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Electrical properties of screen printed $BaTiO_3$ thick films

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Abstract

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. In the present work, the barium titanate thick films were prepared from mechanically activated powders based on $BaCO_3$ and TiO_2. After mixing, the powders were calcined at low temperature by slow heating and cooling rates. The thick films were deposited on to Al_2O_3 substrates through hybrid technology. The obtained films were fired at 850 °C together with electrode material (silver/palladium). The electrical properties of thick films: dielectric permittivity, dielectric losses, Curie temperature, hysteresis loop were reported. The obtained BT thick films can be applied in as multilayer capacitors or in gas sensor application.

Keywords: $BaTiO_3$ and titanates; Capacitors; Electrical properties; Films

1. Introduction

It is a good reason to believe that the gap between the bulk materials and thin films can be filled with materials suitably designed and appropriate processed.[1] Indeed, the difficulty in preparation of thin films in various thickness ranges is the primary reason for their notable lack of availability. As the film thickness increases, the difficulty in preparing thick film is well recognized. Thick film technology is a method whereby resistive, conductive and dielectric pastes are typically applied to ceramic substrates.[2,3] The technology of producing thick films of various types involves a number of steps which are common to all of them. Unlike thin films, the number of processes capable of producing high quality thick films is rather limited to specifically mentioned sol-gel, MOD and screen printing. Previous investigators have employed dip coating, spin coating, electrophoresis 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, de-bonding from substrates, increasing the roughness.[3,4] Otherwise, the deposition of thick film pastes by screen printing is a relatively simple and convenient method to produce thick layers with thickness up to 100 μm. This process is useful to accommodate the demands of miniaturization, circuit complexity, multilayer assembles, or high frequencies.[5,6] Generally, the characteristics of thick film ferroelectric materials are similar to the characteristics of bulk materials.[7,8]

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 the one required for thin films, thus increasing the possibility of interactions with either electrodes or substrates, and consequently leading to a possible degradation. Adhesion between support and film, and 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 permittivity have rather high tendency to appear.[9,10]

In general, the sub-micron powders are widely available, and an effective method to prepare thick film of

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barium titanate is by using reliable ceramic powders. Another possibility to obtain required grains size could be by mechanical activation of raw materials during powder process preparation using high energy milling process. It is known that the mechanical activation generally results in a decrease of particle size, increase in surface area, change of free energy, formation of a new surface, and formation of different crystal lattice defects. Thus, the barium titanate could be easily obtained due to initiation of the solid state reaction between the starting components at lower temperature.

In the present work, $BaTiO_3$ (BT) 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. The upper and bottom electrodes based on Ag–Pd and functional component based on BT were screen-printed on alumina substrate and after that annealed in air atmosphere. The microstructure, electrical properties and effect of the number of layers of thick films on electrical properties were analysed.

2. Experimental procedure

2.1. Powder and paste preparations

The mixture of $BaCO_3$ (Merck PA 99%) and TiO_2 (Ventron PA 99.8%) powders using a 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-ionized water and ethanol. It was reported, previously, that LiF even in small amount works as a sintering aid.[12,13] Through the liquid formation via LIF doping, barium titanate could be sintered at the temperature lower than it is usually for solid state reaction of BT. The homogenized powders were mechanically activated in high-energy vibro-mill with rings (TM MN 954/3) in air for 90 min. An organic binder was added; powders were dried, milled, sieved and pressed at 400 MPa. After calcination at 50 °C for 1 h, the obtained pellets were crashed, milled and sieved.

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

2.2. Film preparation

The electrode materials were specially produced (IRITEL dd.) for the screen printing technique starting from the silver/palladium mixture (Ag–Pd 70/30).The bottom electrode was deposited on the Al_2O_3 support (Alcoa), in the middle was screen-printed dielectric layer of barium titanate and on the top was deposited the upper electrode, sintered all together at 850 °C during 1 h in air flow atmosphere. The obtained films presented a thickness ranging from about 25 to 75 μm, depending on the number of layers.

2.3. Characterization

The particle size analysis after mechanical activation has shown that the obtained particles were less than 0.2 μm. After calcination, milling and sieving the particle size ranged from 0.2 to 0.5 μm. The rather strong agglomerates were destroyed by multi-step ultrasonic treatment. The thicknesses of the films were measured from cross-sectional analysis of the samples, using SEM. The microstructure and chemical composition were analyzed using a scanning electron microscope (TOPCON SM 300) coupled with an energy dispersive spectrometer (EDX, Princeton Gamma-Tech).

The electrical measurements, capacitance and dielectric losses are performed using a HP 4291A coupled with a furnace. The dielectric permittivity and Curie temperature were determined for thick film samples with up to three layers. The hysteresis loop was obtained using ACR 100 meter.

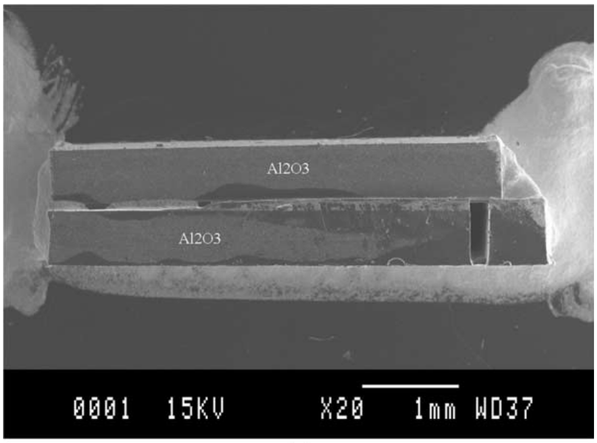
3. Results and discussion

The difficulty in fabricating thin films in needful thickness range is the primary reason for their notable lack of availability and for the use of thick films. Otherwise, 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 thin films. 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 can determine stress levels.[10,11,13] Taken all together, these stresses, especially tensile stresses, can produce disastrous results such as delaminating off the film from the substrate. Besides, when the film become thicker, it may appear micro-cracks or pores, or can lead to the appearance of macro cracking. In general, it should be noted that in thick films most of the problems in the substrate and processing consideration are magnified in comparison to thin films because the extended processing times at temperature and the desire to deposit a maximum film thickness per layer.[11–14]

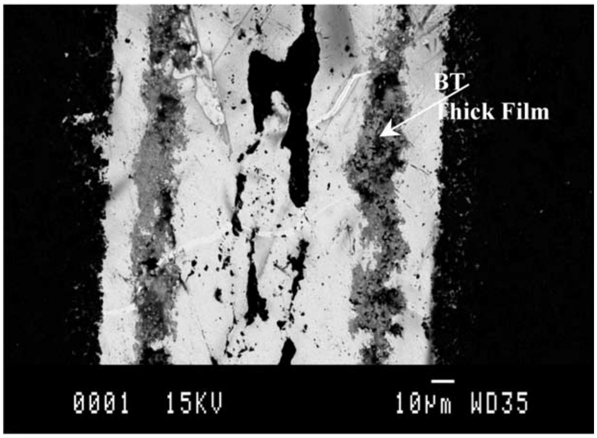
In the investigated case the thick films were deposited on Al_2O_3 substrates. Since the chemical stability of

Al_2O_3, and chemical compatibility with the film is good, the inter-diffusion could be minimized. The cross and transversal sections of one and two layers screen-printed BT films are presented in Fig. 1. The thickness for one layer thick film was approximately 25 µm; 50 µm for 2 layers and 75 µm for a 3 layered thick film. The adhesion of Ag–Pd/BT electrodes was rather strong and the adhesion of the bottom and upper electrode layer overprinted were good; it could not be peeled off with scotch tape.

The grain size of BT thick film is rather regular with rounded grains and withouth detected presence of secondary phases. The grain size was less than 1 µm, approximately 700 nm for one layer and approximately 850 nm for three layered films. The small grain size is caused not only due to low sintering temperature and rather short time for firing process, but also resulted from mechanical activation process of starting powders. No obvious cracks on the fired BT layer were observed, because the presence of low temperature melting glass frits in the BT powder formulation, which wetted the substrate and promoted liquid-phase sintering during firing. Meanwhile, the presence of certain amount of porosity was noticed, especially for one layered BT film. On the other hand, EDX analyses pointed out the composition of barium titanate ($BaTiO_3$) and other barium titanate compositions richer in barium or titanium were not observed. Although, in cross-sectional area of thick film with one layer, it was noticed the presence of rather small amount of another phase composition. The observed phase was located closed to grain boundaries pointed to traces of silver, evidently originated from electrode materials.



(a)



(b)

Fig. 1. SEM analysis of BT thick film: (a) transversal section, (b) cross section of BT films.

It is well known that dielectric properties evaluate the potential application for ceramics and films. The dielectric permittivity is intrinsic behavior of the material, meanwhile many factors during preparation of thick film could affect on the final value of dielectric properties.[15,16] The dielectric properties of barium titanate thick films are presented in Fig. 2. It is indicative that the dielectric permittivity changes with number of layers. The dielectric permittivity at room temperature (25 °C, frequency region from 1 up to 100 kHz) is around 450, 800 and 2000 for one, two and three layers, respectively. The Curie temperature of ~120 °C was observed for all BT thick films independently of number of layers. 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 permittivity at the Curie temperature is rather well expressed with values of 480, 1100 and 2600, depending on the number of layers. No significant difference, during heating and cooling cycles, was noticed on the dielectric properties.

It was noticed that the dielectric losses slightly changed in the frequency region from 1 kHz do 100 kHz. The characteristic diagram for two layered thick films

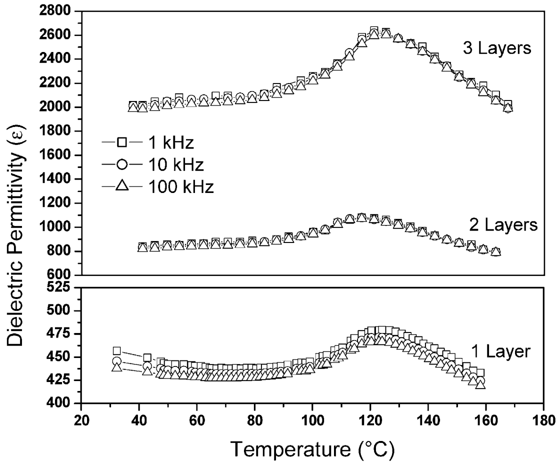


Fig. 2. Dielectric permittivity of one, two and three layered barium titanate thick films. K_1, K_2 and K_3 are frequencies of 1, 10 and 100 kHz, respectively.

was presented in Fig. 3. The values obtained ranged from 0.1 to 2.5×10^{-2}, depending on the number of layers. This observation is comparable with reported data that as the thinner the dielectric layer, the higher is the dielectric loss.[10] It is believed that the dispersion of dielectric loss results are mostly caused by the measurement system used and it is more expressed for low values of frequencies. On the other hand, the lower values obtained for dielectric losses, comparing with some literature data for BT thick film, prepared by electrophoresis method, resulted due to a higher thickness of the films or to the observed grain size in dielectric layers.[14]

The possible reason for the evident variation on the dielectric permittivity with film thickness of BT is that during sample preparation, a few problems could arise. Lower density films were obtained on structures with fewer layers. This means that the barium titanate films were not sintered to fully density, the porosity was rather high, and the grain growth was lower on films with a small number of layers. It is known that in $BaTiO_3$ ceramics, the so-called "grain size effects" which deal with the variation of the dielectric permittivity (ε) of $BaTiO_3$ with grain size, has important influence.[15] It has been found that the decrease in ε is generally attributed to the reduction in grain size and the decrease in defect concentration is related with the reduction in surface area, promoted by grain growth.

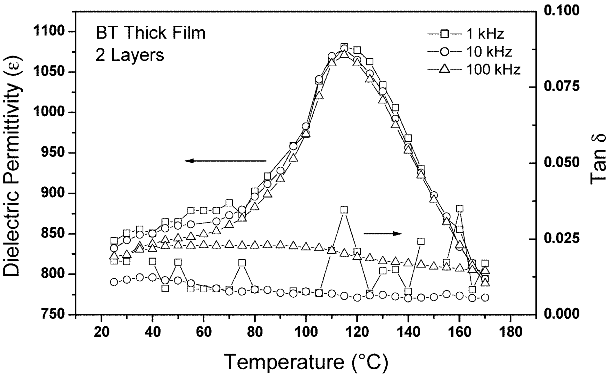


Fig. 3. Dielectric permittivity and dielectric losses vs temperature and frequency, for BT thick films with 2 layers.

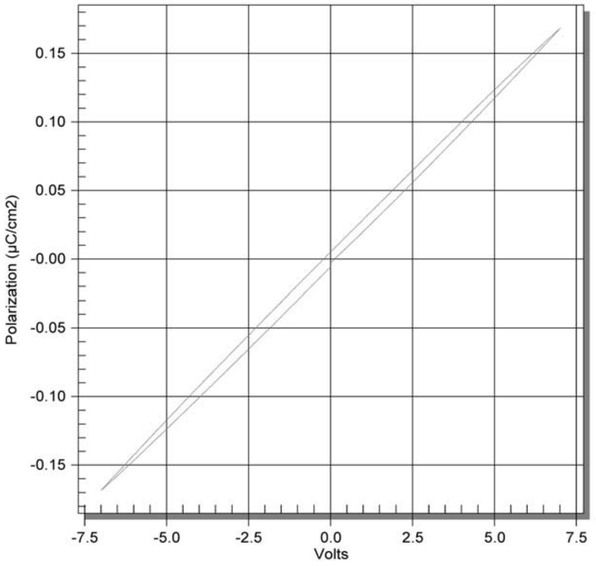


Fig. 4. Hysteresis loop for BT thick films with 3 layers.

On the other hand, after the electrode deposition it is assumed that part of the electrode material could diffuse from the surface of BT layer through intergranular pores, forming a conductive film and changing the dielectric properties of film. Besides, the circular electrodes instead total surface covered could probably diminish the problem of diffusion of electrode material into films. These results are comparable with the data reported by Jang et al., Yamashita et al. and Zhang et al.[15–18]

The hysteresis loop of the three layers of BT thick film is presented in Fig. 4. It could be noticed that the loop is well performed; meanwhile it is very narrow. The remanent polarization was 1.07×10^{-2} μC/cm^2 and the coercive field was 3×10^{-2} V/cm^2. The obtained results pointed to the small values of P_r and E_c probably caused by small grain size (grain boundary effect) and by influence of interface electrode/film.

4. Summary

Thick films of barium titanate up to three layers were prepared with success by the screen-printing technique on Al_2O_3 substrates with thickness ranging from about 25 to 75 μm. The adhesion electrode/support and electrode/barium titanate layer was strong and no delaminating off was noticed.

The dielectric permittivity for barium titanate thick films with three layers was 2600 at the Curie temperature of ~120 °C. The dielectric losses change from 0.1 to 2.5×10^{-2}, depending on the number of layers. The evident variation on dielectric permittivity with film thickness, could be reduced either by increasing the density of the films, grain growth, as well as other materials related parameters, or through electrode configuration, or by controlling the screen-printing parameters.

The remanent polarization measured is 1.07×10^{-2} μC/cm^2 and the coercitive field shows the value of 3×10^{-2} V/cm^2. The small values of P_r and E_c are caused by small grain size (grain boundary effect) and by the influence of interface electrode/film.

Therefore, screen-printed barium titanate thick films could be a potential candidate for application such as multilayer capacitors or sensors.

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