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Effect of rapid thermal annealing on the structural and electrical properties of RF sputtered CCTO thin film

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Abstract: $CaCu_3Ti_4O_{12}$ (CCTO) thin films have been deposited by RF magnetron sputtering on silicon substrates at room temperature. As-deposited thin films were subjected to rapid thermal annealing (RTA) at different temperatures ranging from 850°C to 1000°C. XRD and capacitance - voltage studies indicate that the structural and electrical properties of CCTO thin film strongly depend upon the annealing temperature. XRD pattern of CCTO thin film annealed at 950°C revealed the polycrystalline nature with evolutions of microstructures. Electrical properties of the dielectric films were investigated by fabricating Al/CCTO/Si metal oxide semiconductor structure. Electrical properties were found to be deteriorated with increasing in annealing temperature.

Keywords: RTA, X-ray diffraction, FESEM, C-V measurement

1. Introduction

Materials with high dielectric constants are drawing a great deal of interest among researchers. Recently, $CaCu_3Ti_4O_{12}$ (CCTO) a cubic perovskite material is under active research due to its giant dielectric permittivity [1]. It shows a negligible temperature dependence on dielectric constant [2]. From neutron diffraction, no change in phase was found room temperature to 300°C [1, 2], which suits its application in microelectronics [3]. Miniaturization of electronic devices demands CCTO thin film to be integrated to semiconductor technology. Many research groups have deposited CCTO thin film by different deposition techniques like pulse laser deposition [4], sputtering [5], wet chemical methods [6]. However, sputtering has several advantages like low cost, uniformity, ease of synthesis, low temperature processing, non toxic nature. Post deposition annealing plays a significant role in the morphological and electrical properties of thin films. Rapid thermal annealing (RTA) has several advantages over conventional annealing like low thermal budget, less chance of dopant distribution, rapid grain growth [7]. In this work, an attempt has been made to investigate structural, morphological and electrical properties of CCTO thin film annealed with different RTA temperature.

2. Materials and Methods

CCTO sputtering target have been fabricated by adopting solid state route. Stoichiometric amount of $CaCO_3$, CuO, TiO_2 were mixed by using ball milling in acetone medium. The powder was calcined at 1050°C for 10 hours. Formation of single phase CCTO was confirmed by XRD studies. Thereafter, the target was fabricated by mixing the calcined powder with 5wt.% PVA solution and was pressed into a pellet of 2 inch dia and 3mm thickness using uniaxial compression with pressure 40MPa. Finally, the target was sintered at 1100°C for 8 hours. The details of target fabrication process have been reported elsewhere [8]. CCTO thin films of thickness 100 nm have been deposited on p-Si (100) substrates by RF magnetron sputtering technique with RF power of 105 W and deposition pressure of 5×10^{-3} mbar [9]. Post-deposition RTA was carried out at various temperatures ranging from 850°C-1000°C for 10min in air atmosphere using MTI (OTF- 1200X) system.

The structural and morphological properties were studied by X-Ray diffractometer (Rigaku ultima IV) and field-emission scanning electron microscope (FESEM: NOVA-FEI). For electrical measurements, MOS capacitors were fabricated using thermally evaporated aluminum film as top and bottom electrodes. The electrical properties of the Al/CCTO/Si metal oxide semiconductor (MOS) structures were studied by Agilent E4980A precision LCR meter and Keithley 6487 Picoammeter/voltage source.

3. Results and discussion

Fig. 1. shows the XRD pattern of CCTO thin films annealed at different temperature. The films, annealed at 950°C, show distinct (220) and (400) XRD peak, which depicts the polycrystalline nature of CCTO. The ratio of maximum intensity peak (200) of thin film annealed at 1000°C and 950°C $I_{1000°C}/I_{950°C} = 0.60$ which clearly indicate that there is a reduction in crystallinity for thin film annealed at 1000°C. This may be due to the creation of defects in the CCTO films including incorporation of impurity, variation of morphology and density, formation of unsaturated bonds at higher temperature. This increases the density of disorder due to which there is reduction of crystallinty at high temperature. Fig. 2. shows the FESEM micrographs of the CCTO thin films annealed at various annealing temperature. Thin films, annealed at 850°C and 900°C, depict the formation of microstructures with wide range of size variation (500nm - 4µm). On the other hand, uniform distributions of microstructures were appeared for the films annealed at 950°C and 1000°C. This may be due to the availability of adequate amount of thermal energy to the microstructure to form uniformly on the substrate.

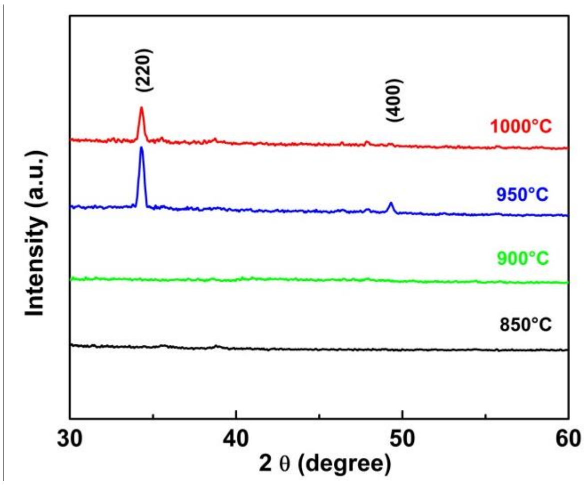

Figure 1. XRD pattern of CCTO thin films annealed at different temperatures

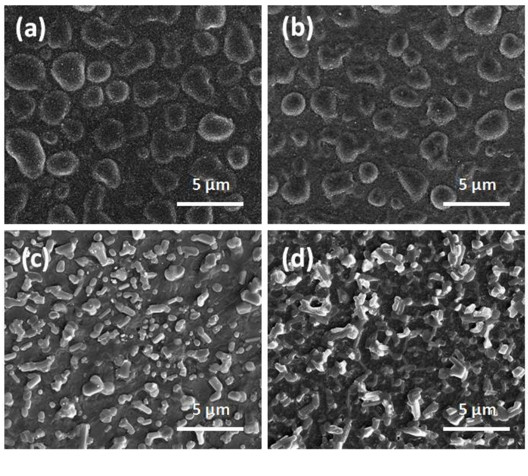

Figure 2. FESEM images of CCTO thin annealed at (a) 850°C, (b) 900°C, (c) 950°C and (d) 1000°C. Scale bar represents 5 µm

Capacitance-voltage (C-V) measurements were carried out for the films annealed at 950°C and 1000°C after the confirmation of CCTO phase. Fig. 3. shows the normalized high frequency (1MHz) (C-V) curves. Three regions of the C-V curves namely accumulation, depletion and inversion are distinctly visible in all the curves. The oxide charge density (Q_{ox}) was calculated from the shift in flatband voltage. Q_{ox} was found to be 0.14 × 10^{11} cm^{-2} and 1.81 × 10^{11} cm^{-2} for thin films annealed at 950°C and 1000°C, respectively. High Q_{ox} value for 1000°C annealed sample can be correlated to the formation of defects in CCTO thin films and therefore, possess large amount of trapping centres. The CCTO/Si interface charge density (D_{it}) is calculated using Hill- Coleman method [10]. Thin film annealed at 1000°C have comparatively high D_{it} (3.6 × 10^{11} $eV^{-1}cm^{-2}$) as compare to the 950°C annealed film (2.0 × 10^{11} $eV^{-1}cm^{-2}$) which may be due to the presence of dangling bonds at the interface and also due to interfacial stress, defects, nonstoichiometry of few initial deposited layers for high temperature annealing [11]. Leakage Current characteristics for CCTO thin films annealed at different temperature is plotted in Fig. 4. Thin film annealed at 1000°C shows high leakage current, which may be due to structural defects and/or incorporation of impurities due to high temperature annealing.

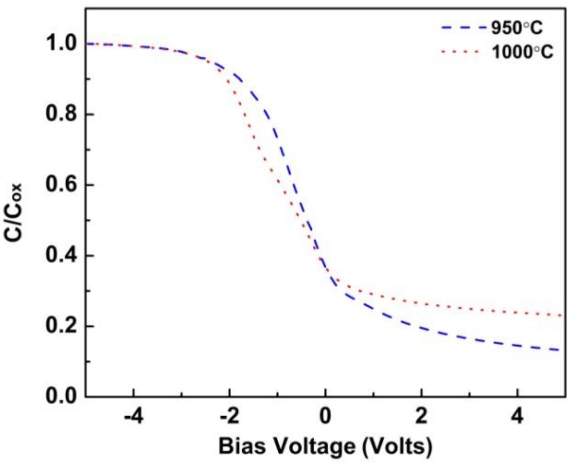

Figure 3. Capacitance - voltage characteristics of annealed CCTO films

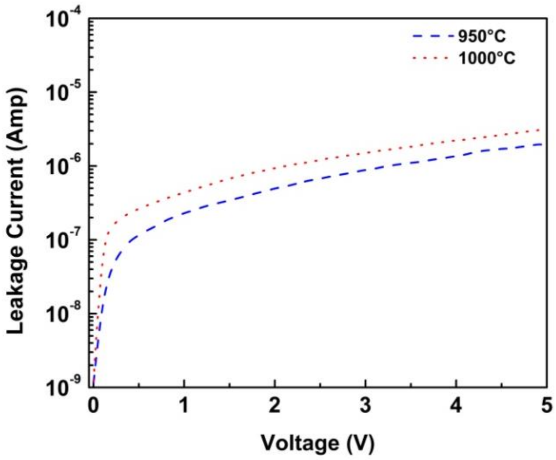

Figure 4. Current - voltage characteristics of annealed CCTO films.

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4. Conclusions

CCTO thin film has been deposited by RF sputtering on silicon substrates. Post deposition annealing was carried out with different temperatures. Evolution of CCTO polycrystalline phase was confirmed from XRD patterns. Thin film annealed at 950°C have shown better crystallinity, uniform microstructures, lower interface and oxide charge density and also lower leakage current.

5. Acknowledgement

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6. References

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