SAND2008-0141C

Fabrication of (Ba,Sr)TiO$_3$ High-Value Integrated Capacitors by Chemical Solution Deposition

Jennifer Sigman, Paul G. Clem, Geoff L. Brennecka, Bruce A. Tuttle
Sandia National Laboratories, Albuquerque, NM 87123, USA

Abstract — This report focuses on our recent advances in the fabrication and processing of barium strontium titanate (BST) thin films by chemical solution depositiion for next generation fuctional integrated capacitors. Projected trends for capacitors include increasing capacitance density, decreasing operating voltages, decreasing dielectric thickness and decreased process cost. Key to all these trends is the strong correlation of film phase evolution and resulting microstructure, it becomes possible to tailor the microstructure for specific applications. This interplay will be discussed in relation to the resulting temperature dependent dielectric response of the BST films.

INTRODUCTION

With the continuing trend of electronic device miniaturization, the need for low cost, high performance and reliable passive components (capacitors, resistors, inductors) is a prominent issue. [1] - [3] Integration of these passives aids in size reduction efforts and can also reduce cost and improve device performance.[1] Size reduction of intergration capacitors can be furthered with increased capacitance values by increasing electrode area, increasing the dielectric constant of the dielectric layer, or decreasing the thickness of the dielectric layer. (Ba,Sr)TiO$_3$ (BST) is one of the leading candidates for integrated capacitors due to its high dielectric constant, compositiional flexibility, lead-free composition, and processing compability with the materials and methods already standard in device fabrication. Using chemical solution deposition to fabricaiton the dielectric layer and replacing conventional Pt based electrodes with base metal (Cu, Ni) electrodes can reduction the cost of fabricating of the capacitors. Therfore in this report, we present our recent efforts improving the fabricaiton next generation BST integrated capacitors by chemical solution deposition with examples of decreased dielectric layer thickness, reduced temperature coefficient of capacitance and the use of Cu electrodes.

EXPERIMENTAL

BST solutions were made by chelating titanium (IV) isopropoxide with propionic acid then mixing in a solution of barium acetate and strontium acetate which had been pre-dissolved in glacial acetic acid and electronic grade methanol. [3], [4] The resulting 0.05-0.3 M solutions were spun on commercially available platinized silicon substrates (170 nm Pt // 30 nm Ti // 200 nm thermal SiO$_2$ // Si, Silicon Quest International, Santa Clara, CA) or commercially available copper foil (Schlenk AG, Roth, Germany) at 3000-5000 rpm for 30 sec. Films were then pyrolyzed on a 200 – 400 °C hotplate for 1-5 min. This process was repeated until the desired number of film depositions was reached and the film was ready to be crystallized. Multiple spinning and crystallization sequences were used to achieve preferred microstructures and thicknesses. BST films on copper foil were crystallized at 750 – 950 °C for 1 hr in an atmosphere of 3% H$_2$ / N$_2$ bubbled through room temperature water (pO$_2$ ~ 10^{-12} atm). BST films on platinized silicon were crystallized in air by direct insertion into a furnace preheated to 700-800 °C for 30 min. Pt or Cu top electrodes were then deposited via RF sputtering through a shadow mask. Dielectric measurements made were using a probe station in conjunction with an HP 4284A Precision LCR Meter and a Source Measure Unit Film microstructure and morphology were studied using field emission scanning electron microscopy and θ-2θ x-ray diffraction was used to identify the crystalline phases in each of the films.

RESULTS AND DISCUSSION

Decreased Dielectric Layer Thickness

Achieving capacitors with BaTiO$_3$ layers of 100 nm by chemical solution deposition requires process modifications. The number of layers is ultimately more important than the overall thickness; however, the standard two-step heat treatment (multiple pyrolysis steps and a single crystallization anneal) produces a granular film microstructure (Fig 1a) because BaTiO$_3$ films deposited from a carboxylate-based chemical solution do not readily achieve a columnar grain structure. Instead, they form an intermediate carbonate phase prior to forming the perovskite phase.[5] Using a typical two-step approach, the minimum thickness with high yield of devices that can be achieved has been ~190 nm. Below this thickness, regardless of the number of pyrolyzed layers and molarity of the solution, the porosity and defect concentration in these granular films has prevented viable high yield fabrication of a large number of devices.

Alternatively, film nucleation kinetics can be altered to favor heterogenous nucleation at the substrate interface by using single heat treatment for each individual layer. The resulting films (Fig 1b) display both a columnar grain structure and higher density. While this approach has been previously reported by Hoffmann, [5], we report here that this approach is necessary for achieving BST films < 100 nm by low cost carboxlyic-based chemical solution depositions. It is predicted that films as thin as 50nm can be achieved by scaling this method. The influence of the microstructure on the dielectric response can be seen in Fig 1c. Consistent with a previous report from Hoffmann et al., [5] there is 5 fold increase in the dielectric response when a columnar grain structure is achieved. Additionally, by controlling the crystallization temperature, overall grain size in the columnar films can remain small to main low temperature coefficient of capacitance values. [4]

Use of Base Metal Electrodes

By controlling the atmosphere during crystallization to low values ($pO_2 < 10^{-12}$ atm) it is possible to achieve high quality undoped $BaTiO_3$ films without the formation of copper oxide (Cu_2O). The grain size of $BaTiO_3$ films deposited on Cu is strongly dependent upon crystallization temperature, increasing from approximately 40 nm in films heated to 750 °C (Fig 2a) to approximately 70-80 nm in films crystallized at 950 °C (Fig 2b). As shown in Fig 2c, this doubling of the grain size is accompanied by a doubling of the measured dielectric constant. Ihlefeld *et al.* have previously suggested that the higher crystallization temperatures used to produce $BaTiO_3$ films on Cu results in more bulk-like grain structures which account for the increase in dielectric constant over the K values measured for ‘standard’ $BaTiO_3$ films, such as those deposited on Pt // Si.[6] Interestingly, our $BaTiO_3$ films on Cu exhibit larger grain sizes and significantly higher dielectric constants than those crystallized under the same conditions on Ni [3] and those crystallized at the same temperatures in air on polished Al_2O_3, [4] despite the granular microstructure of the films on Cu. Without any film optimization, the temperature dependent dielectric responses for $BaTiO_3$ films on both Cu and Ni foils exceed X7R requirements, though they do not yet meet NPO standards. Films are currently able to handle fields of 25 V/μm (Figure 10) with zero-bias capacitance densities of 1.5μF/cm^2 and dielectric losses of 5% or lower.

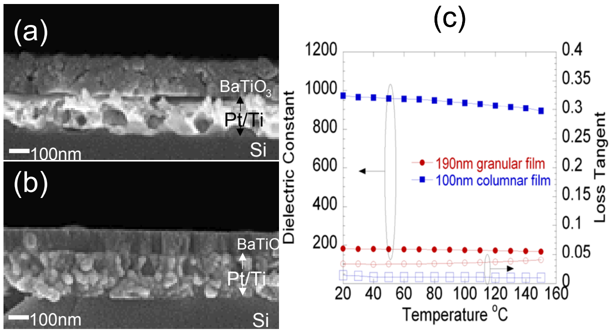

Fig. 1. (a) SEM cross section an 8 layer $BaTiO_3$ deposited in a layer by layer manner. (b) SEM cross section of an 8 layer $BaTiO_3$ film with all layers deposited prior to film crystallization. (c) Dielectric response of films in (a) and (b).

ACKNOWLEDGEMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

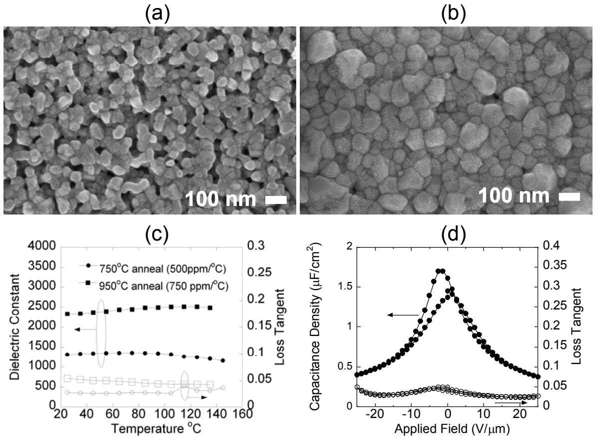

Fig. 2. SEM plan view images of $BaTiO_3$ on copper foil annealed at (a) 750 °C and (b) 950 °C. (c) Dielectric response of films in (a) and (b). (d) Field dependent dielectric response film in (a).

REFERENCES

[1] N. Setter, V. Sherman, K. Astafiev, and A. K. Taganstev, “Polar Ceramics in RF-MEMS and Microwave Reconfiguarble Electronics: A Brief Review on Recent Issues,” J. Electroceram., vol 13, pp. 215-22 (2004).

[2] P. Jain and E.J. Rymaszewski, “Embedded Thin Film Capacitors—Theorhetical Limits,” IEEE Trans. Adv. Packag., vol. 25, no. 3, pp. 454-458 (2002).

[2] J. T. Dawley and P. G. Clem, “Dielectric Properties of Random and <100> Oriented $SrTiO_3$ and $(Ba,Sr)TiO_3$ Thin Films Fabricated on <100> Nickel Tapes,” Appl. Phys. Lett., vol 81, pp. 3028-30 (2002).

[3] C. D. Smith and E. F. Jones, "Title of paper," presented at the EKE Conference on..., City, State, June 6-7, 1993.

[4] J. Sigman, P. G. Clem, J. J. Richardson, J. T. Dawley, and C. D. Nordquist, “Effect of Microstructure on the Dielectric Properties of Compositionally Graded $(Ba,Sr)TiO_3$ Films,” J. Appl. Phys., vol 102, pp. 0541061 1-7 . (2007).

[5] S. Hoffmann and R. Waser, “Control of the Morphology of CSD-Prepared $(Ba, Sr)TiO_3$ Thin Films,” J. Euro. Ceram. Soc., vol 19, pp. 1339-43 (1999).

[6] J. Ihlefeld, B. Laughlin, A. Hunt-Lowery, W. Borland, A. Kingon, and J. P. Maria, “Copper Compatible Barium Titanate Thin Films for Embedded Passives,” J. Electroceram., vol 14, pp. 95-102 (2005).