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Barium titanate screen-printed thick films

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Abstract

Barium titanate (BT) thick films were prepared from mechanically activated powders based on $BaCO_3$ and TiO_2. After homogenization and milling in a high-energy vibro mill, the powders were calcined at 700 °C for 2 h by slow heating and cooling rates. A thick film paste was prepared by mixing BT fine powders with small amount of low temperature sintering aid and organic binder. The thick films were screen-printed on alumina substrates electroded with Ag-Pd. The BT films were sintered at 850 °C for 1 h. The thickness was 25–75 μm depending of number of layers. The microstructure of thick films and the compatibility between BT layers and substrate were investigated by SEM .Results of dielectric property measurements are also reported.

Keywords: A. Films; C. Dielectric properties; D. $BaTiO_3$ and titanates; Multilayer ceramic capacitors

1. Introduction

It is good reason to believe that the gap between bulk materials and thin films can be filled with materials suitably designed and appropriately processed [1]. Indeed, the difficulty in the preparation of thin films in various thickness ranges is the primary reason for their notable lack of availability. Notwithstanding the difficulties, thick films still hold promise as a interesting area of research since it is generally recognized that certain phenomena such as electroptic effects, piezoelectricity or capacity can be profitably applied to devices within them [2].

Barium titanate ($BaTiO_3$) is used extensively as the dielectric in ceramic capacitors, particularly due to its high dielectric constant and low loss characteristics. As advanced miniaturization requires smaller circuit area, the multilayer ceramic capacitors with higher volumetric efficiency (MLCCs) were developed. Conventionally, $BaTiO_3$-based materials are manufactured at high temperature, by solid-state reaction or from chemically derived intermediates. These methods typically produce large, agglomerated particles that consequently are milled to obtain mean particle sizes between 0.5 and 1.5 μm. The large, non-uniform particle size of conventionally prepared $BaTiO_3$, generally limits the ability to fabricate reliable MLCCs with various dielectric layer thickness [3].

Many researchers have been reported on the deposition mechanisms with different powders [4–7]. As the film thickness increases, the difficulty in preparing thick film is well recognized. The sub-micron powders are widely available, and an effective method to prepare a thick film of barium titanate (BT) is by using reliable ceramic powders. One possibility to obtain the required grains size is by the mechanical activation of raw materials during powder process preparation using high-energy milling process. The mechanical activation is one of the most effective methods for obtaining highly disperse systems due to mechanical action stress fields form in solids. This effect results of changes of free energy, leading to release of heat, formation of a new surface,

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formation of different crystal lattice defects and initiation of solid state chemical reaction [8,9]. Energy parameters of the system and the amount of accumulated energy during mechanical activation have been changed during process [10]. Generally, plastic deformation of surface layers of particles due to high local stress on particle contacts is caused by the energy accumulated in the deformed material. The accumulated deformation energy determines irreversible changes of the crystal structure and smaller particles size [11]. As the consequence of deformation, the change of crystal and microstructure of material leads to change of their properties. Usually sub-micron grain size of ceramic powders could exceedingly advance their applications in thick and thin films technology, requiring for application in electronics.

It is known that thin films may be deposited on substrates by various techniques, for example, sputtering, evaporation, sol-gel, etc. processes [12,13]. Typical film thickness are between 0.1 and 1.0 μm. Meanwhile, the layer thicker than a few micrometers could not be achieved by these methods.

Thick film technology is a method whereby resistive, conductive and dielectric pastes are typically applied to ceramic substrates [14]. The technology of producing thick films of various types, involving a number of steps, is common to all of them. Unlike thin films, the number of processes capable of producing high-quality thick films are rather limited to specifically mentioned sol-gel, MOD and screen printing. Previous investigators have employed dip coating, spin coating and chemical vapor deposition technique with limited success on films up to 25 μm in thickness. However, by experience, it was shown that films thicker than 2 or 3 μm, which could be prepared by previously mentioned deposition techniques, had a tendency to undergo cracking, debonding from substrates, increasing the roughness [15,16]. Otherwise, the deposition of thick film pastes by screen printing is a relatively simple and convenient method to produce thicker layers with thickness up to 100 μm.

Screen printing is relatively mature technology. This process is useful to accommodate the demands of miniaturization, circuit complexity, multilayer assembles, or high frequencies [17,18]. Generally, the characteristics of thick film ferroelectric materials are similar to the characteristics of bulk materials.

The circuits defined by screen printing are fired typically at 850 °C to fuse the films to the substrates and to produce the desired functions. This temperature is higher than for thin films, thus increasing the possibility of interactions with either the electrodes or substrates, and consequently to their possible degradation. Adhesion between support and film, as similar temperature expansion coefficients of the thick films and substrate are also important. Low-melting glasses were used to isolate the top layer conductor from the rest of the circuit below. However, because of undesirable interaction between the glass phase and the overlying conductor, crystallizable glasses with low dielectric constants could appeared.

In the present work, $BaTiO_3$ thick films were prepared from mechanically activated powders based on $BaCO_3$ and TiO_2 to obtain sub-micron grain sized powders. A thick film paste was prepared by mixing BT fine powders and organic vehicle, screen-printed on alumina substrates, coated with electrodes based on Ag-Pd and sintered at 850 °C for 1 h. The microstructure and dielectric properties were determined and the effect of the number of layers in the thick film was related.

2. Experimental

2.1. Powder preparation

The mixture of $BaCO_3$ (Merck PA 99%) and TiO_2 (Ventron PA 99.8%) powders in relation Ba/Ti = 1 and LiF (Merck PA 99.3%) in amount of 1.5 wt.% were homogenized in planetary ball mill for 120 min in the mixture 1:1 of de-mineralized water and ethyl alcohol. It was reported previously that LiF in small amount presents a sintering aid [19]. Through the liquid formation via LIF doping, barium titanate could be sintered at the temperature lower than it is usually for solid state BT. It was mentioned in the previous papers [20,21]. The homogenized powders were mechanically activated in a high-energy vibromill with rings (TM MN 954/3) in air for 90 min. An organic binder (aqueous solution of 2 wt.% polyvinyl alcohol) was added, powders were dried, milled, sieved and pressed at 400 MPa. After calcination at 800 °C for 1 h, pellets were crushed, milled and sieved.

2.2. Paste preparation

The paste was prepared from the suspension of organic material (resin, organic solvent and some additive to improve rheological behavior of paste) and calcinated BT powders, in relation 30:70. To get better adhesion between paste and substrate it was added low temperature melting glass in powder form. The viscosity of the prepared paste was adjusted by grindometer in the range $0.6–1.1\times10^2$ mP s for a shear rate of 10 s^{-1}.

2.3. Substrates and electrodes

Alumina substrates were used as a commercial product (Alcoa). The electrode materials were produced specially for the screen printing technique (IRITEL) and presented as a silver/palladium mixture (Ag-Pd 70/30).

2.4. Film preparation

The bottom electrode (Ag-Pd 70/30) was screen printed on the Al_2O_3 substrate and fired at 600 °C for 1 h. On the fired electrode, barium titanate layer was screen-printed and sintered at 850 °C in air flow during 1 h. After firing of the dielectric layer, the upper electrode (Ag-Pd 70/30) was deposited, and after that dried and fired at the same temperature–time regime as for bottom electrode. The obtained films usually had thickness that ranged from 25 to 75 μm, depending on the number of layers.

2.5. Characterization

The particle size analysis after mechanical activation has shown that the obtained particles were less then 0.1 μm. After calcination, milling and sieving the particle size was in the range 0.2–0.5 μm. The rather strong agglomerates were destroyed by ultrasonic milling.

Specimens for SEM examination were prepared in planar and cross-sectional views of the films. The thickness of the films was measured from cross-sectional analysis of the samples. The microstructure and chemical composition were analysed using a scanning electron microscope (TOPCON SM 300) coupled with a EDS (PGT).

The electrical measurements, capacitance and dielectric losses were performed using a HP 4291A coupled with a furnace. The dielectric constant and Curie temperature were determined for thick film samples with up to three layers.

3. Results and discussion

A major change in the past decade is the increase in the number of chips and multilayer dielectrics. Chips and myltilayers still use thick film technology, but the complexity is demonstrated in precisely deposition onto substrates. The difficulty in fabricating films in the needful thickness range is the primary reason for their notable lack of availability. When thick films are being deposited, the differences in thermal coefficients of dielectric materials, electrodes and support can lead to stress (compressive or tensile) much more expressed than in a thin one. Furthermore, the elastic module of the substrate as well as the film must also be taken into consideration during preparation of thick films since their different modules have to determine stress levels [22]. Taken all together, these stresses, specially tensile stresses, can produce disastrous results such as delaminating of the film from the substrate and when the films become thicker the macro-cracking of films may appear or can lead to appearance of micro-cracks or pores in film. In general, it should be noted that with thick films most of the substrate and processing considerations are magnified in comparison to thin films because of the extended processing times at temperature and the desire to deposit a maximum film thickness per layer [15].

The substrates selected for our investigation were based on pure Al_2O_3. Al_2O_3 substrates have a good chemical compatibility with the film, so the inter-diffusion is minimized. Previous experiments have been shown that the substrates do not put the BT thick films neither in compression nor in tension. The most common problems in thick films relating to appearance of cracks was not observed in investigated case.

The cross-section of two layers screen printed BT film is presented at Fig. 1. The thickness of one, two and three layers of thick film, measured by SEM, was approximately 25, 50 and 75 μm, respectively. The adhesion of Ag-Pd/BT layer was rather strong, and it was not possible to easily peel off the alumina substrate. In the same time, the adhesion of the bottom electrode layer overprinted with alumina, and upper electrode overprinted with BT was good; it could not be peeled off with Scotch tape. The results indicate that the adhesion

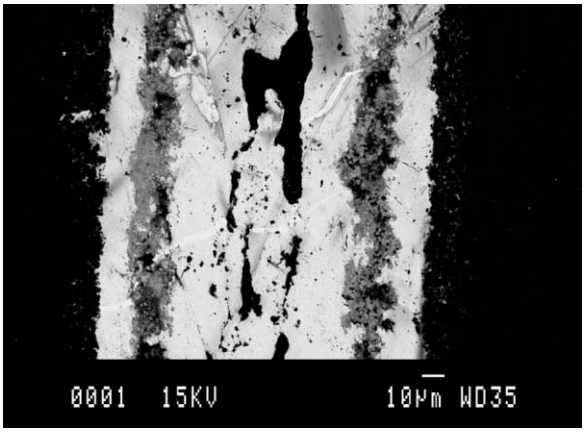

Fig. 1. The cross-section of two layers barium titanate thick film deposited on Al_2O_3 substrate.

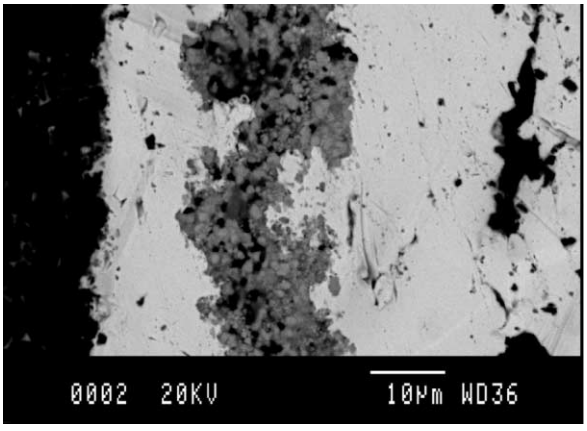

Fig. 2. SEM analysis of barium titanate thick films presenting the small grain sized barium titanate.

of the electrode film to alumina substrate and to barium titanate are quite well and that the firing process does not decrease the stability of inter connections.

The grain size of BT thick film is rather regular with rounded grains and withouth obvious presence of secondary phases (Fig. 2). The grain size was less than 1 μm, approximately 800 nm. The small grain size is caused not only due to low sintering temperature and the rather short time for firing process but also resulted from a tribophysical activation process that increases the surface area of starting powders.

The dielectric properties of BT thick films are presented in Figs. 3–5. The dielectric constant and dissipation factor of BT thick films with up to three layers as a function of temperature and frequency is shown. It should be noticed that the dielectric losses slightly change in frequency region from 1 to 100 kHz. The dielectric losses values ranged from 0.1×10^{-2} to 2.5×10^{-2} depending on the number of layers. At the lowest frequency it was very difficult to obtain the exact results, because of the noise caused by the system used for measurements. Otherwise, the decrease in the dielectric losses with the increase of film thickness could be noticed. This observation is comparable with reported data that the thinner dielectric layer, the higher is dielectric loss [23]. On the other hand, the rather low values obtained for dielectric losses compared with the literature data [13] related to BT thick film prepared by

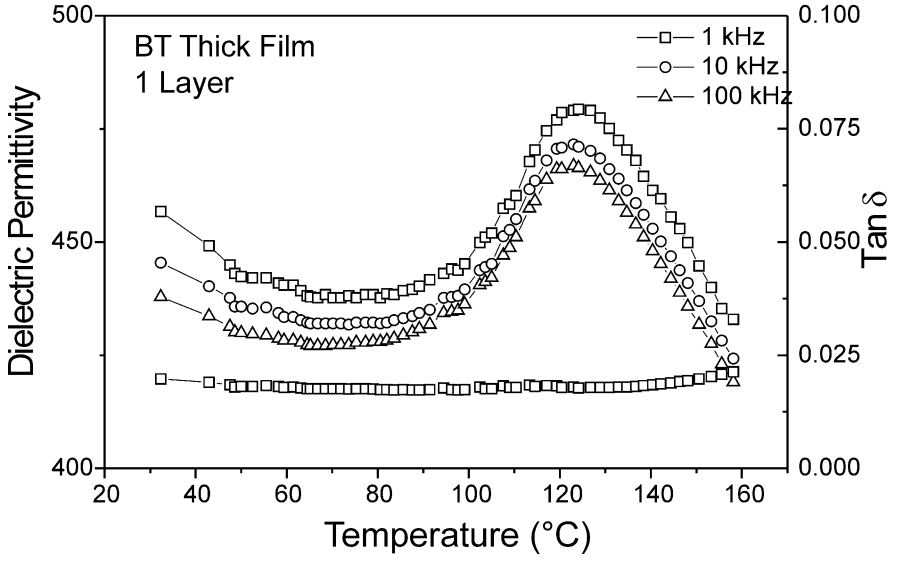

Fig. 3. Dielectric permittivity and dielectric loss vs temperature and frequency, for barium titanate thick films with one layer.

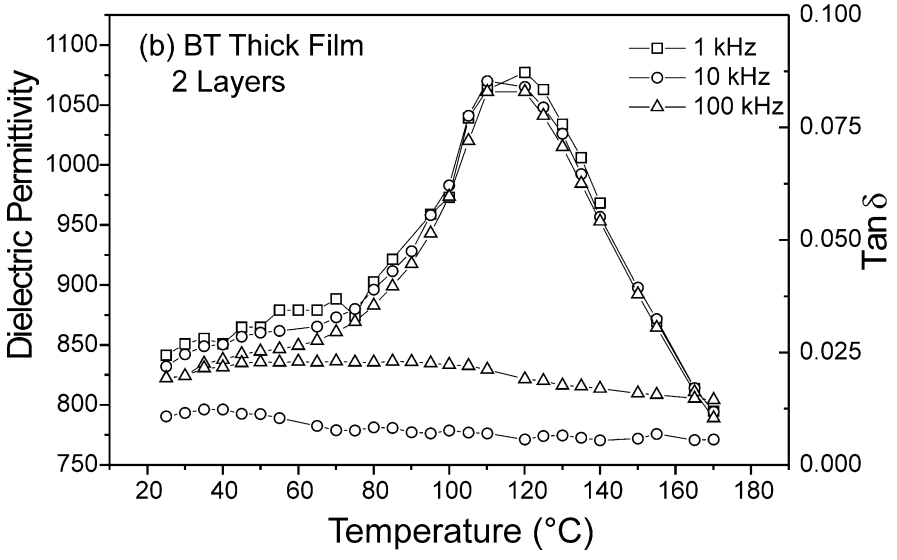

Fig. 4. Dielectric permittivity and dielectric loss vs temperature and frequency, for barium titanate thick films with two layers.

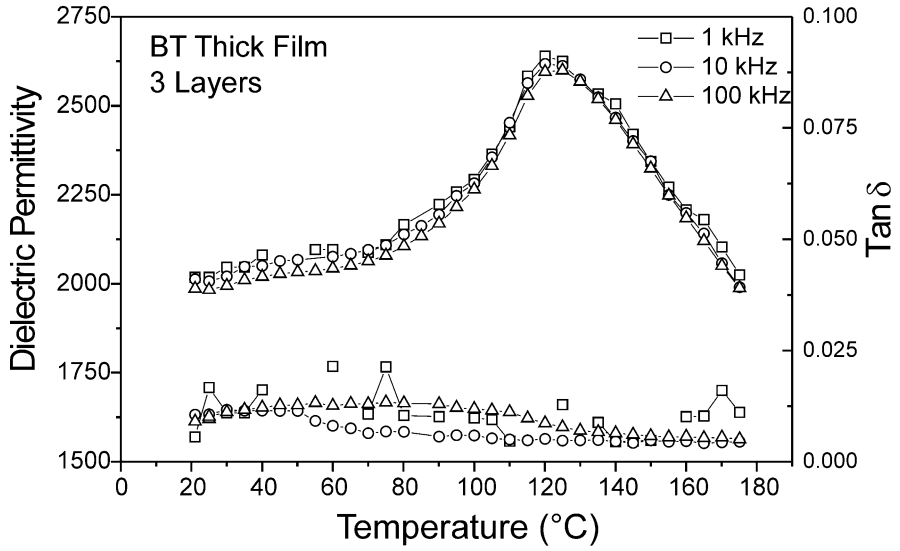

Fig. 5. Dielectric permittivity and dielectric loss vs temperature and frequency, for barium titanate thick films with three layers.

electrophoresis method was not only due to the higher thickness of films but also due to the microstructure and grain size of the dielectric layer.

The dielectric constant at room temperature (25 °C, in the frequency region from 1 kHz up to 100 kHz) changes from 300 to 2000, depending of the number of layers. Dielectric constant at the Curie temperature is well expressed (Figs. 3–5). The Curie temperature of ~120 °C was observed for all BT thick films independently of number of layers. The dielectric constant at the Curie temperature was 480, 1100 and 2600 and no significant difference during heating and cooling cycles was noticed. It is believed that the position of dielectric peak without shifting in comparison with the $BaTiO_3$ bulk is due to known phase transition from tetragonal to cubic.

Dielectric properties indicate that the BT thick films show similar characteristics with bulk material. This means that the screen-printed BT thick films have a good opportunity to evaluate their potential application as multilayer dielectrics.

4. Summary

Thick films of barium titanate in one, two and three layers were prepared with success by the screen-printing technique on Al_2O_3 substrates. The films had thickness ranging from about 25 to 75 μm measured by cross-sectional analysis. The most common problem in thick films such as cracking was not observed. The adhesion electrode/support and electrode/barium titanate layer was strong and no delamination off was noticed. The microstructure of BT thick film deposited by screen-printing is uniform and dense with rounded grains and withouth presence of secondary phases.

The BT thick films show the dielectric constant ranging from 500 to 2600 at the Curie temperature of ~120 °C.The dielectric losses are from 0.1 to 2.5×10^{-2} depending on the number of layers. Dielectric properties obtained indicate that the barium titanate thick films show the similar characteristic with bulk material. This strongly suggests that the screen-printed BT thick films have a good opportunity to evaluate their potential applications as multilayer dielectrics.

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