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Humidity Sensing Properties of CCTO Thin Films Grown by Radio Frequency Magnetron Sputtering:Substrates Dependent

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ABSTRACT. CCTO thin films are of great importance for applications in various electronic devices. CCTO thin films with 200 nm thickness were grown onITO andAl_2O_3 substrates by RF magnetron sputtering at 300 °C. The crystallographic properties of the films were studied by X-ray diffraction (XRD), and their morphologies were investigated by field emission scanning electron microscopy (FESEM). The I-V characteristic were measured by using direct current (DC) analysis method at humidity range of 30–90% relative humifity (RH). The XRD and FESEM results indicate that the CCTO thin films are polycrystalline nature, and porousfor both substrates. The average crystallite size was 30 nm and 50 nm for CCTO deposited on ITO and Al_2O_3 substrate, respectively, as it is in good agreement with the FESEM results. The response times, recovery time and sensitivity were obtained 12 s, 500 s, and 17, respectively for 200 nm CCTO thin films deposited on ITO substrate, while those sensing properties were 30 s, 450 s, and 75for CCTO thin films deposited on Al_2O_3 substrate. The CCTO thin films deposited on Al_2O_3 substrate show better I-V characteristics than that deposited on ITO substrates.

Keywords: *CCTO, RF magnetron sputtering, Structural, I-V characteristic;*

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1. INTRODUCTION

The $CaCu_3Ti_4O_{12}$ (CCTO) thin film with cubic structure is a novel electroceramic material with high dielectric permittivity (ε) and moderate dielectric loss (δ)[1,2]. Contrast to other metal oxide thin film materials, the CCTO thin film usually exhibits better chemical resistance, and thermal stability than electrolyte and organic polymer sensors. Recently, CCTO- based materials has concerned a great attention in the various applications from capacitor [3,4], to sensors [5,6] due to its distinctive electronic, physical and sensing properties. However, fabrication of the reliable CCTO thin film based possible device applications require to understand the factors influencing on the structural, morphological and properties of the thin films that are sensitive to the process conditions [7,8].

The substrate is an important factor which should be taken into consideration. As we all know, the thin films with better crystallinity will show excellent properties. Different substrates will led the change in crystallinity of thin films. Several researchers have reported the effect of the substrates on the different properties of the thin films. The suitable substrate cause better crystallinity and large grainsize, leads to better humidity sensing properties, and increment in other properties for thin films. However, so farthere is no effort to study the influence of substrate on properties of CCTO thinfilm.

In this work, cubic structure CCTO thin films had deposited on ITO and Al_2O_3 substrates by RF magnetron sputteringat substrate temperature 41 ºC. The effect of different substrates was investigated by studying the structural, morphologcal, and humidity sensing properties.

2. MATERIALS ANDMETHODS

2.1 CCTO thin film humidity sensor preparation. The CCTO thin films with 200 nm thicknesses were deposited on ITO and Al_2O_3substrates by RF magnetron sputtering system. The cylinder shaped pure CCTO (99.9%) target with a thickness of 0.19 inch and diameter 3inch was used. The ultrasonically cleaned ITO and Al_2O_3 were used as substrates and fixed in rotatable substrate holder. The distance between target and substrate was kept constant approximately 120 mm. The sputtering chamber was first pumped down from atmospheric pressure to a base pressure of 30×10^{-5} mbar. Then Ar gas was introduced into the chamber at a rate of 65 standard cubic centimeter per minute (SCCM) and when the pressure reached 2×10^{-5} mbar, the RF power supply was switched on and kept at 150W. sensor fabrication and humidity measurement using these CCTO thin film sensors was carried out by a climate chamber (Memmert HPP108) which was the same as our previous work [9]. The sputtering conditions for thin film deposition are summarized in Table1.

Table 1 Sputtering condition for CCTO thin film deposition

Parameter	Condition
Target	CCTO (99.9% purity)
Substrate	ITO, Al_2O_3
RF power	200 W
Sputtering gas	Pure argon (10 Sccm)
Deposition time	60 min
Operation pressure	1.23×10^{-5} mbar
Substrate temperature	41 ºC

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction and morphology analysis. The X-ray diffraction (XRD) patterns of the sputtered CCTO a thin film on ITO and Al_2O_3 substrates is shown in Fig. 1 (a, b). Diffraction peaks of the film can be specified to body centered cubic perovskite related structures (ICDD data card no. 98-005-8088) with space group of Im-3. As shown in Fig. 1, the four comment peaks with hkl value (022), (013), (123), and (244) are observed for CCTO thin films. The intensities of peaks are sharps and narrow, approving that the samples are in high quality and good crystallinity. Furthermore, the crystallite size (D) can be calculated according to the Williamson-Hall [10]Eq. (1):

$$\beta\cos\theta = \frac{0.9\lambda}{D} + (4.\varepsilon.\sin\theta) \qquad (1)$$

Whereby ,λ is the X-ray wavelength (0.15406 nm), and β is the full width at half maximum [FWHM] of the film diffraction peak, and θ is the Bragg diffraction angle. The values of D can be obtained through the extrapolation and shown in Table 2. The extra peaks also were observed in Fig. 1 (a andb) that is belong to substrates.

Fig. 2 (a and b) illustrates FESEM images of the sputtered CCTO thin film on ITO and Al_2O_3 substrates. The CCTO thin film layer present uniform surface morphology. The average grain size is 30 and 50 nm distribute on the film surface for ITO and Al_2O_3 substrates, respectively that was measured by imgagej software. It can be obviously perceived that CCTO thin films layer are intergranular porous. The thickness of the CCTO thin films was measured by thin film analyzer (Filmetric, F20) and found to be 200 nm.

Table 2 XRD data for CCTO films on ITO and Al_2O_3 substrates for comment peaks

Substrate	2θ				d-spacing (Å)				Crystallite size (nm)			
	(022)	(013)	(123)	(244)	(022)	(013)	(123)	(244)	(022)	(013)	(123)	(244)
ITO	24.5	38.7	45.1	78.1	2.52	2.32	1.93	1.22	25	56	39	37
Alumina	34.6	38.3	45.1	77.2	2.59	2.34	1.94	1.23	55	52	55	63

3.2 Humidity sensitivity of CCTO thin film

3.2.1 Response/Recovery Time. Response time is defined as the time taken by the sensor to achieve 90% of the final steady resistance value, while the recovery time is the time required for the sensor to return 30% above the original resistance value in air. The humidity sensing properties of CCTO thin films was analyzed at constant temperature (30 °C). Underthese conditions, the response/recovery time were measured at voltage 3 V and humidity range 30 – 90% RH. The electrical characteristics of CCTO thin films are shown in Figs. 3 and 4. The response time is 12 s and 40 s while the recovery time is 500 s and 450 s, CCTO thin film deposited on ITO and Al_2O_3 substrates, respectively.

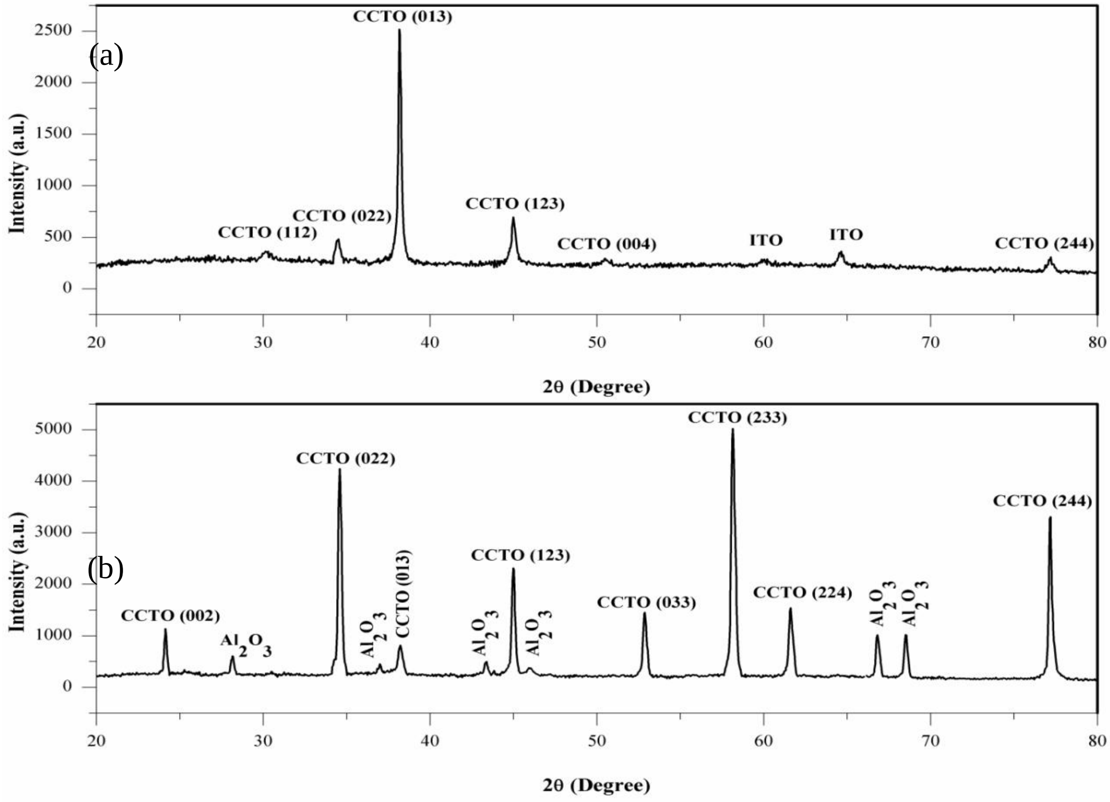

Fig. 1 X-ray diffraction patterns of the sputtered CCTO thin films layer on (a) ITO substrate and (b) Al_2O_3 substrate

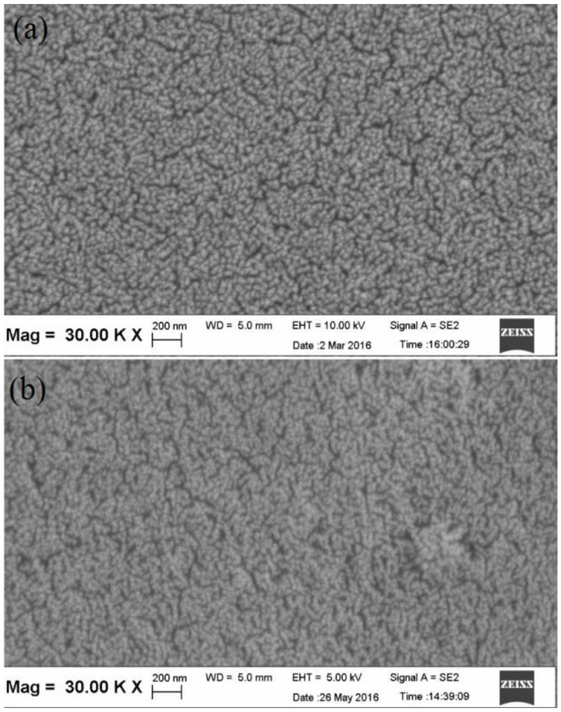

Fig. 2FESEM image of CCTO thin film deposited on (a) ITO substrate and (b) Al_2O_3 substrate

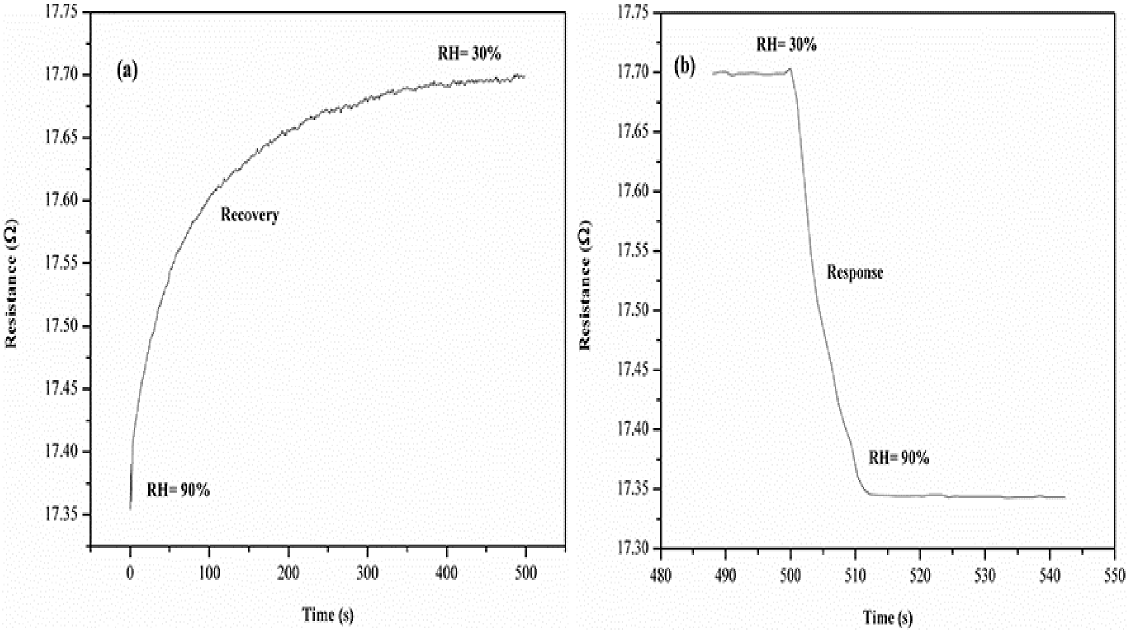

Fig. 3 Humidity behavior CCTO thin film deposited on ITO substrate at relative humidity 90%-30% and 3 V (a) Response and (b) recovery curve

3.2.2 Sensitivity**.** The humidity sensitivity (S_H) is measured by using Eqs. 2 and 3 and response curve (Fig.3). S_H is defined as the change in the resistance of the sample per unit change in the applied relative humidity.

$$S_H = \frac{\Delta R}{\Delta R_H}$$

$$(2)\Delta R_H = \frac{R_{LH} - R_H}{R_{LH}}$$

(3)

The R_{LH} is the resistance of the sample measured at lower humidity (R_{LH} = 30% RH) and R_H is the resistance of the sample at any relative humidity (RH%). It is found that, S_H is about 17, 75 for CCTO thin film with 200 nm deposited on ITO substrate and Al_2O_3 substrate respectively, at 30-90% RH. CCTO deposited on Al_2O_3substrate show better S_H that is attributed to grain size effect. Because of small grain size, the film with 200 nm thickness has large grain boundary density.

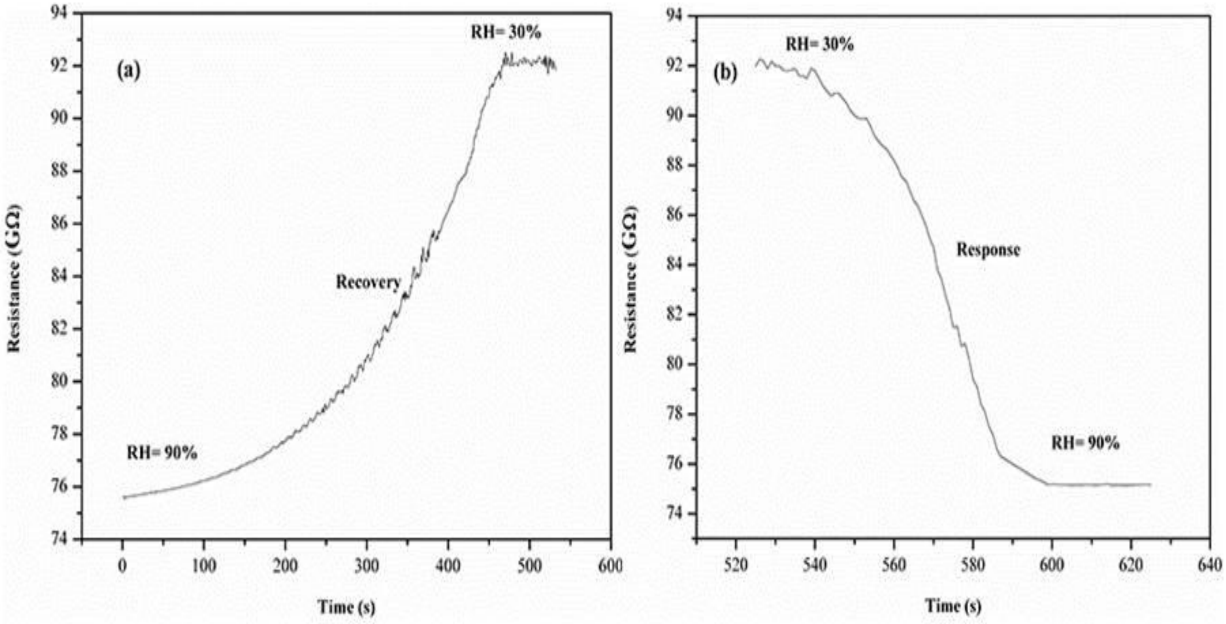

Fig. 4 Humidity behavior CCTO thin film deposited on Al_2O_3 substrate at relative humidity 90%-30% and 3 V (a) Response and (b) recovery curve

4. SUMMARY

CCTO thin film layer with 200 nm thicknesses was successfully deposited on ITO and Al_2O_3substrates by RF magnetron sputtering process at 300 ºC and power 150 W. The FESEM shows the CCTO thin film layer are intergranular porous microstructures, uniform, and porous with average grain size is30 and 50 nm for ITO and Al_2O_3substratesrespectively. CCTO thin film deposited on Al_2O_3substarte shows better humidity sensing properties.

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