High Dielectric Constant Thin-Films for Embedded Passive Components

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Pure and doped barium titanate thin films have been prepared by chemical solution deposition on 18 µm thick, industry standard copper foils. Films are approximately 0.6 µm thickness and exhibit randomly oriented equiaxed $BaTiO_3$ grains. The $BaTiO_3$ films are sintered in a high temperature nitrogen-based atmosphere such that copper oxidation is avoided. The high sintering temperature, as compared to typical thin-film processing, provides for large grained films with properties consistent with bulk barium titanate-based capacitors. Grain diameters are between 0.05 and 0.2 µm depending on sintering temperature, dopant level and type. The dielectric constant ranges between 800 and 2000, representing capacitance densities in excess of 1µF/cm$^{2.}$ Loss tangents are less than 2.5%. Temperature dependent measurements on pure barium titanate films indicate a ferroelectric transition near 100 °C with a very diffuse character. The Curie point may be depressed to lower temperatures with dopants. This early work on $BaTiO_3$ based films on copper foil represents an important first step towards very high capacitance density embedded passive components.

Introduction

Embedding decoupling capacitors within the layers of a printed wiring board (PWB) frees up surface space, increases device reliability, and reduces electromagnetic interference and inductance losses. Freeing up surface space allows additional integrated circuits (IC's) and other devices to be added or allows the designer to shrink the size of the board. Device reliability increases due to fewer soldered connections. The ability to locate decoupling capacitors directly below ICs shortens interconnect lengths, which in turn decreases the lead inductance and increases the maximum frequency of operation (1-2).

For printed wiring boards, embedding thin-film high capacitance density materials is especially challenging. High capacitance density layers can only be achieved by ceramic systems so there is a natural thermal incompatibility between ceramic processing and the organic substrate. To overcome this issue, several groups have pursued the fired-on-foil capacitor process(3-7). Various approaches to this exist but typically a capacitor dielectric solution is coated on to a metallic foil and dried. The coating process may be any number of processes but at the R&D level it is generally spin coated. This is repeated until the required number of layers are applied, typically 3-6. The foil is then fired at an elevated temperature to form a dense ceramic film.

Following this, a top electrode is formed on top of the dielectric to form the fired-on-foil capacitor. Various approaches exist but generally sputtering is a simple and viable method. The foil may then be bonded to prepreg, and the top electrode etched to form an inner-layer containing individual capacitors and any associated circuitry. Finally, the inner-layer structure may be incorporated inside a multilayer printed wiring board using standard printing wiring board processes.

Much of the previous fired-on-foil capacitor research(3-6) has used leaded dielectrics, primarily due to their ability to be processed at temperatures at or below 600 °C. Additionally, nickel based coating of copper foils has generally been employed to reduce or eliminate copper interactions with the dielectric. Some of these combinations have allowed firing the capacitors in air rather than in reducing atmospheres. Though successful, and currently pursued for commercialization, these low temperature approaches lead to relatively low capacitance density films (~150 nF/cm^2) and leaded dielectrics represent a short term solution when considering the industrial need to eliminate lead-containing technology. Barium titanate based dielectrics are an obvious materials choice for lead-free applications, but crystallization of barium titanate based dielectrics requires temperatures in excess of 600°C(8). Therefore, for such temperatures, a low oxygen atmosphere is required so that the metal foil is not oxidized.

In this report, we combine deposition of barium titanate based dielectrics via chemical solution deposition (CSD) techniques onto bare copper foils and high temperature processing in controlled atmospheres. Using this approach, we provide a high capacitance density fired-on-foil capacitor structure that can be integrated into printed wiring boards.

Film Preparation

Chemical solutions containing Ti/Zr ratios of 100/0, 95/5, 90/10 and 75/25 were prepared by mixing titanium isopropoxide and zirconium propoxide in the prescribed ratios with acetylacetone to stabilize the titanium component. These precursor solutions were then combined with a barium acetate solution such that the A:B site ratio was 1:1. The solutions were diluted to 0.3 molar by additions of methanol.

The solutions were spin coated on to the drum side of untreated Oak-Mitsui 18 micron thick copper foil and dried for 7-8 minutes at 250ºC. This process was repeated until the desired thickness was achieved. Typically, three coats were necessary. The films were then fired in a reducing atmosphere of reagent grade nitrogen and forming gas containing water vapor at 900ºC for 30 minutes. The equilibrium reaction of water vapor, hydrogen, and residual oxygen in the nitrogen gas is sufficient to provide for atmospheres amenable to maintaining the dielectric in an oxidized state without oxidizing the copper foil. The partial pressure of oxygen in the furnace atmosphere was maintained at a *P*O2 of 10^{-11} atmospheres as measured by an *in situ* solid state oxygen sensor. After firing, the films were re-oxidized at 550ºC for 30 minutes under a partial pressure of oxygen of 10^{-6} atmospheres (~ 1ppm O2) to reduce the oxygen vacancy defects associated with the high temperature and the low partial pressure of oxygen used in the firing. 50 nm thick, platinum top electrodes were then applied via RF magnetron sputtering through a shadow mask that defined the top electrode area.

Phase development, crystallinity, and lattice parameters of the films were investigated with a Bruker AXS D-5000 x-ray diffractometer equipped with a GADDS area detector. Lattice parameters were calculated utilizing a Nelson-Riley correction function and assuming a pseudo-cubic crystal symmetry for all compositions. A CP-Research Thermo Microscope atomic force microscope was used to study the film surface morphology and grain size. Dielectric properties were characterized using a Hewlett-Packard 4192A Impedance Analyser and an MMR technologies Inc. cryogenic temperature stage.

Film Characterization

Figure 1 shows the x-ray diffraction patterns for the barium titanate and barium zirconate titanate thin-films on copper foils. The pattern displays single phases, narrow peak widths, random orientation, and low, flat background noise level. This is more consistent with x-rays prepared from crystalline powders than with traditional thin-films processed at low temperature and suggest highly crystalline films with relatively large grain sizes(9).

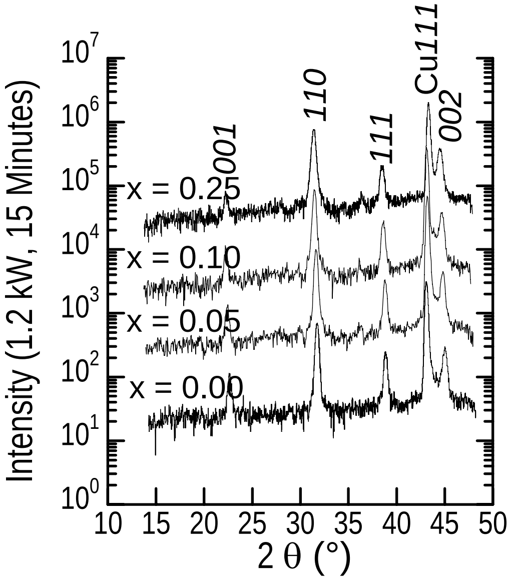

Figure 1 - 2θ x-ray Diffraction Scans of $Ba(Ti_{1-x}Zr_x)O_3$ Thin Films on Copper Foil

Figure 1 also suggests that no Cu2O or CuO phase development occurred during the firing process as would be expected from analysis of the free energy curves for copper and copper oxide at 900ºC and an atmosphere containing ~ 10^{-11} atm O2. This suggests an abrupt Cu/dielectric interface, i.e., no interfacial layer. Further characterization of the *001* family of peaks, with the aid of the Nelson-Riley function for correction of systematic diffractometer errors(10), revealed the dependency of lattice parameter with the mole fraction of BaZrO3 as shown in Figure 2.

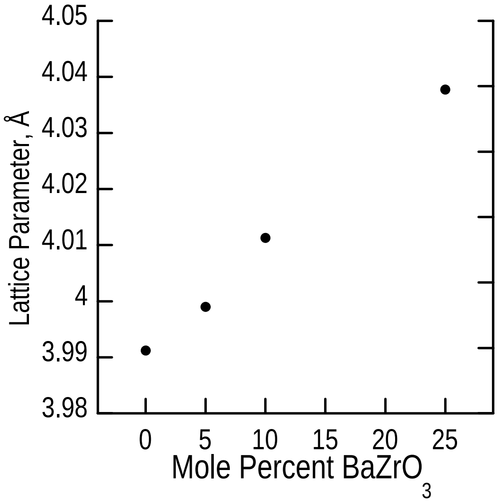

Figure 2 - Lattice Parameters of $Ba(Ti_{1-x}Zr_x)O_3$ Thin Films Deposited on Copper Foils

As expected, the substitution of zirconium for titanium results in enlarged cell dimensions. The increase in cell dimensions is approximately linear with respect to mole fraction of substituted zirconium and is indicative of a continuous increase in cell volume as zirconium dopant fraction increases.

Figure 3 shows the atomic force microscope scans taken in contact mode of the 4 film compositions. Increasing the fraction of BaZrO3 results in a decrease in average grain size. This type of microstructure is not typical of non-leaded ferro-electric thin films, which most often exhibit much finer grain sizes(8). We attribute this ceramic like topography to the high firing temperature used during the process. This structure is also consistent with the x-ray lines shown in Figure 1.

The decrease in grain size with increasing zirconium content may be attributed to the highly refractive nature of the zirconium addition hindering diffusion during firing. Alternatively, the addition of zirconium may increase the nucleation rate of BZT crystals, thereby limiting grain growth and thus final grain size.

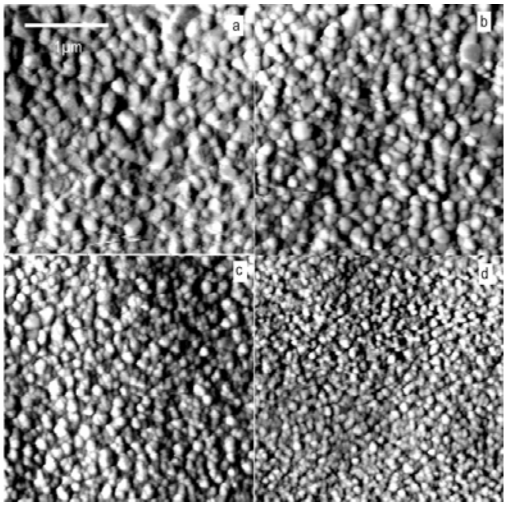

Figure 3. 3 µm x 3 µm Contact Mode AFM Error Signal Scans of a) $BaTiO_3$ b) $Ba(Ti_{0.95}Zr_{0.05})O_3$ c) $Ba(Ti_{0.90}Zr_{0.10})O_3$ and d) $Ba(Ti_{0.75}Zr_{0.25})O_3$ on Copper Foil Substrates

Given the relatively large grain sizes present in these films, dielectric properties more consistent with fine-grained barium titanate based ceramics prepared from powders are to be expected. These include high dielectric constants and clear evidence of hysterisis in the ferro-electric regime.

Figure 4 shows the field dependence of the capacitance density of pure barium titanate for increasing and decreasing voltage sweeps. Hysterisis and a strong dependence of capacitance on the electric field is evident for the barium titanate film. This demonstrates the ferro-electric nature of the film and is indicative of a tetragonal structure.

Figure 5 shows the dielectric constant and loss tangent versus temperature at a frequency of 10 KHz for each composition. It can be seen that increasing the mole fraction of barium zirconate broadens the peak and reduces the relative permittivity maximum to lower values. In addition the temperature at which the maximum occurs (Curie point) is also shifted to lower temperatures. From this, we estimate that a 92.5/7.5 ratio of Ti/Zr will give a composition that exhibits less than a 15% change from its value at 25ºC at the temperature of -55ºC and +125ºC, i.e., an X7R composition.

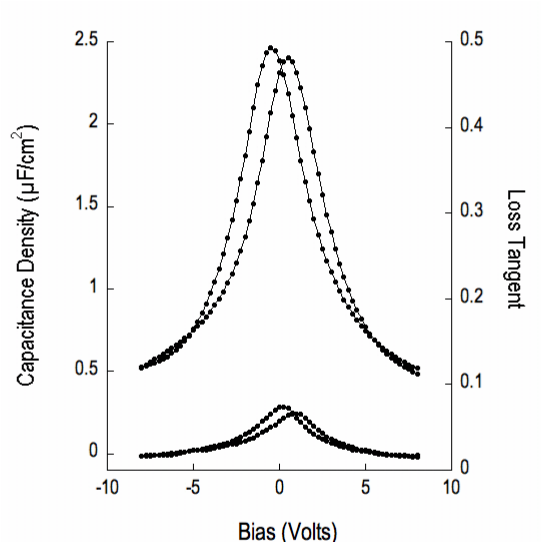

Figure 4 - Capacitance Density of Pure Barium Titanate as a Function of Increasing and Decreasing Voltage Sweeps

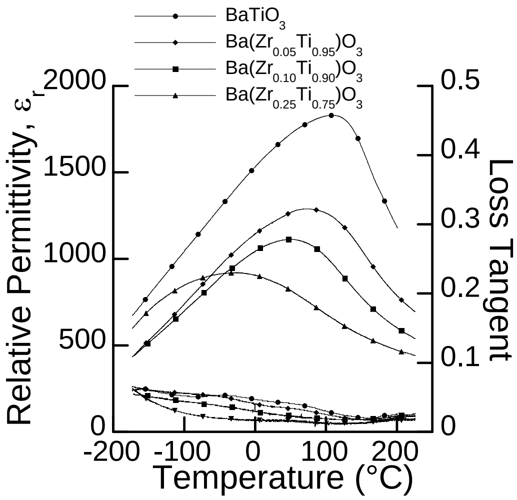

Figure 5 - Dielectric Constant Versus Temperature for $Ba(Ti_{1-x}Zr_x)O_3$ Thin Films Deposited on Copper Foil Substrates

Figure 6 plots the temperature and value of the dielectric maximum versus the composition. It is observed that the Curie point decreases linearly with mole percent of BaZrO3. This trend is slightly more exaggerated than that observed with bulk ceramic material(11) but the effect of thin-films and fine grain sizes may be a factor in this behavior.

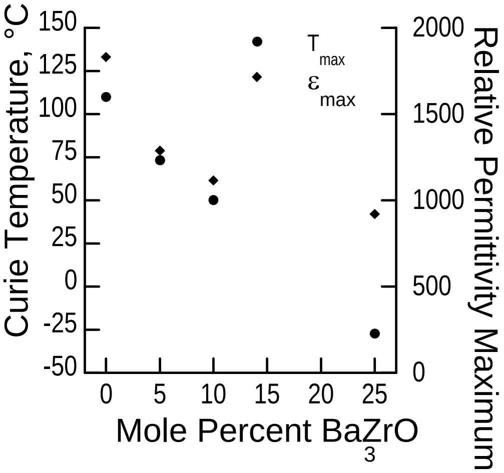

Figure 6 - Curie point and Maximum Permittivity Values versus Composition for $Ba(Ti_{1-x}Zr_x)O_3$ Thin Films Deposited on Copper Foil Substrates

Conclusions

It has been shown that barium titanate and barium zirconate titanate thin films can be deposited directly on copper foil and be processed to yield attractive dielectric properties. Key to the attractive properties are high temperature processing and the atmosphere control during firing to maintain an atmosphere that is oxidizing to the dielectric but reducing to the copper. The ability to substitute zirconium for titanium in barium titanate and produce single-phase dielectric structures facilitates both moving the Curie point and broadening the peak, allowing an X7R composition to be generated.

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