Formation of polymer/ceramic composite grain boundary capacitors by mechanical alloying

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A new technique to process ceramic/polymer grain boundary capacitors has been developed and demonstrated using $BaTiO_3$ as the ceramic conducting phase and LaRC-TPI polymer as the insulating phase. The particles were characterized by transmission electron microscopy and the dielectric properties of the capacitors were measured at room temperature and 100 kHz. The overall best composite grain boundary capacitor was made with 40 vol% polymer after milling the powder for 1 h. It had a dielectric constant of 58 and a dielectric loss of 0.01. The dielectric properties of the grain boundary capacitors could be manipulated by changing processing variables such as milling time and volume fraction of polymer.

(Keywords: grain boundary capacitors; dielectric performance; polymer/ceramic composites)

INTRODUCTION

The demand for smaller capacitors has increased in recent years as electronic components have become smaller. Ceramic grain boundary capacitors have been identified as a method to miniaturize capacitors and maintain a high dielectric constant[1,2]. A grain boundary capacitor is a particulate composite made of discrete conducting grains surrounded by a continuous insulating layer. When an electric field is applied to the grain boundary capacitor, each pair of adjacent conducting grains separated by an insulating layer forms a miniature capacitor. The insulating layer acts as the dielectric. The permittivity, E, of a grain boundary capacitor can be calculated by:

$$E = E_{ri}(d_a/d_i) \qquad (1)$$

where E_{ri} is the relative permittivity of free space ($8.854 \times 10^{-12}\,F\,m^{-1}$), d_a is the diameter of the conductive grain, and d_i is the thickness of the insulating layer.

Several methods to make ceramic grain boundary capacitors have been reported in the literature. One method is to reduce ceramic particles such as $BaTiO_3$ to produce semiconducting particles, then reoxidize the surface to produce an insulating layer[1]. A second method is to use a two-phase insulating ceramic/conducting ceramic system, where the insulating ceramic is chemically different from the semiconducting material[1]. A third method is to coat an insulating polymer onto ceramic particles to form a two-phase system[3]. In previous work, a polymer/ceramic grain boundary capacitor was fabricated by solution coating an insulating polymer, LaRC-TPI, onto a semiconducting ceramic layer capacitor. Its dielectric loss was approximately one order of magnitude less than that of a one-layer capacitor at room temperature, and became comparatively more efficient as temperature increased. Since the permittivity of a grain boundary capacitor depends only on the ratio of the diameter of the semiconducting grains to the thickness of the insulating layer, it should be possible to increase the dielectric constant by decreasing the thickness of the polymer coating. Unfortunately, it is difficult to control the thickness of the polymer coating via the solution coating technique used in previous studies[3].

In this paper, we report on a new processing technique to make a polymer/ceramic composite grain boundary capacitor which provides more control over the thickness of the polymer coating. In this technique, the polymer and ceramic powders are mechanically alloyed together. Mechanical alloying is a solid state process developed by Benjamin[4] for production of oxide dispersion strengthened superalloys. The same technique can be used to intimately combine ceramic and polymer powders. As a result of the mechanical alloying, each ceramic particle is coated with a thin layer of polymer. In traditional metal or ceramic mechanical alloying, a new composition is formed at the interface; however, in this system, mechanical alloying implies improving the dispersion of the two phases and the uniformity of the coating, without creating a new phase. The coated particles are then pressed together to form a composite grain boundary capacitor. This technique provides better control over polymer coating thickness and uniformity.

EXPERIMENTAL

Barium titanate ($BaTiO_3$) ceramic powder (2–6 μm), supplied by Alfa Chemical, was reduced in a hydrogen

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atmosphere at 1144°C for 8 h. This semiconducting powder was then mixed with a thermoplastic polyimide (LaRC-TPI) powder, supplied by Mitsui Toatsu, in various volumetric combinations. The powder blends were mechanically alloyed together in a SPEX 8000 Mixer/Mill. The ceramic and polymer powders were placed in a tungsten carbide vial with two tungsten carbide balls. The powder and ball charges in the vial were fixed to maintain a constant energy input for every batch. The vial was agitated in the ball mill, resulting in a series of high energy impacts in which the powders were fractured, deformed and fused together. The result was $BaTiO_3$ particles, smaller than the initial powder, with polymer fused around them. The milling time and volume fraction of polymer in each batch were varied to obtain different sizes of ceramic particles with varying polymer coating thicknesses (i.e. varying d_a/d_i in equation (1)). These mechanically alloyed particles were then hot pressed into composite discs at 300°C and 69 MPa (10 000 psi) for 30 min.

The $BaTiO_3$ particles, milled alone and milled with polymer, were examined using transmission electron microscopy (TEM). Copper leads were attached to the surfaces of the pressed discs using silver epoxy paste supplied by Epoxy Tech, Inc. The capacitance and dielectric loss were measured using an HP 4192A LF impedance analyser at room temperature and 100 kHz. The dielectric constant (K) was calculated using the formula:

$$K=(Cd)/(E_{ri}A) \qquad (2)$$

where C is the measured capacitance, A is the surface area of the capacitor, d is the thickness of the silver coated disc, and E_{ri} is the relative permittivity of free space, as defined previously.

RESULTS

Transmission electron microscopy

Typical TEM micrographs of the $BaTiO_3$ particles milled alone for 1 h and milled with 40 vol% polymer for 1 h are shown in *Figures 1* and *2*, respectively. The black areas represent material through which the electron beam was not transmitted (i.e. ceramic) and the lighter, grey areas represent material through which the electron beam was transmitted (i.e. polymer). The average size of the milled $BaTiO_3$ particles was less than 2 μm. The $BaTiO_3$ particles milled with polymer were coated with polymer, as evidenced by the grey areas surrounding the black particles in *Figure 2*. Most of the particles were agglomerated into groups of varying sizes with polymer intermixed. During mechanical alloying, the high energy impacts caused the polymer to flow and coat the particles and fuse them together. A minimum of 40 vol% polymer was required to fully coat the ceramic particles. Otherwise, every $BaTiO_3$ particle was not surrounded by polymer. After just 1 h of milling with 40 vol% polymer or more, all the ceramic particles were surrounded with polymer. However, if the volume fraction of polymer was 60 vol% or more, additional milling time was required for all of the polymer to adhere to the ceramic particles. With such a large volume fraction of polymer and 3 h or less of milling, the ceramic particles were coated, but additional free polymer appeared in TEM micrographs. Unfortunately, additional milling time also decreased the average particle size of $BaTiO_3$. Since dielectric constant in a grain boundary capacitor is proportional to the ceramic grain size, it was undesirable to decrease the $BaTiO_3$ particle size. TEM suggested that mechanical alloying was an effective procedure to coat $BaTiO_3$ particles with LaRC-TPI polymer and that the thickness of the coating increased with polymer volume fraction.

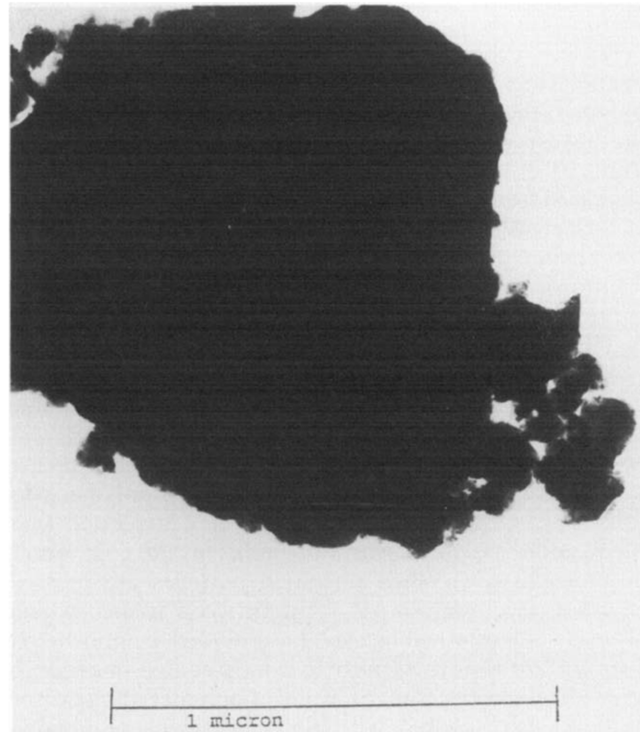

Figure 1 Transmission electron micrograph of $BaTiO_3$ particles milled for 1 h

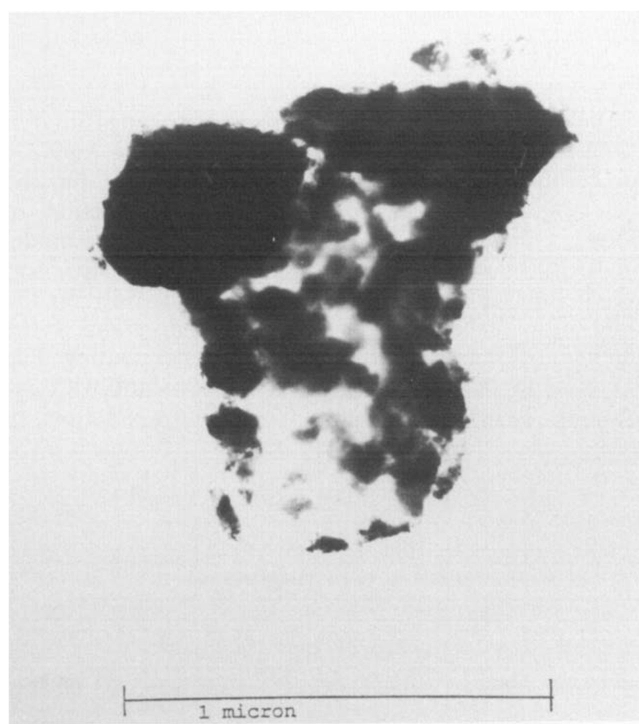

Figure 2 Transmission electron micrograph of $BaTiO_3$ particles milled with 40 vol% LaRC-TPI polymer for 1 h

Dielectric loss

Dielectric loss of each capacitor was measured at room temperature and 100 kHz. For every volume fraction of polymer, the composite moulded after 1 h of milling had the lowest value of dielectric loss; these values ranged from 0.02 to 0.009 as volume fraction of polymer increased from 20 to 70%. This was lower than the value of dielectric loss achieved by the best polymer/ceramic composite grain boundary capacitor made by the solution coating technique (dielectric loss = 0.04) and is considerably lower than the value of 0.7 typical[3] of $BaTiO_3$.

As shown in *Figure 3* for composites made from powder milled for 1 h, the dielectric loss decreased as volume fraction of polymer increased. The same trend was observed for milling times of 1, 3 or 5 h. The decrease in dielectric loss at approximately 40 vol% polymer was consistent with the TEM results, which suggested that 20–30 vol% polymer was not sufficient to coat every ceramic particle. When uncoated particles are pressed together, electrical shorts form between grains, which promotes charge leakage in the moulded composite. It is important that each particle is fully coated in order to have low dielectric loss. At 40 vol% polymer, the ceramic particles were coated with polymer, which eliminated electrical shorts and decreased the value of dielectric loss significantly. Adding more than 40 vol% polymer had little effect on dielectric loss; however, it did have an effect on the storage capabilities or capacitance of the composite grain boundary capacitor, as measured by the dielectric constant.

Dielectric constant

Dielectric constant of each capacitor was measured at room temperature and 100 kHz. As shown in *Figure 4* for composites made from powder milled for 1 h, the dielectric constant decreased as volume fraction of polymer increased. This was consistent with the model for dielectric constant for a grain boundary capacitor, which states that the capacitance depends only on the ratio of the diameter of the semiconducting grains to the thickness of the insulating layer or polymer coating. The same trend of decreasing dielectric constant with increasing polymer thickness (i.e. volume fraction of polymer) was observed for every milling time, as shown in *Figure 5*. If the powders were not alloyed together before moulding (or alloyed for just 15–45 min), the polymer did not effectively surround the ceramic particles. This was suggested by TEM and verified by the nearly constant value of the dielectric constant as a function of volume fraction for composites made from powder blends that were not milled. The composites made with powder milled for 1 h had the highest dielectric constant. Milling for longer periods was not required to coat the ceramic particles with polymer, and resulted in smaller ceramic grains, as noted with TEM, thereby decreasing the capacitance. The highest value of the dielectric constant obtained for the capacitors manufactured in this study was 64, for a composite with 20 vol% polymer after 1 h of milling. This was approximately twice the value of the dielectric constant (K) for the best composite grain boundary capacitor made by the solution coating technique reported earlier ($K = 31$), yet lower than that of $BaTiO_3$ ($K = 1500$). The dielectric loss of the same capacitor was 0.02. This dielectric loss was an order of magnitude lower than that of $BaTiO_3$; however, it

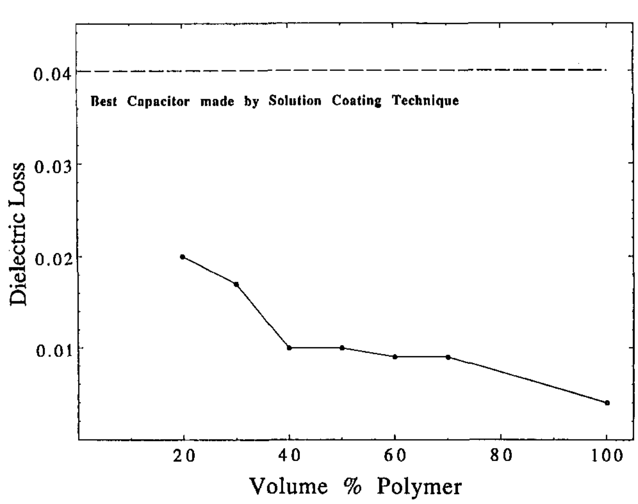

Figure 3 Dielectric loss measured at room temperature and 100 kHz *versus* vol% polymer for $BaTiO_3$/LaRC-TPI grain boundary capacitors moulded after milling powder for 1 h

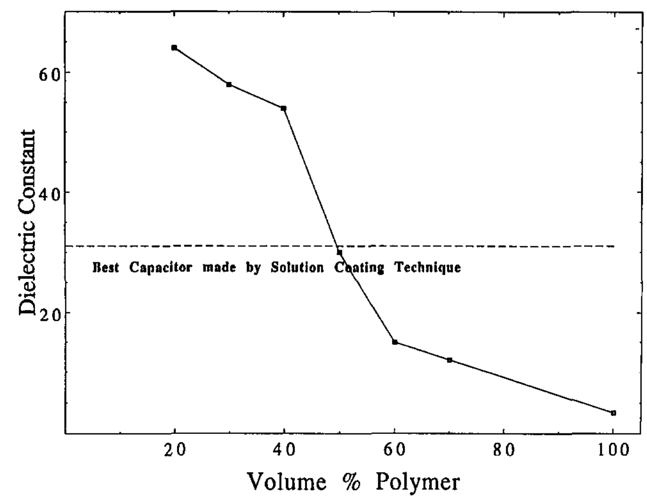

Figure 4 Dielectric constant measured at room temperature and 100 kHz *versus* vol% polymer for $BaTiO_3$/LaRC-TPI grain boundary capacitors moulded after milling powder for 1 h

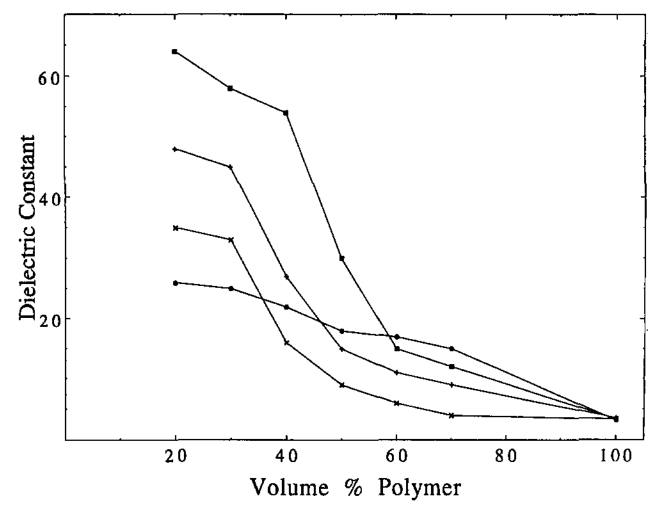

Figure 5 Dielectric constant measured at room temperature and 100 kHz *versus* vol% polymer for $BaTiO_3$/LaRC-TPI grain boundary capacitors. Results are shown for composites moulded after milling powder for 1 h (□), 0 h (+), 2 h (×), and 3 h (○)

could be further decreased (at the expense of the dielectric constant) by increasing the polymer coating thickness. By looking at *Figures 3* and *4*, it is apparent that the dielectric constant did not drop significantly until after 50 vol% polymer was added; however, the dielectric loss dropped abruptly when 40 vol% polymer was added. This indicated that a 40 vol% polymer/ceramic grain boundary capacitor moulded after 1 h of milling exhibited the best overall performance. It had a relatively high value of the dielectric constant (58) and a low value for the dielectric loss (0.01). These values are much better than those obtained from the best polymer/ceramic grain boundary capacitor made by the solution coating technique, which had a dielectric constant of 31 and a dielectric loss of 0.04 at the same frequency and temperature[3].

SUMMARY AND CONCLUSIONS

Polymer/ceramic composite grain boundary capacitors with $BaTiO_3$ semiconducting grains and LaRC-TPI polymer were made using a mechanical alloying technique, and were characterized. By controlling the volume fraction of polymer and alloying time during processing, the dielectric loss and dielectric constant could be manipulated. Dielectric constant and dielectric loss decreased as volume fraction of polymer increased. TEM results suggest that at least 40 vol% polymer was needed to fully coat the ceramic particles with polymer in order to make a low loss composite capacitor, and this is supported by the dielectric measurements. Mechanically alloying for 1 h was sufficient to coat the $BaTiO_3$ particles with LaRC-TPI polymer without greatly reducing the $BaTiO_3$ particle size. For composite grain boundary capacitors made with powders milled for 1 h, the dielectric constant did not drop significantly until after 50 vol% polymer was added; therefore, the composite moulded from a powder mix of 40 vol% polymer milled for 1 h performed the best. It had a relatively high value of dielectric constant (58) and a low value of dielectric loss (0.01); these values are better than those obtained from the best composite capacitor made by the solution coating technique. The capacitance of polymer/ceramic composite grain boundary capacitors may be improved by using ceramic powder with a larger initial particle size.

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