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Transformation of sputtered calcium copper titanate thin film into nanorods by sequential annealing

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ABSTRACT

Rapid synthesis of long calcium copper titanate (CCTO) nanorods was carried out by sequential annealing. CCTO thin films have been deposited on p-Si substrate by RF sputtering technique and afterwards, the samples were thermally treated using a preheated furnace by varying the annealing temperature from 850 °C to 1100 °C. CCTO nanorods of 12 μm lengths and 400–600 nm diameters were synthesized at 1100 °C. Based on the FESEM observations, a plausible growth mechanism has been proposed to explain the formation of nanorods. The (220) XRD peak of the CCTO film became prominent for the annealing temperature of 950 °C. The presence of nanoscale crystals in amorphous matrix has been observed by HRTEM studies. The elemental mapping of CCTO nanorod has shown a spatial variation of elements throughout the nanorod. The oxide and interface charge density was found to be increased with the rise in annealing temperature.

1. Introduction

In recent years, calcium copper titanate (CCTO) has drawn considerable attention for potential applications in supercapacitors [1], varistors [2], resonators [3], sensors [4] and memory devices [5] due to its nontoxic nature, excellent dielectric properties with high thermal and electrochemical stability [6,7]. CCTO has shown extraordinary dielectric constant (10^4–10^5) at room temperature in bulk form [8]. Several intrinsic and extrinsic models like domain boundaries, off-center displacement of Ti ions, twin boundary effect, Debye-type relaxation have been proposed to explain the origin of high-k in bulk CCTO [8–10]. The mostly accepted concept behind this enhanced dielectric constant is internal barrier layer capacitor (IBLC) model, where the thin dielectric layer between the adjacent semiconducting grains is responsible for this enhanced dielectric properties [11].

In order to fabricate low cost, portable, high performance electronic devices, the realization of functional materials in form of thin films/nanostructures are highly required. Since last decade, enormous efforts has been undertaken to synthesize CCTO thin films by various techniques in order to replace the conventional dielectrics [12–15]. However, a versatile and robust technique for the synthesis of CCTO nanostructures has not been fully explored. Very short (< 1 μm) CCTO nanorods were synthesized on platinized silicon substrates by sputtering technique [16,17]. The current technology demands the realization of long nanostructures for the fabrication of crossbar structures in order to achieve portable and high performance devices [18]. Recently, Tang et al. have observed long (14 μm) CCTO nanostructures by two step hydrothermal reaction [19]. Banerjee et al. have fabricated CCTO nanotubes by sol-gel method using closely packed porous nanochannel alumina template [6]. Jesurani et al. have synthesized CCTO nanoparticles using sol gel technique [20]. Recently, Tubío et al. have fabricated three dimensionally ordered macroporous CCTO structures by combining sol gel techniques with colloidal crystal templating [21]. However, these techniques are very complex and require longer process duration. In wet chemical methods, it is very difficult to observe contamination-free, reproducible characteristics of functional materials even through the precise control of the process parameters. Hence, there is a requirement of synthesis of long CCTO nanostructures by adopting complementary metal oxide semiconductor (CMOS) compatible process. In this research work, the synthesis of long CCTO nanostructures has been carried out by modified sequential annealing procedure for the first time.

2. Material and methods

A 2 in. CCTO sputtering target was fabricated by adopting conventional solid state route. Stoichiometry amount of $CaCO_3$, CuO and TiO_2 powder were thoroughly mixed in acetone medium for 12 h using ball milling method. The powder was grinded finely and calcined at 1050 °C for 10 h. Formation of pure phase CCTO was confirmed by XRD studies. 5 wt% polyvinyl alcohol (PVA) was added as binder with the calcined power and was pressed into a target of 2 in. diameter and 3 mm thick

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Table 1
Deposition parameters of RF sputtered CCTO thin film.

Target	CCTO
Base vacuum	3×10^{-6} mbar
Sputtering gas	Ar
Pre-sputtering time	10 min
RF Power	105 W
Deposition Pressure	5×10^{-3} mbar
Substrate temperature	RT

using uniaxial compression. The final sintering for the CCTO target was done at 1100 °C for 8 h. CCTO thin films were deposited on p-type silicon [(100), 1–10 Ω cm] by RF magnetron sputtering with RF power of 105 W and deposition pressure of 5×10^{-3} mbar at room temperature. The details of thin film deposition parameters are mentioned in Table 1. The CCTO nanostructures were synthesized by adopting a modified rapid thermal annealing of sputtered films in air ambient. Prior to the post deposition annealing, the temperature of the tubular horizontal furnace was kept at 800 °C. The sputtered sample was slowly inserted inside the preheated furnace. Samples were kept at 800 °C for 30 s and thereafter, the temperature was increased upto the dwelling temperature with the ramp up rate of 50 °C/min. The dwelling temperatures in this research were varied from 850 °C to 1100 °C. The morphological and structural properties of CCTO nanorods were studied by field-emission scanning electron microscope (FESEM: NOVA- FEI), X-Ray diffractometer (Rigaku ultima IV) and high resolution transmission electron microscopy (HRTEM; FEI TECNAI F30 G^2 STWIN) system. Al/CCTO/Si metal oxide semiconductor (MOS) structures were fabricated by thermally evaporated Aluminum as top and bottom contacts. The electrical properties were studied by Agilent E4980A precision LCR meter and Keithley 6487 picoameter/voltage source.

3. Results and discussions

Fig. 1 depicts the FESEM micrograph of CCTO thin films processed by modified annealing for 10 min in air ambient with various dwelling temperature. The films, processed at 850 °C, have shown the homogeneous distribution of spherical granular morphologies with average size of 2 μm. The films annealed at 950 °C have shown the appearance of bimodal microstructures with spherical and polyhedral shape. In this case, restructuring of the surface texture has taken place due to the grain growth through grain boundary diffusion at 950 °C. The grain growth in CCTO is primarily driven by the grain boundary mobility, which greatly depends on the diffusion of ions, atoms and/or charge species of the grain across the grain boundary [22]. The size of the spherical microstructures has been significantly reduced and the tiny cuboids of average size 500 nm are appeared for the process temperature of 1050 °C. In addition to the appearance of different types of microstructures, bulges were also appeared on the surface of the CCTO films for the annealing temperature of 950 °C and 1050 °C. The evolution of nanorods of average length around 12 μm has taken place at 1100 °C. The average diameter of the nanostructures was found to be in the range of 400–600 nm. In order to investigate the growth mechanism, the annealing was carried out at 1100 °C for very short period. Short CCTO nanorods were appeared for the process duration of both 10 s and 60 s as shown in Fig. 2(a-b). This study confirms that the evolution of nanostructure mostly depend on the process temperature rather than the process duration. However, the length as well as the aspect ratio of the nanorods is found to be increased with the rise in process duration. On the other hand, the evolution on CCTO nanorods were not observed for the conventional annealing of CCTO films, where the films were slowly heated from room temperature to 1100 °C. From the above observations, it is very clear that the modified annealing process plays vital role to form long CCTO nanorods due to the restructuring of the microstructures of sputtered CCTO thin films.

The formation of CCTO nanorods can be explained by the combined

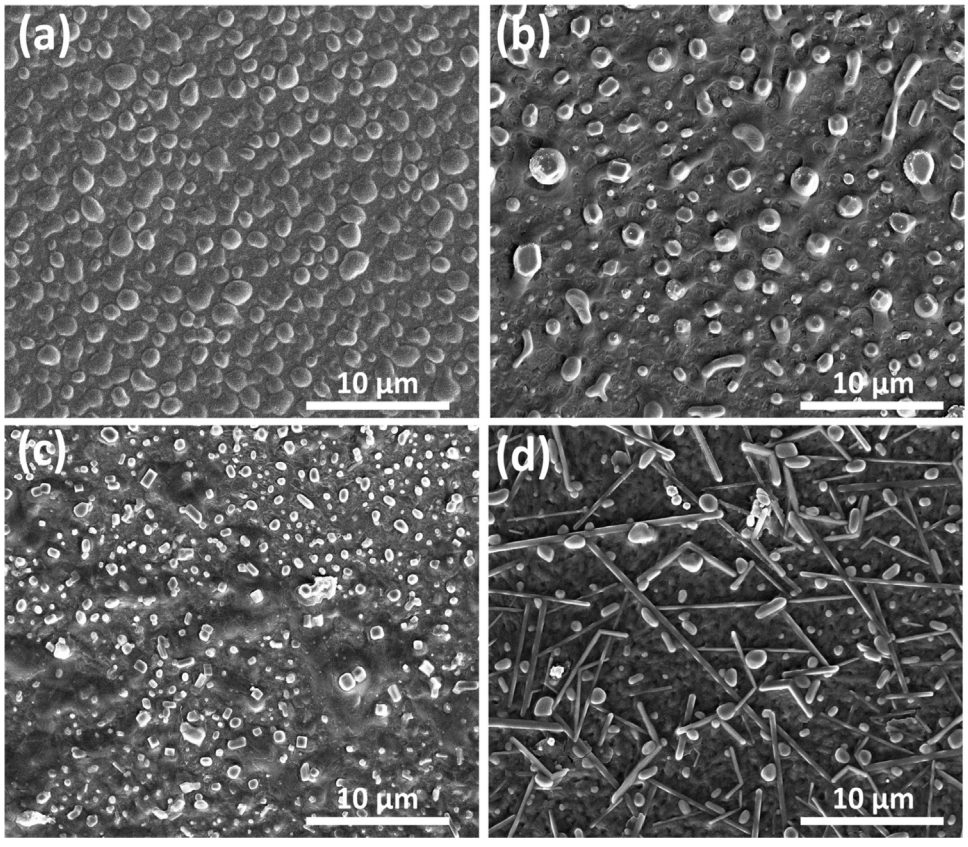

Fig. 1. FESEM images of CCTO thin films sequentially annealed at temperatures (a) 850 °C, (b) 950 °C, (c) 1050 °C and (d) 1100 °C.