are sprayed onto the substrates. The deposition condition of AD process as follows. The deposition time, working pressure, distance between the nozzle and the substrates, deposition area, carrier gas, and gas flow were 30 min, 3.2 torr, 5 mm, 10×10 mm^2, N_2 gas, and 5 Standard Liter per Minute (SLM), respectively. The

*Corresponding author:
Tel : +82-2-940-5164
Fax: +82-2-915-8084
E-mail: yhlee@kw.ac.kr

deposited films were investigated for their structural and electrical properties. The thickness of the aerosol deposited composite films was measured using a surface profiler (Ambios Technology XP-2). The surface morphologies of composite films was observed using field-emission scanning electron microscopy (FE-SEM; JSM-7001F, Jeol). The crystal structure of deposited composite films was confirmed by X-ray diffraction (XRD; Ultima IV, Rigaku) and Al powder contents in deposited composite films were measured using X-ray fluorescence (XRF).

In order to measure the electrical properties, upper copper electrodes of 1.5 mm in diameter were coating by electron beam evaporation with a shadow mask on the Al-filled $BaTiO_3$ composite films. In addition, the leakage current density (I-V measurement 4200-SCS, Keithley), percolation threshold and impedance analysis (HP 4294A, Agilent) were analyzed.

Results and Discussion

With the mixed starting powder, $BaTiO_3$ films and Al-filled $BaTiO_3$ composite films with the thickness of 5 μm were successfully fabricated by AD process. Figure 1 shows the SEM images of the (a) mixed $BaTiO_3$ and Al powder, (b) surface morphologies of Al-filled $BaTiO_3$ composite films, and (c) surface morphology of the pristine $BaTiO_3$ film on Cu substrates. From the Figure 1 (a), it was confirmed that the size of the $BaTiO_3$ and Al powder is approximately 0.5 and 5 μm, and the powder is randomly dispersed. The 5 μm-thick Al-filled $BaTiO_3$ composite films were fabricated on Cu substrates using mixed starting powder with various weight percent of 0 (≈ 0 vol%), 10 (≈ 20 vol%), 20 (≈ 36 vol%), 30 (≈ 49 vol%), 40 (≈ 60 vol%), 50 (≈ 69 vol%), 60 (≈ 77 vol%), 70 (≈ 84 vol%), and 80 (≈ 89 vol%) All Al-filled $BaTiO_3$ composite films showed dense surface morphologies without any pores. In addition, from the SEM image of Al-filled BaTiO3 composite film, we could observe the impaction trace of starting $BaTiO_3$ or Al powder onto pre-deposited film surface.

Figure 2 shows the XRD pattern of 20 wt% Al-filled $BaTiO_3$ composite film fabricated by AD process. It can be confirmed that the fabricated composite films were well crystallized with a cubic crystal system and secondary phase did not exist. However, diffraction patterns of the $BaTiO_3$ and Al powder were overlapped, so that we could not verify the existence of Al powder in Al-filled $BaTiO_3$ composite films. For this reason, the X-ray fluorescence (XRF) was used in order to investigate the exact content of Al.

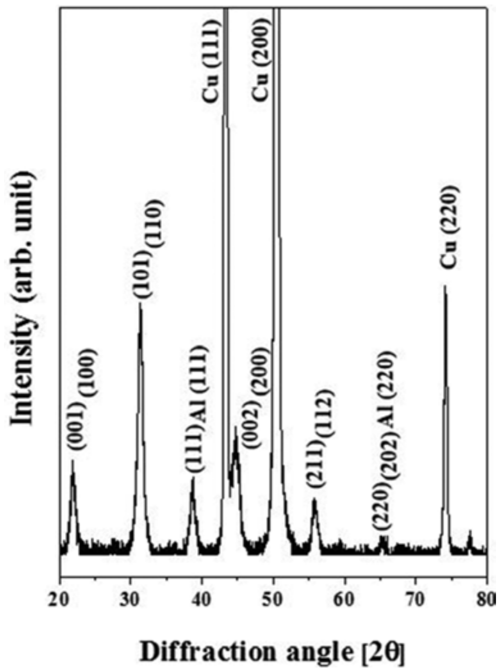

Fig. 2. XRD patterns of the 20 wt% Al-filled $BaTiO_3$ composite film.

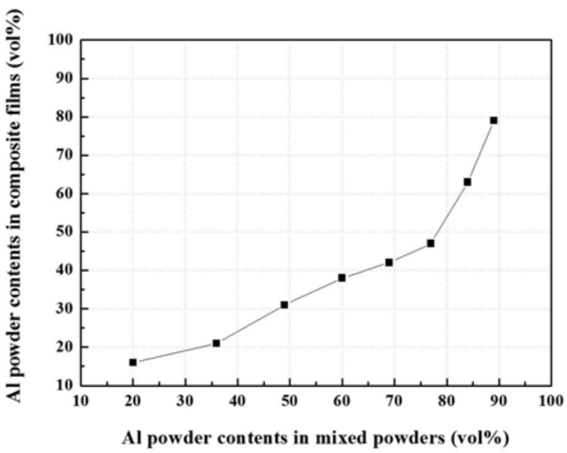

Fig. 3. Al powder contents on composite films versus Al powder contents in mixed powders.

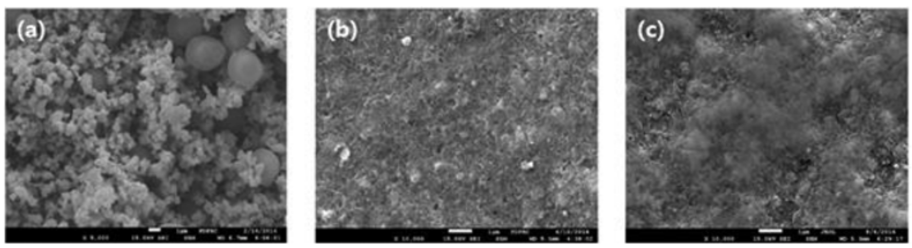

Fig. 1. SEM images of the (a) Al-filled $BaTiO_3$ composite powder, (b) Al-filled $BaTiO_3$ composite film surface, and (c) $BaTiO_3$ film on Cu substrates.

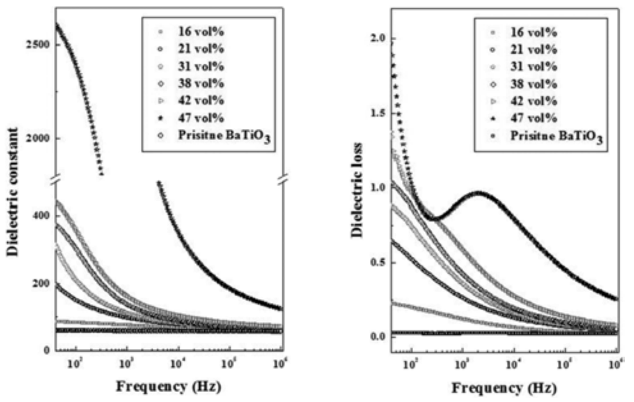

Fig. 4. Dependence of the dielectric constant and dielectric loss of Al-filled $BaTiO_3$ composite film samples with 16, 21, 31, 38, 42, and 47 vol% versus frequency.

Figure 3 show the XRF data of the Al-filled $BaTiO_3$ composite films with the various Al contents. The Al contents in composite films increased with increasing Al contents in starting powder. The Al contents in composite films using the starting powder with the Al powder contents of 20, 36, 49, 60, 69, 77, 84, and 89 vol% are 16, 21, 31, 38, 42, 47, 63, and 79 vol%, respectively However, the measured Al contents of the composited films were less than the prepared Al contents of starting powder. Because, the density and particle size of the Al powder are larger than the $BaTiO_3$ powder resulting in less aerosolization of Al powder in aerosol chamber. From the reason, less Al powder is impacted to the substrates compared with the prepared Al powder. The $BaTiO_3$ and Al powder density are a twofold difference (2.7 and 6.02 g/cm^3), and the particle sizes are an almost tenfold difference (0.45 and 5 μm).

Figure 4 shows the dielectric properties of the pristine $BaTiO_3$ film and Al-filled $BaTiO_3$ composite films with a various Al contents as functions of frequency. The dielectric properties of the 63 and 79 vol% Al-filled $BaTiO_3$ composite films could not be measured due to their short-circuit characteristics originated by huge Al contents. As shown in Fig. 4 (a), the relative dielectric constants of the composite films were increased in accordance with increased Al contents, especially in low frequency ranges. The relative dielectric constants of 0, 16, 21, 31, 38, 42, and 47 vol% Al-filled $BaTiO_3$ composite films at 1 kHz are 60.24, 76.05, 97.7, 112, 137.5, 162.25, and 1028.8, respectively. Even the relative dielectric constant of the 47 vol% Al-filled $BaTiO_3$ composite film was drastically increased up to 2395.2 at 100 Hz. However, the relative dielectric constants of Al-filled $BaTiO_3$ composite films showed high frequency dependence, whereas the pristine $BaTiO_3$ film have stable relative dielectric constants with frequency variation. The relative dielectric constants of 0, 16, 21, 31, 38, 42, and 47 vol% Al-filled $BaTiO_3$ composite films at 1 MHz are 58, 56, 62, 62.3, 61, 71.98, and 124.9, respectively. From this result, it was confirmed that the Al effects on the dielectric constants of the 16 ~ 38 vol% Al-filled $BaTiO_3$ composite films become offset at 1 MHz excepting the 47 vol% Al-filled $BaTiO_3$ composite film.

These phenomenon can be explained by the Maxwell-Wagner-Sillars (MWS) polarization (or interfacial polarization) and the micro-capacitor structure [11, 13]. The MWS polarization effect is induced by the space charge or interfacial polarization caused by traveling charge carriers in heterogeneous dielectrics. In our composite films, we considered that the free-electrons in the Al filler are piled up at the interfaces between Al filler and $BaTiO_3$ matrix by the applied electrical field leading to the interfacial polarization, and this causes large-scale field distortions in contrast to the other types of polarization (atomic, electronic, dipolar). Therefore, we can expect that the interfacial polarization by the traveling charge carriers (free-electrons) begin to lag as the frequency increases, and it confirmed from the Fig. 4 (a). In the theoretical viewpoint, this situation can be described as a Debye-type relaxation process, as follows:

$$\varepsilon^* = \varepsilon'_\infty + \frac{\varepsilon'_S - \varepsilon'_\infty}{1 + j\omega\tau} - j\frac{\sigma}{\omega} \tag{1}$$

$$\varepsilon' = \varepsilon'_\infty + \frac{\varepsilon'_S - \varepsilon'_\infty}{1 + \omega^2\tau^2} \tag{2}$$

$$\varepsilon'' = \frac{(\varepsilon'_S - \varepsilon'_\infty)\omega\tau}{1 + \omega^2\tau^2} + \frac{\sigma}{\omega} \tag{3}$$

here, ε', ε'' are the real and imaginary parts of the complex dielectric constant ε^* of the heterogeneous dielectric, ε_S and ε_∞ are the static and high-frequency dielectric constant, respectively, σ represents the conductivity and τ and ω are relaxation time and frequency. The Debye-type relaxation well describes the tendency of the dielectric constants of the composite films. However, the dielectric constant of the 47 vol% Al-filled $BaTiO_3$ composite film at 1 MHz was higher than the pristine $BaTiO_3$ film and the other Al-filled $BaTiO_3$ composite films. The reason for this, it was considered that the 47 vol% Al-filled $BaTiO_3$ composite film are affected by the micro-capacitor structure due to higher Al contents.

Figure 4 (b) show the dielectric loss of composite films. The dielectric loss of the pristine $BaTiO_3$ film was stable (0.02 at 1 MHz), whereas the dielectric losses of the 16, 21, 31, and 38 vol% Al-filled $BaTiO_3$ composite films were decreased with frequency variation. The high dielectric losses of the composite films are significant in low frequency ranges, and this decreases quickly when the frequency is increased. From the conductivity term σ/ω of the equation (3), this result can be expected and can be explained the

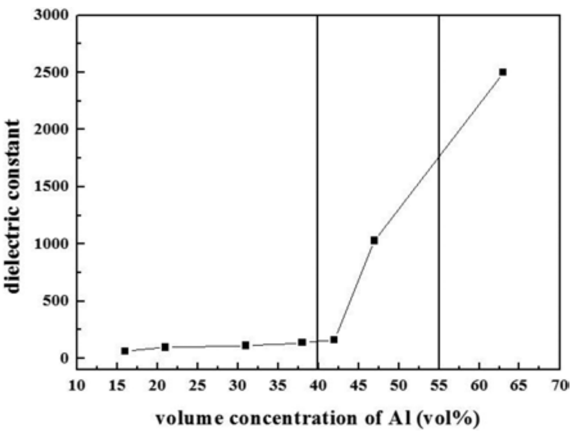

Fig. 5. Percolation threshold of Al-filled $BaTiO_3$ composite films at a frequency of 100 Hz.

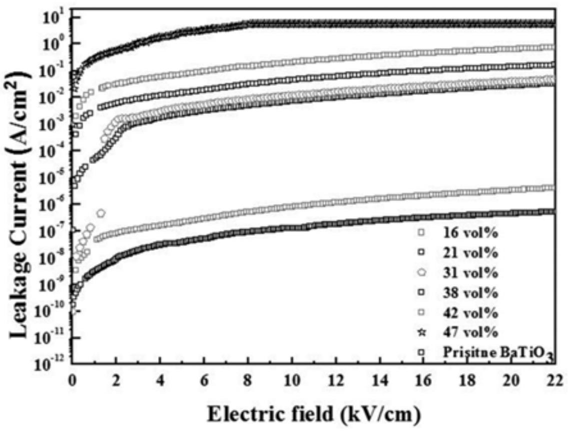

Fig. 6. Leakage current behavior for Al-filled $BaTiO_3$ composite film samples with 0, 16, 21, 31, 38, 42, and 47 vol% deposited on Cu substrate.

increased conductivity in the composite films caused by increased Al contents. On the other hand, the 47 vol% Al-filled $BaTiO_3$ composite films have the sum of losses from the conductivity term σ/ω and the Debye-type relaxation which is originated by the interfacial polarization.

The concentration dependence of the dielectric constant in the neighborhood of the percolation threshold is given by the following power law [14]:

$$\langle\varepsilon\rangle = \frac{\varepsilon_0}{|f_c - f|^q}$$

where ε is the matrix dielectric constant, fc is the filling factor, fc is the percolation threshold, and q is a critical exponent [15]. By the above Fig. 5, the percolation threshold is observed as ranging from 40 to 55 vol%. From calculated percolation threshold, the obtained values of q and f_c are 0.71 and 47 vol%, respectively. For these results, Al-filled $BaTiO_3$ composite film occurs the phase transition and increases the dielectric constant sharply over the 47 vol% Al constant.

The leakage current behavior for Al-filled $BaTiO_3$ composite films deposited by AD process with various aluminum content of 0 ~ 47 vol% on Cu substrates is shown in Fig. 6. The leakage current density of various volume percent (0, 16, 21, 31, 38, 42, and 47 vol%) Al-filled $BaTiO_3$ composite films was, 4.5×10^{-7}, 3.34×10^{-6}, 2.75×10^{-2}, 3.98×10^{-2}, 0.64, and 5.66 A/cm^{-2}, respectively at a high electric field of 20 kV/cm. The cause of this high current density of Al-filled $BaTiO_3$ composite films was considered to be the presence of a good deal of the aluminum metal powder in the $BaTiO_3$ matrix. The aluminum function of the conductive networks move charges by space charge polarization, and the electrical characterization confirms that the AD-deposited Al-filled BaTiO3 composite film had improved electrical properties. These findings were a result of the analysis of the good dielectric properties and the dielectric mechanism of the Al-filled $BaTiO_3$ composite films.

Conclusions

In this research, percolative Al-filled $BaTiO_3$ composite films of 5 μm thickness were fabricated by aerosol deposition process at room temperature. The aluminum particles were mixed in the $BaTiO_3$ matrix with 0, 16, 21, 31, 38, 42, 47, 63, and 79 vol%. The relative dielectric constants of 0, 16, 21, 31, 38, 42, and 47 vol% Al-filled $BaTiO_3$ composite films at 1 kHz are 60.24, 76.05, 97.7, 112, 137.5, 162.25, and 1028.8, respectively. The 47 vol% Al-filled $BaTiO_3$ composite films had high relative dielectric constant and low dielectric loss owing to the percolation effect. Also, the dielectric constant of Al-filled $BaTiO_3$ composite films appeared a strong dependence on frequency. The percolation threshold was observed as ranging from 40 to 55 vol%, for these results, Al-filled $BaTiO_3$ composite film occurred the phase transition and increased the dielectric constant sharply over the 47 vol% Al constant. The leakage current density of Al-filled $BaTiO_3$ composite films with 0, 16, 21, 31, 38, 42, and 47 vol% was 4.5×10^{-7}, 3.34×10^{-6}, 2.75×10^{-2}, 3.98×10^{-2}, 0.14, 0.64, and 5.66 A/cm^{-2}, respectively at a high electric field of 20 kV/cm. The AD-deposited Al-filled $BaTiO_3$ composite film is confirmed to have improved electrical properties.

References

1. Y. Imanaka and J. Akedo, Int. J. Appl. Ceram. Technol. 7 (2010) E23.
2. T. Sudo, H. Sasaki, N. Masuda, and J. L. Drewniak, IEEE Trans. Adv. Packag. 27 (2004) 304.
3. R. R. Tummala, M. Swaminathan, M. M. Tentzeris, J. Laskar, G. K. Chang, S. Sitaraman, D. Keezer, D. Guidotti, Z. Huang, K. Lim, L. Wan, S. K. Bhattacharya, V. Sundaram, F. Liu, and P. M. Raj, IEEE Trans. Adv. Packag. 27 (2004) 250.
4. C. Pecharroman, F. Esteban-Betegon, J. F. Bartolome, S. Lopez-Esteban, and J. S. Moya, Adv. Mater. 13, (2001)

1541.
5. Z. M. Dang, Y. H. Li, and C. W. Nan, Adv. Mater. 15, (2003) 625.
6. Y. Imanaka, M. Takenouchi, and J. Akedo, Journal of Crystal Growth 275 (2005) e1313.
7. J. Akedo, J. Am. Ceram. Soc. 89 (2006) 1834.
8. D. Popovici, H. Tsuda, and J. Akedo, Jpn. J. Appl. Phys. 47 (2008) 7490.
9. K. Sahner, M. Kaspar, and R. Moos, B: Chemical 139 (2009) 394.
10. H. Abe, M. Takashima, K. Sato, M. Natio, and J. Akedo, in *Proceedings of the 16th IEEE International Symposium on Applications of Ferroelectrics ISAF & Processing*, p. 539, IEEE, Piscataway, USA (2007).
11. T. Prodromakis and C. Papavassiliou, Applied Surface Science 255 (2009) 6989.
12. X. Ning, P. Y. Ping, and W. Zhuo, J. Am. Ceram. Soc. 95 (2012) 999.
13. B. Zazoum, E. David, and A. D. Ngo, Trans. Electr. Electron. Mater. 15(5) (2014) 235.
15 C. Pecharroman and J. S. Moya, Adv. Mater. 12 (2000) 294.