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Thickness-dependent microstructures and electrical properties of $CaCu_3Ti_4O_{12}$ films derived from sol–gel process

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Abstract

$CaCu_3Ti_4O_{12}$ (CCTO) thin films with various thicknesses were prepared by a sol–gel multiple coating processes on $Pt/Ti/SiO_2/Si$ substrates. Microstructures and surface morphologies of CCTO thin films were analyzed by grazing incident X-ray diffractometer (GIXRD) and scanning electron microscope (SEM), respectively. The correlation between the thickness and electrical properties of CCTO films was investigated. The dielectric constants of CCTO films decreased with increasing film thickness (coating cycle). Both the dielectric constant of CCTO films and interlayer are calculated. Possible mechanisms are explored to explain the thickness dependence of the dielectric constant of CCTO films.

Keywords: Sol–gel; $CaCu_3Ti_4O_{12}$ (CCTO); Thickness-dependent properties; Dielectric

1. Introduction

Recently, the new pervoskite-type material $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much attention because of its high dielectric constant over a broad temperature range. Each successive dynamic random access memories (DRAM) generation has to maintain the same storage charge, while the area of the capacitor has significantly decreased [1–6]. CCTO is a promising candidate for application of DRAM in very large scale integrated (VLSI) circuits due to its large dielectric constant. With the shrinking of device dimensions, high dielectric constant materials become more important and necessary to be used for capacitor in DRAM. Increasing the dielectric constant of the material or the area of a capacitor can achieve a large capacitance.

The high dielectric constant is attributed to the grain-boundary capacitance (internal barrier layer capacitance, IBLC) instead of an intrinsic property associated with the crystal structure [7]. In order to apply CCTO in microelectronic devices and give a more fundamental understanding of its physical property, some groups have grown CCTO films by pulsed-laser deposition (PLD) with different substrates [8,9]. In the work of Jiang et al., high quality epitaxial CCTO films were prepared on a (001)-oriented $LaAlO_3$ substrate and presented a high dielectric constant of 10^4 at 1 MHz at room temperature [8]. While in the studies of Fang and Shen, the CCTO thin film deposited on $Pt/Ti/SiO_2/Si$ substrates showed a polycrystalline characteristic and achieved a dielectric constant of near 2000 at 10 kHz and room temperature [9,10]. The process window of the above methods of CCTO thin film is very narrow. In addition, the PLD method for CCTO is expensive. Sol–gel was chosen as the preparation technique in this study because it offers a homogeneous distribution of elements on a molecular level, ease of composition control, high purity, and the ability to coat large and complex area substrate. Both the dielectric constants of CCTO films and interlayer are calculated by Mixture Rule. A pore fraction of dielectric film is also estimated.

2. Experimental procedures

The CCTO thin films were prepared by a sol–gel technique. Four inch diameter p-type (100) Si wafers with nominal resistivity of 5 to 10 Ω cm were used as substrates. After standard RCA cleaning, a 200 nm SiO_2 film was grown on Si substrate, then 10 nm Ti and 100 nm Pt layers were deposited sequentially by dc

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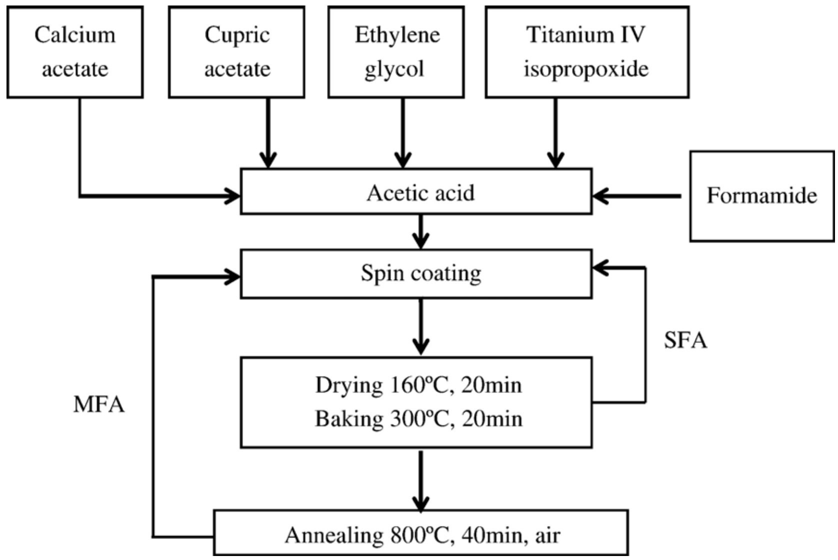

Fig. 1. Flow chart for the fabrication of CCTO films.

sputtering to obtain a $Pt/Ti/SiO_2/Si$ substrate for the deposition of CCTO thin-film capacitors. Fig. 1 shows the flow chart of CCTO thin film fabrication. Precursor solution of CCTO with a 0.18 molar concentration was prepared by dissolving the appropriate amount of calcium and cupric acetates in acetate acid, and then it was added a stoichiometric amount of titanium IV isopropoxide. Following, ethylene glycol was added into the CCTO solution to increase solution stability. Formamide was selected as an additive to adjust the solution viscosity to prevent the cracking of CCTO thin films during baking. Then, the CCTO solution was heated at 165 °C for 80 min.

After the synthesis of CCTO solution is completed, the solution was spun-coated onto $Pt/Ti/SiO_2/Si$ substrate at 7000 rpm for 30 sec. The CCTO thin films were baked at 160 °C for 20 min to dry the gel, and then heated in a furnace at 300 °C for 20 min to remove residual organic compounds. After the heating of the first CCTO film, a second CCTO film was spun, baked, and heated as described above. The process was repeated and CCTO thin films with different coating layers were obtained in order to avoid through pin-hole. Then, the CCTO films, denoted single-cycle furnace annealing (SFA) samples, were annealed at 800 °C in a furnace for 40 min with various thicknesses. Alternative preparation is the multi-cycle furnace annealing (MFA) specimens, each CCTO layer is spun, baked, heated, and annealed, and then the following deposition layer process is performed. Finally, the top electrodes of the Pt (100 nm) were deposited by DC sputtering system through a shadow mask.

A Setaram-Labsys thermogravimetric analyzer (TGA) and a Setaram-Labsys differential scanning calorimeter (DSC) were employed to measure the decomposition and crystallization temperatures of CCTO gel films. Both TGA and DSC experiments were carried out in a dry air atmosphere with a heating rate of 10 °C/min.

The phase of the films was characterized by a grazing incident X-ray diffractometer spectra collected by using CuK_α (λ=0.15406 nm) radiation with 40 kV and 150 mA in the 2θ range of 30 ° to 65 °(XRD, RU-H3R, Rigaku Co.). The cross sections of films were observed with a scanning electron microscope (SEM, Hitachi S4700). The capacitance was measured with a C–V analyzer (model 590, Keithley Instruments Inc.) in the applied voltage range of −5 ± 5 V and at the frequency of 100 kHz. An electron probe microanalyzer (FE-EPMA, JXA-8500F) was used to analyze the composition of the films.

3. Results and discussion

3.1. Microstructure

The TGA/DSC graphs of the CCTO films are shown in Fig. 2. The DSC curve exhibits two endothermic peaks and one exothermic peak. The first endothermic peak at 60 °C records the rapid volatilization of water in the gel. The presence of an exothermic peak at 250 °C is concerned with the decomposition of organic compound. In the meantime, a significant weight loss due to the evaporation of water and decomposition of organic compound is observed in the TGA curve for the temperature below 300 °C. The second endothermic peak at 765 °C in the DSC curve is related to the phase formation of perovskite CCTO,

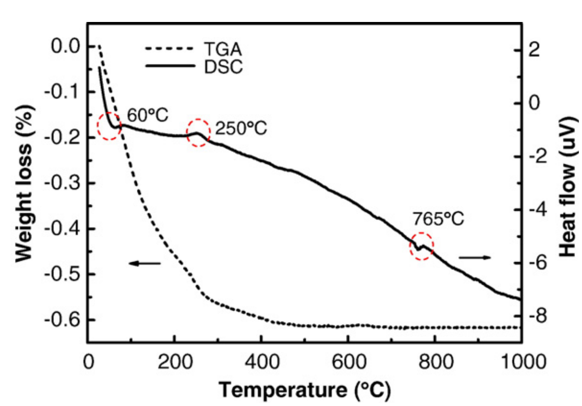

Fig. 2. TGA and DSC of the CCTO gel films heated in a dry air atmosphere at 10 °C/min.