

Improvement in the volume efficiency of multilayered ceramic capacitors (MLCCs)

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Abstract An attempt was made to improve the conventional lamination process in the multilayered ceramic capacitors (MLCCs) fabrication by adapting a solvent treatment on the BaTiO₃ green sheets. During the lamination process, additional particle rearrangement in the BaTiO₃ green block was stimulated by solvent treatment. This rearrangement resulted in a more compact structure of the BaTiO₃ green sheets compared to that obtained through the conventional lamination process. The overall thickness of BaTiO₃/Ni/BaTiO₃ laminates was also reduced after solvent treatment. It is suggested that miniaturization in the fabrication of MLCCs can be improved by adapting a solvent treatment during the lamination process.

Keywords Multilayered ceramic capacitors (MLCCs) · Interface properties · Microstructure · Dielectric properties

1 Introduction

Multilayer ceramic capacitors (MLCCs) are considered to be one of the most passive components in electronic devices [1]. Currently, the miniaturization trend in the fabrication

of electronic devices demands capacitors with increasingly smaller size and higher dielectric permittivity [1–6]. To meet this requirement, manufacturers have attempted to reduce the thickness of the active layer (i.e. the ceramic dielectric layer). To achieve this, smaller size powder has been used as a dielectric material [7–10], and the optimization of casting and lamination has been explored [11, 12]. The thickness of the active layer can be reduced by particle rearrangement during casting and lamination. There are a number of reports [1–6] that describe the effect of particle rearrangement during casting on the thickness of the active layer. On the other hand, few have studied the effect of particle rearrangement during lamination [12]. Nevertheless, these studies focus mainly on the effect of chemical structure and molecular mass (*M_r*) of the binder, and lamination pressure on the rearrangement of particles surrounded by the polymer vehicle.

This work describes the enhancement of particle rearrangement during the lamination process and the resulting decrease in thickness of the BaTiO₃/Ni/BaTiO₃ laminates. To bring about intensive particle rearrangement during the lamination process, BaTiO₃ green sheets were treated by various solvents of different solubility parameters and surface tensions. Solvent flows into the open pores of BaTiO₃ green sheets and raises the viscous flow of the binder. Simultaneously, it has the capability to facilitate the movement or rearrangement of the particles inside the green sheet. This rearrangement can reduce the sheet thickness as well as result in a homogeneous compaction of the BaTiO₃ green sheet.

In this study, the physicochemical properties of various solvents such as the solubility parameter and surface tension were correlated with particle rearrangement and the resulting thickness of the BaTiO₃/Ni/BaTiO₃ laminates.

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Table 1 Physicochemical properties of selected solvents; functional group, surface tension, and solubility parameter [13, 14].

Solvent	Functional group	Surface tension (dynes/cm)	Solubility parameters (MPa ^{1/2}) ^a	
			Polarity	Hydrogen bonding
Mineral spirit	None	25.84	0	0.2
Toluene	None	28.50	2	1.4
Ethanol	hydroxyl (OH)	22.75	19.5	8.8
Toluene	hydroxyl (OH)	20.11	7.9	10.2
Poly (vinyl butyral)	hydroxyl (OH)	–	4.4	13

^aSources: Refs 13 and 14.

2 Experimental procedure

A commercial BaTiO₃ powder (BT-01, Sakai Chemicals, Japan) was used in this study. The powder had a BET specific surface area of 12.1 ± 0.05 m²/g with a nominal particle diameter of 100 nm. To remove any physically adsorbed water and volatile organics on the powder surface, the powder was vacuum dried at 100°C for 24 h. A mixture of toluene and ethanol with a ratio fixed at a mass fraction (%) of 60/40 toluene/ethanol was chosen as the suspending medium based upon a previous study [2].

Phosphate ester (RE610, Toho Chemical Industry, Tokyo, Japan) with a molecular mass of $M_r = 1500\text{--}2000$ g/mol was used as a dispersant. Poly (vinyl butyral) resin (PVB, Sekisui Chemical, Osaka, Japan), was used as a binder.

Mineral spirits (Shell, USA), toluene (Samchun Chemicals, Korea), ethanol (Samchun Chemicals, Korea), and terpineol (Fluka, Switzerland) were used for the solvent treatment. Equilibrium surface tension measurements were performed by the Wilhelmy plate method using a Krüss processor tensiometer K100 at 25°C. In the Wilhelmy plate method, the sample is held by an electrobalance and is then immersed and retracted, at a constant speed, into and out of the liquid contained in a beaker. During these cycles the force acting on the plate vs. depth of immersion are recorded. The physicochemical properties of solvents and PVB are summarized in Table 1 [13, 14]. Mineral spirits were chosen as a representative of nonpolar solvents. Toluene has little polar nature due to the presence of the benzene pendant group. Ethanol was selected as a solvent for the PVB binder and has a highly polar component of solubility parameter of 19.5 [15].

The BaTiO₃ suspensions were prepared at a volume fraction of 10%. Stock solutions of RE610 and PVB were prepared in mixtures of toluene and ethanol. The BaTiO₃ powders were first mixed with the dispersant stock solution and then ball-milled for 3 h using zirconia grinding media to ensure thorough and uniform wetting of all particles. PVB stock solution was then added to the suspension. The prepared suspensions were ball-milled for additional 20 h at room temperature.

Green sheets were cast using a table caster (Samsung Electromechanics Co. Ltd, Suwon, Korea) with a single doctor

blade at a casting speed of 177 cm/min. The thickness of a single layer of green tape was approximately 6 μm. The tapes were dried in the drying zone of the tape caster using a bottom heating system at 50°C.

The solvent evaporation method was used for homogeneous sheet treatment. BaTiO₃ sheets were warmed in a double boiler to a limited extent. For the solvent treatment of the green sheet surface, green sheets were exposed by solvent vapor which was generated at the temperature equivalent to 80% of boiling temperature of each solvent. The exposure time was 20 min.

The green tapes were finally laminated with a Ni inner electrode and then were isostatically pressed under 300 MPa pressure at 65°C for 20 min.

The thickness of the BaTiO₃/Ni/BaTiO₃ laminates was measured using a micrometer. Each reported measurement was obtained by averaging 10 values.

The surfaces of the pressed laminates were examined using a scanning electron microscope (SEM, JSM 5900LV, Jeol, Tokyo, Japan). A small segment of each solvent-treated, pressed sample was mechanically removed and transferred into a sample holder. For cross-sectional observation of the laminates, the laminates were quenched in liquid N₂ and then fractured to yield observable sandwich structures. The samples were coated with gold and their microstructures were observed by using SEM, operated at an accelerating voltage of 20 kV.

3 Results and discussion

Figure 1 shows the influence of the solvent treatment on sheet thickness. The BaTiO₃ sheet with the thickness of 18 μm was prepared by using tape casting method. It was obtained that the thickness of the sheet is apparently reduced by the solvent treatment. The sheet thickness by the solvent treatment with mineral spirit, toluene, ethanol, and terpineol was decreased by 11.8, 19.4, 30.4, and 32.6% as the reduction percentage. It indicates that the polar solvents such as ethanol and terpineol are more effective for the decrease in sheet thickness by solvent treatment, compared to the non-polar solvent including mineral spirit and toluene (see Table 1). However, it is of

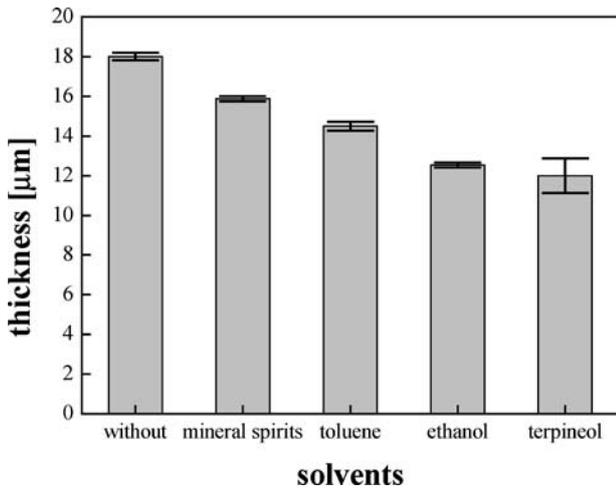


Fig. 1 Thickness measurements of BaTiO₃/Ni/BaTiO₃ structures treated by selected solvents

interest that terpineol-treated sheet exhibits significantly different sheet properties from the ethanol-treated sheet, even though the volume efficiency of the sheets by terpineol and ethanol is almost same. It was found that the terpineol treatment renders the BaTiO₃ sheet to extremely wet and crumple and thus it significantly deteriorates the homogeneity, the microtopography, and the mechanical properties such as tensile strength and elongation of the sheet. This is likely attributed to the high affinity between terpineol and PVB due to the similar solubility parameter of two species. As the terpineol-treated sheet is easily warped and torn down in the fabrication process, it was impossible to successfully fabricate the dielectric active layer in MLCC. Therefore, this result reflects that the careful design of a proper solvent system should be made with the concept not only considering of solubility parameter of the solvent but also sustaining the basic mechanical properties of the sheet during the solvent treatment.

Fig. 2 Microstructures of the fractured surface of BaTiO₃/Ni/BaTiO₃ structures treated by ethanol

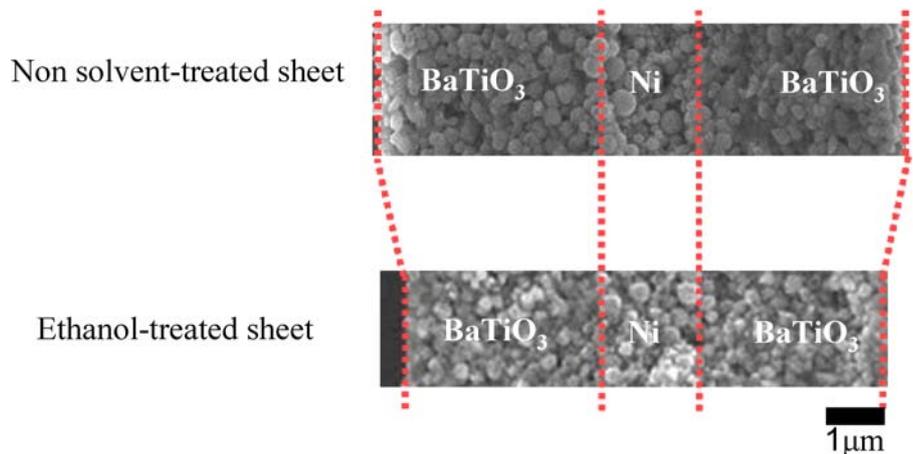


Figure 2 is the green microstructures in the fractured surface of BaTiO₃/Ni/BaTiO₃ laminates fabricated with BaTiO₃ sheets with and without ethanol treatment observed by SEM. The layer thickness of ethanol-treated BaTiO₃ sheet in the laminate is significantly decreased compared to the non-treated sheet and the mechanical properties of the ethanol-treated sheet are well sustained. Also, it was found that the packing density of the particles in the sheet is increased with ethanol treatment. This result corresponded well with the decrease in thickness of the green block by solvent treatment, as shown in Fig. 1.

The volume efficiency of the sheet in MLCCs by the solvent treatment was mainly attributed to the intrusion behavior of the solvent vapor molecule into the sheet. During solvent treatment, the solvent intruded into the open pores which were formed during the drying process for the preparation of green sheet. The intrusion of solvent vapor molecules was affected by the interaction between the solvent vapor molecules and polymer matrix as well as flow rates, pressures, pore sizes, and the fluid viscosity [16]. The interaction between the solvent molecules and polymer matrix can be manipulated by alterations in the solubility parameter, which provides an easy numerical method for rapidly predicting the extent of interaction between materials, particularly of liquids and polymers [17]. PVB binder used in this study is swollen by the polar solvent due to the residual PVA hydrophilic chains present in the PVB binder. Ethanol has hydrophilic OH functional groups and thus it has high affinity for the PVB binder. Therefore, the PVB binder matrix in the BaTiO₃ green sheet treated by ethanol was swollen and thus it allowed a viscous flow of PVB binder in the BaTiO₃ green sheet. This leads to the decrease in frictional forces between the BaTiO₃ particles and resultant particle bridging. This was simultaneously capable of allowing the movement or rearrangement of particles inside the green sheet. The packing density was increased through the particle rearrangement and thus the thickness of the BaTiO₃ sheet was decreased. On the other

hand, non-polar solvents like mineral spirit and toluene have lower affinity with PVB binder and thus they are not beneficial for the viscous flow of the PVB binder matrix and the resulting particle rearrangement, which resulted in the relatively low volume efficiency.

Additionally, the intrusion depth of the solvent was directly related to the diffusion of solvent molecules into the polymer matrix. The polymer matrix, which was swollen by the solvent, acted as a porous medium, which resulted in an internal pressure similar to capillary pressure. Molecular interaction is the driving force for diffusion and can be predicted by surface tension. The molecular interaction between the matrix and the solvent decreased as surface tension of solvent increased. Thus, it is suggested that ethanol with lower surface tension (22.75 dynes/cm) can deeply diffuse and intrude into the PVB matrix compared to mineral spirit (25.84 dynes/cm) and toluene (28.50 dynes/cm) with higher surface tension.

Consequently, these results propose that the particle rearrangement and the resulting decrease in the thickness of the BaTiO₃ green sheet in MLCC can be modulated by a proper solvent treatment, while considering physicochemical properties of solvent such as the solubility parameter and the surface tension of the solvent.

4 Conclusions

The improvement of the lamination process in the fabrication of MLCCs was attempted by solvent treatment on the BaTiO₃ green sheet surface before the printing of inner electrode. The particle rearrangement in the BaTiO₃ green block was successfully modulated by solvent treatment. The thickness of green blocks treated by mineral spirits, toluene, ethanol, and terpineol was decreased by 11.76, 19.44, 30.38, and 32.58%, respectively.

It was revealed that solvents with a high polar component of the solubility parameter resulted in thinner BaTiO₃ green blocks and the intrusion depth of the solvent was affected by the surface tension of solvent. These results are consistent with the observation of the BaTiO₃/Ni/BaTiO₃ laminate

microstructure. MLCCs with high volume efficiency can be obtained by introducing solvent treatment to the fabrication process. These findings may impact the fabrication of ultra thin multilayer ceramic capacitors under 1 μm.

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