CCTO thin film synthesis by radio frequency magnetron sputtering

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Abstract. In the present work CCTO thin film has successfully deposited on FTO substrate in a non-reactive (argon) atmosphere with frequency (RF) magnetron sputtering at 300 W. This work aims to determine the structural, morphological and optical properties of thin film using X-ray diffraction (XRD), atomic force microscopy (AFM) and Ultraviolet–visible spectroscopy (UV-Vis), respectively. The result shows that the nature of CCTO thin film is polycrystalline with cubic structure. XRD peaks confirmed the presence of CCTO phase with the crystal planes of (022), (013), (033), (024), and (224). The average crystallite size was 32 nm as measured by Williamson-Hall method. The surface roughness (Ra) and root mean square (RMS) of CCTO thin film were 26 nm and 33 nm, respectively. The maximum optical transmittance of CCTO thin film was more than 80% in the visible region (550-1000 nm) while calculated optical energy bandgaps was 3.2 eV.

1. Introduction

Recently, CaCu₃Ti₄O₁₂ (CCTO) perovskite-like compound has received increasing interest because of the attractive attribute like high dielectric constant (εᵣ) at wide range of temperature (100 - 600 K). This special feature has increased the potential of CCTO as a useful material in the microelectronics field. In various CCTO studies, the chemical methods have applied to prepare bulk materials and the main aim its focusing on possible mechanism that account for the unusual CCTO properties [1]. The remarkable properties such as high εᵣ, low dielectric loss (tan δ) [2,3], high electrical and thermal stability [4] can be achieved when CCTO is in the form of thin film owing to superior uniformity and porosity in contrast to bulk materials. With these properties, the CCTO thin film becomes very attractive to utilize in several applications such as capacitor [5], antennas [6], sensors [7], and solar cell [8]. Nevertheless, further comprehension of the structural characteristics of the CCTO thin films that is correlated to growth parameters, are essential prior to practical application as electronic devices.

There are various chemical and physical methods to deposit CCTO thin film such as, sol–gel process [9], pulsed laser deposition (PLD) [10], sputtering [11], and metal organic chemical vapor deposition (MOCVD) [12]. RF magnetron sputtering possesses huge beneficial as it’s capable to control a deposition parameter, good adhesion and deposit uniformly in large surface area, among
these methods. It is reported previously [13-15] the effect of thickness, annealing temperature, and RF power on the properties of CCTO thin films deposited on ITO substrates. All works show that the properties of CCTO thin film changes with changing the parameters. Thus far there is no scientific report to investigate the properties of CCTO thin film deposited on fluorine tin oxide (FTO) substrate by RF sputtering.

Therefore, in this study, 250 nm thickness of CCTO thin film has been deposited on FTO substrate by using RF magnetron sputtering and the crystallite structural, surface morphological, and optical properties of CCTO thin films were investigated for the first time.

2. Experimental Method

2.1 Preparation CCTO thin film

CCTO thin film with a 250 nm thickness has been deposited on FTO substrate by using RF magnetron sputtering (HHV Auto 500) technique. The FTO demonstrates to be a favorable electrode substrate in sensors and solar cell applications. CCTO target was used with in this experiment with 76 mm diameter and 5 mm thickness. In order to eliminate the surface impurities, the substrate (FTO) was cleaned with acetone, ethanol and deionized water before deposition process. Furthermore, the pressure in the deposition chamber was maintained at 30×10^{-5} mbar and the CCTO target was pre-sputtered for about 300 s at 30 W to eliminate surface contamination, prior to deposition process. The operating pressure during film deposition was 1.23×10^{-2} mbar, while an argon gas flow rate and RF power were 10 sccm and 300 W, respectively at room temperature. The film thickness was measured by thin film controller of RF magnetron sputtering machine and was also confirmed by thin film analyzer (Film metric, F20). X-ray diffraction (XRD Bruker, D8 Advance system) and atomic force microscope (AFM, Nano Navi, SPA 400) were used to examine the crystalline phases and surface topography of the sputtered CCTO films. UV-Vis spectrophotometer (Varian, Cary 50 conc) with the wavelengths range of 280 nm to 880 nm was used to determine the transmittance of CCTO thin film while energy bandgap had calculated from Tauc plot method.

3. Results and Discussion

3.1 X-ray diffraction analysis

Figure 1 depicts the X-ray diffraction (XRD) patterns of the CCTO thin film on a FTO substrate with 250 nm thickness. The diffraction peaks of the film are corresponds to cubic perovskite related structures (ICDD data card no. 095-005-8088) with space group of Im-3 [16]. It is visible that five peaks centered at 34.20°, 38.55°, 52.51°, 55.65°, and 61.42° which match to crystal planes (022), (013), (033), (024), and (224), respectively. The characteristic peak of FTO substrate can be seen in the pattern at 20 = 27.20 ° which is related to the crystalline structure of FTO [17]. However, not all of the expected peaks for CCTO thin film are appeared in the spectrum. This phenomenon can be attributed to the small amount of CCTO being deposited on the FTO substrate. The average crystallite size was determined referring to Williamon-Hall method [18] and it was found to be 32 nm.
3.2 Morphology analysis (AFM)

The AFM analysis (tapping mode at ambient condition) was conducted to evaluate the surface morphology of the sputtered CCTO thin films. The 2D images of the sputtered CCTO thin film are presented in Figure 2. The roughness (Ra) and its root mean square (RMS) of a scan area (10 × 10 µm²) were determined by the AFM. It can be seen (Figure 2 a) that the CCTO film illustrated a microstructure which contains a mixture of small and large grains. Furthermore, the recorded values of Ra and RMS are 26 nm and 33 nm, respectively. These values may have originated from the initial roughness of the substrate itself. Roughness values for FTO substrates before deposition were: RMS = 20 nm. It was also perceived from surface profile variations (corresponding average profile line) Figure 2 (b) that the pore size is about 85 nm. However, both surface roughness and pore size can be potential parameter to influence practical applications like optical and gas sensors.
3.3 Optical properties

The UV-Vis transmission spectra of CCTO thin films deposited on FTO substrates is shown in Figure 3. The transmittance of samples was measured as a function of wavelength in the range of 300-1000 nm. The transmittance of CCTO thin films was detected in the range of 60% to 80% (Figure 3inset) on FTO substrate in the visible region. The optical energy bandgap ($E_g$) was measured by using the Tauc model [19]. The $E_g$ of CCTO thin films on FTO substrate was 3.2 eV as shown in Figure 3. The wide bandgap is particularly important for allowing wide bandgap devices to operate at much higher temperatures. Additionally, most wide bandgap materials also have a much higher critical electrical field density. Combined, these properties allow them to operate at much higher voltages and currents, which makes them highly valuable in military, radio and energy conversion settings.

Figure 2. Atomic force micrographs of CCTO thin film (a) 2D image (b) the corresponding average profile line
Figure 3. Optical transmittance spectra and Tauc’s plot (inset) of CCTO films deposited on FTO substrate

4. Conclusion

CCTO thin film layer with 250 nm thicknesses was deposited on FTO substrate by using RF magnetron sputtering process at room temperature and power 300 W. The average crystallite size of CCTO thin films was obtained to be 32 nm while the surface roughness was 33 nm. CCTO film also showed good optical transparency (over 60%) in the visible region while the obtained energy bandgap was 3.2 eV. Therefore, having knowledge on properties of CCTO thin film on FTO substrate could be suitable for specific applications.

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6. References

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