### CHAPTER 2

### LITERATURE REVIEWS

### 2.1. Origin of the high dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>

### 2.1.1. Intrinsic effects

The unusually high dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> has led researchers to speculate on the possible mechanisms that can explain its origin. From further dielectric measurements at low temperatures, the interpretation of this giant dielectric constant has been introduced separately by two different research groups on the basis of the intrinsic point of view. First, Ramirez et al. [14] found out that the high dielectric constant was temperature independent over 100 - 400 K. However, the dielectric constant dropped by the factor of 100 at temperatures below 100 K along with a broad peak in the loss tangent, shown in Figure 2.1. Also, measurements of the dielectric constant and tan  $\delta$  as a function of temperature revealed a strong frequency dependence and an increasing trend in the characteristic frequency ( $\omega_0$ ) over temperature. Lastly, Raman scattering data measured at the different temperatures showed a temperature independent gap frequency (28 meV), which is analogous to the thermal activation energy of the dielectric constant at the low frequency region. Considering that  $\omega_0$  can be defined as the jump rate for an electron between two lattice sites, its change as a function of temperature indicates that the anomalous dielectric responses in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> might be linked to a Debye-like relaxation



behavior. Also, the gap frequency correlated with the energy difference between those sites suggests the possibility of highly polarizable relaxation modes.

Figure 2.1 Plots of the dielectric constant and tan  $\delta$  versus temperature of two different CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> samples [14]

Homes *et al.* [18] also reported similar results such as the temperature dependence and the huge reduction (below T = 100 K) of the dielectric constant. From optical data on a single crystal of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>, they found that the dielectric constant as a function of frequency exhibited a strong temperature dependence. Also, the room temperature dielectric constant in the far infrared (FIR) region was about 75, which is much smaller than the reported value of  $10^4$  at 100 kHz [12]. This large

difference was considered as a strong absorption occurring at low frequency range, which can be explained by the dipolar relaxation process. Using the Debye model where the dielectric constant is expressed by Eq. (2.1) [18]:

$$\varepsilon_{r}' = \varepsilon_{r\infty} + \frac{\varepsilon_{rdc} + \varepsilon_{r\infty}}{1 + (\omega\tau)^{2}}$$
 (2.1)

where  $\mathcal{E}_{r\infty}$ : dielectric constant at high frequency,  $\varepsilon_{rdc}$ : dc (static) dielectric constant they showed that the calculated data are well matched with the measured dielectric constant plotted as a function of frequency (Figure 2.2 A). Moreover, the decrease of the relaxation time at increased temperatures, shown in Figure 2.2 B, is expected from Eq. (2.2) [5]:

$$\tau = \tau_h \exp\left(\frac{H}{kT}\right) \tag{2.2}$$

where  $\tau_h$ : pre-exponential factor, H: activation energy

Based on these observations, they suggested "the relaxor-like slowing down of the dipolar fluctuations in nano-sized domains" as the possible mechanism for the unusually high dielectric constant in  $CaCu_3Ti_4O_{12}$ .



**Figure 2.2** (A) a curve fit between the measured and the calculated dielectric constant as a function of frequency; (B) a plot of the relaxation time versus inverse temperature [17]

#### 2.1.2. Extrinsic effects

#### 2.1.2.1. Interfacial polarization effect: Maxwell-Wagner model

Based on first principle calculations, He et al. [19] reported that there was no direct evidence for the intrinsic lattice contribution to the dielectric constant. The subsequent study about the structural and lattice dielectric response of both CdCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> and CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> [20] supported their mathematical results and thus implied the extrinsic model. Afterwards, there have been many other reports about the various extrinsic behaviors in the form of interfacial contributions to the dielectric response of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. These include twin boundaries in single crystals [12], grain boundaries in polycrystalline CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> [21], and electrode interfaces [22]. In an effort to obtain evidence of extrinsic effects, Lunkenheimer et al. [23] investigated the effects of the electrode contact on the dielectric response. Through the measurement of the frequency dependent dielectric constant among four different materials (Indoped CdF<sub>2</sub>, pure LaMnO<sub>3</sub> and single crystal La<sub>2</sub>CuO<sub>4+ $\delta$ </sub>, single crystal SrNbO<sub>3.41</sub>, and polycrystalline Gd<sub>0.6</sub>Y<sub>0.4</sub>BaCo<sub>2</sub>O<sub>5.5</sub>), they concluded that the colossal dielectric constant resulted from these materials is caused by either the electrode contact or grain boundary effects. Furthermore, their ensuing research based on the effects of a variety of contacts and sample thickness on the dielectric response (shown in Figure 2.3 (a) and 2.3 (b), respectively) proved that the unusually high dielectric constant in  $CaCu_3Ti_4O_{12}$  was erroneously attributed to an intrinsic mechanism [24].



Figure 2.3 Plots of the frequency dependent dielectric constant of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> measured with (a) different types of contacts and (b) different thicknesses [24]

The effects caused by the sample-electrode contacts in many high dielectric constant materials can be attributed to an interfacial polarization. It has been known

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from Jonscher [25] a few decades earlier that this interfacial or space charge polarization can be realized from the capacitive layer near the electrode due to the formation of a Schottky barrier. For the application of this polarization mechanism to the high-K CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>, however, it is necessary to consider the nature of interfaces in this compound. Recently, Sinclair *et al.* [21] reported that the limited reoxidation along the grain boundary regions in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> creates an electrically inhomogeneous structure that is characterized by the spatially varying permittivity at the micro- or nanoscale. Consequently, this electrical heterogeneity in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> can be interpreted by using a Maxwell-Wagner type two-layer dielectric model [26]. As shown in Figure 2.4 (a), the dielectric has two parallel layers of materials grain and grain boundary whose dielectric constant, conductivity and the thickness are indicated as  $\varepsilon_g'$ ,  $\sigma_g$ ,  $d_g$  and  $\varepsilon_{gb'}$ ,  $\sigma_{gb}$ ,  $d_{gb}$ , respectively. If a DC voltage is applied to the dielectric and the concept of parallel equivalent circuit of two layers represented in Figure 2.4 (b) is utilized, the voltages of material grain and grain boundary can be expressed as the following equation:

$$\nu_{g} = \nu \frac{R_{g}}{R_{g} + R_{gb}} \left\{ 1 - \left(1 - \frac{C_{gb}R_{gb}}{\tau a}\right) \exp\left(-\frac{t}{\tau}\right) \right\}$$

$$\nu_{gb} = \nu \frac{R_{gb}}{R_{g} + R_{gb}} \left\{ 1 - \left(1 - \frac{C_{g}R_{g}}{\tau}\right) \exp\left(-\frac{t}{\tau}\right) \right\}$$
(2.3)

Furthermore, the relaxation time,  $\tau$ , can be displayed as the function of dielectric constant, conductivity and the thickness:



Figure 2.4 Schematic illustration of (a) Maxwell-Wagner two-layer dielectric model and (b) two-layer parallel equivalent circuit [26]

The concept of the admittance, Y, can be used when an AC voltage is applied to the given dielectric. Since  $V = V_0 \exp(i\omega t)$  and from the following relationship of Y  $= 1/R = I/V = Y_g Y_{gb}/(Y_g + Y_{gb})$  where  $Y_g = (1+j\omega t_g)/R_g$  and  $Y_{gb} = (1+j\omega t_{gb})/R_{gb}$ , the admittance can be written as the following equation:

$$Y = \frac{1}{R_g + R_{gb}} \left\{ \frac{(1+j\omega \tau_g)(1+j\omega \tau_{gb})}{1+j\omega\tau} \right\}$$
(2.5)

where  $\tau = (R_g \tau_{gb} + R_{gb} \tau_g)/(R_g + R_{gb})$ . Using  $Y = j\omega \epsilon^* Co$  where  $\epsilon^* = \epsilon' - j\epsilon''$ ,

the overall dielectric constant ( $\epsilon'$ ) is

$$\varepsilon' = \frac{\tau_g + \tau_{gb} - \tau + \omega_{gb} \tau_g \tau_{gb}}{C_o (R_g + R_{gb})(1 + \omega_{gb} \tau_{gb})}$$
(2.6)

Introducing the static frequency (i.e.  $\omega \sim 0$ ) as well as the maximum

value (
$$\omega = \omega_{\infty}$$
), Eq. (2.6) is simplified as  

$$\varepsilon' = \varepsilon'_{\infty} \{1 + \frac{(\varepsilon'_{s} - \varepsilon'_{\infty})}{\varepsilon'_{\infty}(1 + \omega^{2}\tau^{2})}\}$$
(2.7)

Therefore, by comparing Eq. (2.7) to Eq. (2.3), the two-layer dielectric modeled by the Maxwell-Wagner type polarization provides a relaxation behavior that is indistinguishable from the Debye model. However, at high frequency the second terms become dominate. For CCTO system, the dielectric behavior could be rationalized using the following equation:

$$\varepsilon_s' = \frac{C_{gb}}{C_0} \tag{2.8}$$

Where  $\varepsilon_{s}^{'}$  is the static dielectric constants and  $C_{0}$  is the empty cell constant.

It was also proposed that the apparent dielectric constant  $(\mathcal{E}'_r)$  can be related the grain size (d) and the thickness of grain boundary (barrier width, t) and internal dielectric constant of the barrier material  $(\varepsilon_{gb})$  as the below expression:

$$\varepsilon_r' = \varepsilon_{gb}(\frac{d}{t}) \tag{2.9}$$

From the internal barrier layer capacitor model (IBLC), the equivalent circuit of CCTO system can be consisted of two parallel RC elements connected in series. The two parallel RC circuits represent to semiconducting bulk grain (which consists of grain resistor ( $R_g$ ) and grain capacitor ( $C_g$ )) and insulating grain boundary(which consists of grain boundary resistor( $R_{gb}$ ) and grain boundary capacitor  $(C_{gb})$ ). In case  $R_{gb} \gg R_g$  and  $C_{gb} \sim C \gg C_g$  and  $\omega R_b C_b \ll 1$ , the loss tangent can be express as:

$$\tan \delta = \frac{1}{\omega R_{gb}C} + \omega R_g C \tag{2.10}$$

The first term is dominated at low frequency, therefore the loss tangent decreased with increasing frequency.

### 2.1.2.2 Internal barrier layer capacitor (IBLC) model

As Subramanian *et al.* [12] mentioned earlier, their observation of the twin boundaries in the single crystal CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> provides the possibility of the creation of the barrier layer capacitance effect. Moreover, the fact that the aforementioned Maxwell-Wagner polarization can be derived from the internal interface or barrier suggests another probable extrinsic model to elucidate the abnormally high dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. It has been recognized that non-stoichiometric materials such as TiO<sub>2</sub> become conductive after sintering in reducing conditions [18]. Furthermore, this reduction process during sintering can be significantly affected by the nature of the composition. That is, donor ions enhance the reduction while acceptor ions inhibit the process. When the reduced material undergoes only a limited oxidation, however, a thin layer of higher resistivity material is formed whereas a more conductive region exists in the center of the material. In this type of material, called a barrier or boundary layer capacitor, an improvement in its overall dielectric constant is realized at low frequencies [27]. The most well known examples of this barrier layer capacitor are barium and strontium titanates (BaTiO<sub>3</sub>, SrTiO<sub>3</sub>). For SrTiO<sub>3</sub>, normally an insulator with a moderate dielectric constant of K ~ 332 at room temperature [28], it becomes a non-stoichiometric n-type semiconductor (SrTiO<sub>3-x</sub>) under reducing atmospheres. This phenomenon can be expressed as the following equation:

$$SrTiO_3 \rightarrow SrTiO_{3-x} + \frac{x}{2}O_2 + 2xe^-$$
 (2.11)

Based on the defect chemistry, the oxygen deficiency during the reduction reaction creates oxygen vacancies that can be shown from the expanded form of Eq. (2.11):

$$Sr_{Sr}^{x} + Ti_{Ti}^{x} + 3O_{0}^{x} \rightarrow Sr_{Sr}^{x} + Ti_{Ti}^{x} + 2O_{0}^{x} + \frac{1}{2}O_{2} \uparrow + V_{0}^{"} + 2e^{-}$$
(2.12)

Here, the free electrons shown in Eq. (2.12) contribute to the increased conductivity, forming semiconducting grains. When SrTiO<sub>3</sub> is annealed in oxygen, however, the reoxidation occurs along the grain boundaries leading to a higher resistivity. That is

 $\frac{1}{2}O_2 + V_0^{"} + 2e^- \rightarrow O_0^x \qquad (2.13)$ 



Figure 2.5 Schematic diagram of a brick wall model for a barrier layer capacitor

In order to verify the enhanced dielectric constant in the barrier layer materials consisting of semiconducting grains and insulating grain boundaries, the simple brick wall model was suggested [11]. Assuming the simplified microstructure (shown in Figure 2.5) where the grain boundary thickness is much smaller than the grain size, the capacitance of a single element can be expressed by:

$$C_i = \frac{\varepsilon_o \varepsilon_t t_{gr}^2}{t_b} \tag{2.14}$$

Also, if a column of elements is connected in series (i.e.  $1/C = 1/C_1 + 1/C_2 + \dots$ ), Eq. (2.13) becomes

$$\frac{c_i}{\# of \ elements} = \frac{\varepsilon_o \varepsilon_t t_{gr}^2 / t_b}{(\frac{t}{t_{gr}})}$$
(2.15)

By calculating the capacitance per unit area (C/A =  $\epsilon_r\epsilon_o t_{gr}/tt_b),$  the

effective dielectric constant of the barrier layer material is

$$\varepsilon_{eff}' = \frac{\varepsilon_o t_{gr}}{t_b}$$
(2.16)

Therefore, if  $t_g = 50 \ \mu m$ ,  $t_b = 0.2 \ \mu m$ ,  $\epsilon_r = 200$ , the effective barrier layer

dielectric constant is increased to 50,000.

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Figure 2.6 (a) Schematic diagram of an equivalent parallel circuit(b) impedance complex plane plot showing two semi-circle components [30]

Along with the many efforts to provide the clear extrinsic mechanism in  $CaCu_3Ti_4O_{12}$ , the first evidence of this barrier layer capacitor model was reported by Sinclair *et al.* [28] by using the impedance spectroscopy. Assuming an ideal equivalent circuit that includes two parallel resistance-capacitor (RC) elements connected in series shown in Figure 2.6 (a). The impedance data represented as the reactance (Z") in the y-axis and the resistance (Z') in the x-axis indicate two semi-

circles representing both the grain and grain boundary response. Here, the resistances are obtained from the intercepts on the x-axis while the capacitances can be calculated by using the given equation [29]:

$$\omega_{max} RC = 1 \tag{2.17}$$

where  $\omega_{max}$  is the frequency at the maximum Z" of each semi-circle, equivalent to the reciprocal of the characteristic relaxation time  $(1/\tau)$ . On the other hand, these grain and grain boundary resistances can be identified by the magnitude of capacitance. For example, the impedance analysis for Ca12Al14O33 shows the capacitance of grain on the order of  $1 \times 10^{-12}$  F (~ 1 pF) which is lower than the grain boundary capacitance of 4 x 10<sup>-9</sup> F (~ 4 nF) [30]. The grain and grain boundary resistances from semi-circles are presented in Figure 2.6 (b). For the impedance data on CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> at room temperature obtained by Sinclair et al. [28], it is clearly shown that there exists a non-zero resistance in the inset of Figure 2.7 (a). Considering the semi-circle at low frequency shown in the main figure, this result strongly indicates that there should be another semi-circle at high frequency over  $10^5$ Hz. When the impedance plot was made below 130 K, however, the new data presented in Figure 2.7 (b) confirmed the high frequency semi-circle showing the grain resistance. Thus, similar to the case of a SrTiO<sub>3</sub> barrier layer capacitor, the giant dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> can be attributed to the formation of thin insulating boundaries with the conducting grains.



After the suggestion of the internal barrier layer capacitor (IBLC) model as the clear evidence of an extrinsic effect, there have been a number of reports supporting IBLC effects. As an explanation of the huge reduction of the dielectric constant in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> at low temperature, Homes *et al.* [31] suggested that the increased electronic localization caused by increasing the Born effective charge per oxygen atom ( $Z_0^*$ ) at lower temperature affects the increase in the insulating region based on the IBLC model. On the other hand, a report by Fang and Shiau [32] suggested that there are two different kinds of barrier layers depending upon the microstructure in CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. From their subsequent results via SEM and HRTEM, this microstructure features the semiconducting domains and insulating domain boundaries in the large grains as well as the insulating grain boundaries [33], shown in Figure 2.8 (a). The equivalent circuit including these three RC elements is represented in Figure 2.8 (b).

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Figure 2.8 (a) Schematic illustration of the microstructure of the internal domains (b) equivalent circuit representing the resistance and capacitance of domain (R<sub>d</sub>, C<sub>d</sub>), domain boundary (R<sub>bd</sub>, C<sub>db</sub>), and grain boundary (R<sub>gb</sub>, C<sub>gb</sub>) [33]

### 2.2. Bulk CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> via solid-state synthesis

### 2.2.1. Defect contributions to the dielectric properties via doping schemes

While the extrinsic effect has been accepted as the origin of abnormally high dielectric constant in  $CaCu_3Ti_4O_{12}$  via internal barrier layer model [28], there have been a number of studies about the doping effects on the dielectric

properties in this material. The first study of doping effects was carried out by Kobayashi and Terasaki [34]. From the study of Mn doping on the A"-site (i.e. CaCu<sub>3</sub>- $_{x}Mn_{x}Ti_{4}O_{12}$ ), they reported a huge drop of dielectric constant by the 2% substitution of Mn<sup>2+</sup> for Cu<sup>2+</sup>, which was explained by the fluctuating domain wall caused by the interaction of dipole moments. On the other hand, a Mn doping study by Li et al. [35] was focused on the origin of semiconductivity in CaCu<sub>2.94</sub>Mn<sub>0.06</sub>Ti<sub>4</sub>O<sub>12</sub> in terms of a cation non-stoichiometry model. It was found out that Mn-doped CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> increases the bulk resistivity by six orders of magnitude higher than CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> via impedance analysis. They suggested that different compositions in grains and grain boundaries may cause the suppression of bulk conductivity in Mn-doped CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub>. In addition to Mn doping, the effects of La doping on the A'-site were reported by two different groups. Based on the results by Feng et al. [36], Ca1- $_xLa_xCu_3Ti_4O_{12}$  (x = 0, 0.1, 0.2, 0.3, 0.4) exhibited a decrease in tan  $\delta$  over the entire range of measured frequencies and temperatures. Their impedance analysis data indicated a conductivity rise in the grains due to the effect of donor doping (i.e. La<sup>3+</sup> substitution for  $Ca^{2+}$ ), which eventually suppressed the dielectric loss. In comparison, different results were obtained by Shri Prakash and Varma [37]. In their study of Ca<sub>1</sub>- $_{x}La_{(2/3)x}Cu_{3}Ti_{4}O_{12}$  (x = 0, 0.5, 1), dielectric constant decreased with the amount of  $La^{3+}$  in the frequency range of 100 Hz – 10 MHz. Also, their scanning electron micrographs clearly showed the reduction of grain size from 50 µm to 3-5 µm by La doping. From the results of impedance spectroscopy, the decrease in the dielectric constant of La-doped CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> was explained by a decreased conductivity in the grains and a lower resistivity in grain boundaries. On the other hand, a variety of elements doped onto both the A'-site (i.e.  $Ca_{1-x}A_xCu_3Ti_4O_{12}$  where A = La, Sr, x =

0.02, 0.05) and the B-site (i.e.  $CaCu_3Ti_{4-y}B_yO_{12}$  where B = V, Cr, Mn, Ni, Fe, Co, y = 0.08, 0.20) were utilized by Capsoni *et al.* [38] in order to study their effects on the dielectric properties. It was observed that the grain boundary capacitance ( $C_{gb}$ ) increased by increasing the CuO content (in mol %) for all dopants except Fe. Based on the change in the lattice parameter with both doping types and the minimal influence on the bond length, they suggested that the improved dielectric constant might be due to the grain boundary effects. This explanation was supported by the negligible change in bulk capacitance ( $C_b$ ) via doping.

### 2.2.2. Effects of processing conditions on the dielectric properties

Like the influences of doping on  $CaCu_3Ti_4O_{12}$ , it seems that different processing conditions can significantly affect the dielectric properties as well. In the case of the internal barrier layer capacitors, it has been reported that the dielectric properties are very sensitive to the processing conditions [39-40]. For  $CaCu_3Ti_4O_{12}$ , Bender and Pan [41] examined the effects of the processing conditions in detail by using various conditions including the powder mixing, firing temperature (both calcination and sintering), and annealing. It was revealed that the dielectric constant increased when the  $CaCu_3Ti_4O_{12}$  powder was mixed via a milling method accompanied with a higher sintering temperature and a longer sintering time. They suggested that the improved dielectric constant can be attributed to the higher concentration of defects in the grain core. Also, they explained the sensitivity of the dielectric properties to the processing from the changes in the resistivity of grain boundaries. Aygün *et al.* [42] used a similar approach to the effects of processing conditions on  $CaCu_3Ti_4O_{12}$ . As seen in Figure 2.9, the dielectric constant at 10 kHz increases with sintering time. However, they found out that the grain size remained nearly unchanged over 20 hours of sintering, indicating that there is little relationship between the dielectric constant and grain size (Figure 2.10).



Figure 2.9 Dielectric constant of  $CaCu_3Ti_4O_{12}$  as a function of sintering time

[42]

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**Figure 2.10** Grain size and the dielectric constant of CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> as a function of sintering time [42]

In addition, the results from the effects of oxygen partial pressure  $(pO_2)$  on the post-annealed CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> at 800°C clearly showed the increased dielectric constant at higher pO<sub>2</sub> as shown in Figure 2.11. Since the Nb-doped CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> drastically suppressed the dielectric constant compared to the pure CaCu<sub>3</sub>Ti<sub>4</sub>O<sub>12</sub> at the same pO<sub>2</sub> = 1.0, it was suggested that the change of the dielectric constant is related to the generation of charge carriers among the defects.



Figure 2.11 A plot of dielectric constant versus temperature of the postannealed  $CaCu_3Ti_4O_{12}$  at 800 °C for 24 hours as a function of oxygen partial pressure [42]

### **2.3. Thin film CaCu\_3Ti\_4O\_{12}**

On the other hand, there has been increasing number of reports about CCTO thin films mainly due to the many potential applications for microelectronic devices. Among these reports, the relationship between the dielectric properties and microstructures of the deposited thin films were studied in terms of the different substrates via a pulsed laser deposition (PLD) method. Because of the importance of choosing appropriate materials to minimize the lattice mismatch, lanthanum aluminate (LaAlO<sub>3</sub>) was used as a substrate in the PLD system [43-45] due to the relatively small lattice mismatch of 3.4% to the CCTO thin film [43]. The XRD patterns with  $\theta$ -2 $\theta$  scan data plotted in Figure 2.12 [44] shows that only (001) peaks are detected and very small value (~0.6°) of the full-width at half maximum (FWHM) is obtained from the rocking curve measurement, indicating that CCTO films were obtained with a strong c-axis orientation. For the pole figure reflection from (202) plane of CCTO thin films shown in Figure 2.13 [44], sharp four-fold reflection points (white-colored) can be seen clearly, implying that the grown CCTO film has a high degree of crystallinity.





Figure 2.13 The pole figure reflection from (202) CCTO thin films [44]

Lin *et al.* [44] reported that the dielectric constant of the CCTO films measured at 1 MHz was about 10,000 at room temperature, but only 5,400 for polycrystalline CCTO at the same frequency. They suggested that the higher dielectric constant in the single crystal CCTO thin film be due to the larger number of domain boundaries and relatively larger grains, which contributed to the higher capacitance. On the other hand, dc conductivity measurements by Chen *et al.* [45] showed the change of slope on the  $\sigma$  – 1/T plot at 773 K as seen in Figure 2.14 [58]. They thought that the shift of the activation energy at high temperatures might be due to a vacancydisorder transition. Also, their ac impedance analysis examined the electrical properties of the grown CCTO film at high temperatures (T = 923 K). The results indicated a single semicircle at the frequency range of 10 kHz – 1 MHz shown in Figure 2.15[45]. From the data passing through the origin and showing only one semicircle, the impedance plot clearly indicates that grain response is dominant at high frequencies.



Figure 2.14 Temperature dependence of four probe dc conductivity for a

CCTO thin film [45]

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Figure 2.15 An ac impedance plot for a CCTO thin film at 923 K [45]

In comparison, Si-based substrates such as a multilayer Pt/Ti/SiO<sub>2</sub>/Si has also been utilized in recent CCTO thin film studies [46-50] since Pt is used as a stable conductor at high temperature and Ti as a good adhesive to SiO<sub>2</sub>. As seen in Figure 2.16 [47], XRD peaks of the (211), (220), (400), and (422) planes of the thin film grown on the Pt/Ti/SiO<sub>2</sub>/Si substrate are well matched with the CCTO target implying that the grown film is polycrystalline. From XRD patterns and AFM micrographs of the multilayer CCTO thin films shown in Figure 2.17 (b) [48], the position of the SiO<sub>2</sub> layer in the multilayer CCTO film changes the film crystallinity and the surface morphology. A recent study revealed that a higher crystallinity of the CCTO film was achieved when the SiO<sub>2</sub> layer was inserted on top of Pt/Ti/SiO<sub>2</sub>/Si layer or in the middle of the CCTO film [49]. This improved crystallinity of CCTO thin films might





Figure 2.16 XRD diffraction patterns of (a) CCTO target and (b) CCTO thin

film grown on Pt/Ti/SiO2/Si substrate [47]

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Figure 2.17 XRD patterns of (a) single and (b) multilayer CCTO film layer on Pt/Ti/SiO2/Si substrate [49]

The dielectric measurements by Fang *et al.* [47] showed that the dielectric constant was reduced as the temperature decreased with the relaxation behavior of tan  $\delta$  (Figure 2.18 [47]). This dielectric constant of about 2,000 is similar to the measured values (~ 1,500) of CCTO thin film grown on LaAlO<sub>3</sub> substrate [43], but much lower than the value (K ~ 10<sup>4</sup>) reported by Lin *et al.* [44]. Whereas, both dielectric constant and tan  $\delta$  of the multilayer CCTO/SiO<sub>2</sub>/CCTO films have lower values than the single layer CCTO film, shown in Figure 2.18[49]. Based on the electrical measurement data, the leakage current density of multilayer CCTO film decreases by increasing the thickness of the SiO<sub>2</sub> layer and is lower than the case of a single layer CCTO, implying a more resistive multilayer CCTO film [49]. This result was explained from



the decreased number of free carriers when the  $SiO_2$  layer trapped these carriers, eventually reducing their mobilities [49-50].

Figure 2.18 Temperature dependence of the dielectric constant and tangent

loss of a CCTO film as a function of frequency [47]



Figure 2.19 Frequency dependence of the dielectric constant and tangent loss

for a multi-layer CCTO/SiO2/CCTO film [49]

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