Fabrication and Film Qualification of Sr Modified $Pb(Ca)TiO_3$ Thin Films

Naw Hla Myat San[1], Khin Aye Thwe[1], Than Than Win[1], Yin Maung Maung[1] and Ko Ko Kyaw Soe[1]
Department of Physics, University of Yangon, Myanmar
hlamyatsannaw@gmail.com

***Abstract*— Strontium and calcium - modified lead titanate ($Pb_{0.7}$ $Ca_{0.15}$ $Sr_{0.15}$) TiO_3 (PCST) thin films were prepared by using spin coating technique. Phase transition of PCST was interpreted by means of ε_r-T characteristics. Process temperature dependence on micro-structure of PCST film was studied. Charge conduction mechanism of PCST thin film was also investigated for film qualification.**

***Keywords* —Thin films, spin coating technique, Charge conduction mechanism**

I- INTRODUCTION

Nowadays, ferroelectric thin films are emerging as a key material for widespread applications in both electronic and optical fields. Ferroelectric materials are an important class of materials whose main characteristic is the presence of a spontaneous polarization that can be changed with an external electric field [1].

There has been considerable interest in the ferroelectric ceramics due to their possible applications in transducers and in the piezoelectric, pyroelectric, electro-optic, acousto-optic and memory devices [4].

Among the Ferroelectric, the most studied, doped $PbTiO_3$ (PT) is a perovskite-type compound. On chemical substitution with Ba, La, Sr, Sm or Ca, the system should undergo a series of structural transitions from a tetragonal to a pseudocubic or orthorhombic phase and finally to a cubic phase. Strontium and Calcium-modified lead titanate (PCT) thin films have recently raised interest as a good candidate because of their applications as piezo and pyroelectric sensors and due to their good ferroelectric and dielectric properties. Therefore, a considerable amount of research has been focused on the preparation and the dielectric properties study of (Pb, Ca) TiO_3 thin films [2, 3].

Microstructural properties and charge conduction mechanism of PCST thin films are investigated.

II. EXPERIMENTAL PROCEDURE

In our procedure of Pb (Ca) Sr TiO_3 ceramic synthesis, ceramic powder produced by means of solid-state reaction route, as illustrated by the following reaction schemes,

$$PbO + CaO + SrO + TiO_2 \xrightarrow{\Delta} Pb\,(Ca\,Sr)\,TiO_3$$

Firstly, PbO, CaO, SrO and TiO_2 were weighed by digital balance for powder preparation. The powders were slightly crushed in an agate motor and were uniformly mixed for 1 hour with 30 g of the ($Pb_{0.7}$ $Ca_{0.15}$ $Sr_{0.15}$ TiO_3) previously, prepared and it was added in small portions. After the homogenization of the powder containing Pb, Ca and Sr contain in the following stoichiometic relations Pb (70%), Ca (15%) and Sr (15%). Acetone was added to promote mixed 30 g of powder and stirred with glass stirrer for 1 hour.

Secondly, the mixed powder was added with acetone and placed in a beaker and stirred with magnetic stirrer (500 rpm) for 1 hour. Stirred mixture was left in a room temperature to let dried.

Thirdly, grinding process was done. The mixture powder was placed in a ball milling at 26 V for 1 hour to get constant velocity for mixing the powder thoroughly. The treatment was carried out by air-jet milling at 40 bar for 30 minutes. And then followed by three-stages of Mesh sieving the powder as (100, 250, 400) mesh respectively.

After powder preparation, heating up the powder at 800°C for 1 hour and the powder colour was changed into yellowish colour.

The mixture of PCST powder was placed in cleaned beaker. Then the mixture was grounded for 1 hour. One drop of HCL and 20 ml of methanol were added to the mixture and then stirred and heated in a vessel with water at 100°C for 1 hour. The homogeneous precursor solution was obtained.

The Cu - coated Si substrate with dimensions (1.0 x 1.0) cm^2 was cleaned with HF: H_2O (1:10) for a few minutes and subsequently dried at room temperature. Then the substrate was immersed in acetone for 30 minutes to remove the impurities. After that, it was immersed in deionized water and rinsed.

After cleaning process, the precursor solution was deposited onto Cu - coated Si substrates by spin coating method. The deposited layers were first dried at room temperature and annealed at 300°C, 400°C, 500°C, 600°C and 700°C respectively for 1 hour. Finally, PCST thin films were achieved. The flow chat of PCST thin film preparation was shown in Figure 1.

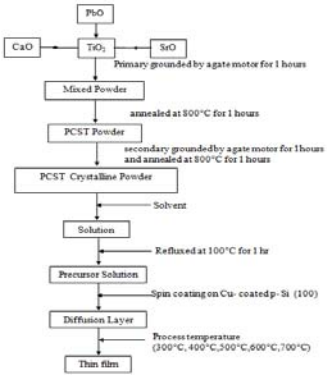

Fig. 1 Flow chart of PCST thin film preparation on Cu- coated p-Si (100) substrate

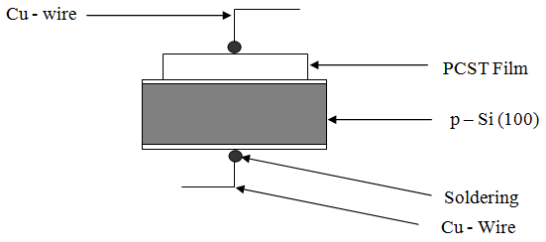

Fig. 2 Illustration of PCST / Si cell structure

III. RESULTS AND DISCUSSION

The XRD pattern in Fig 3 (a - e) shown the different reaction at 300 ºC, 400 ºC, 500 ºC, 600 ºC and 700 ºC. All diffraction peaks indicate a polycrystalline perovskite structure which can be assigned to PCST (70/15/15) phase without any indication of other crystalline by products such as calcium titanate, strontium titanate or dioxide titanium. However, films present texture degree with (201) and (210) as main components and lower contributions along (101) and (002) were also observed on XRD profiles. The rest peaks were coincided with the standard (JCPDF) spectrum. The lattice constants (*c* and *a*) of the unit cell calculated using *hkl* values for PCST (70/15/15) thin films are 4.08 and 3.91 respectively. Table 1 described the lattice parameters (lattice edges) reported by Pontes D S L et al, 2008. The lattice parameters of PCST film at 600ºC were quoted in Table 2. According to the Table 1 and 2, it was found clear that the lattice parameters of observed film were almost the same as Table 1.

TABLE I

LATTICE PARAMETERS AT 600ºC

Temperature (°C)	a-axis (°A)	c - axis (°A)
600	3.92	4.02

Pontes D S L et al, 2008 reported that the lattice parameters were a = 3.92°A, and c = 4.02°A for Pb (Ca) Sr TiO_3.[3]

TABLE II

LATTICE PARAMETERS AT 600ºC

Temperature (°C)	a-axis (°A)	c - axis (°A)
600	3.91	4.08

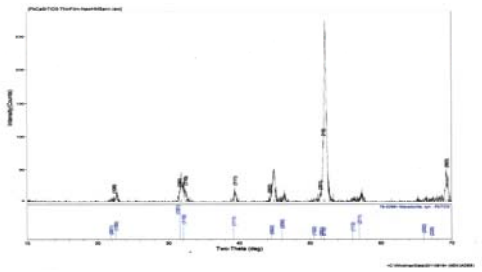

Fig. 3 (a)XRD pattern of Pb(Ca) Sr TiO_3 film annealed at 300 ºC

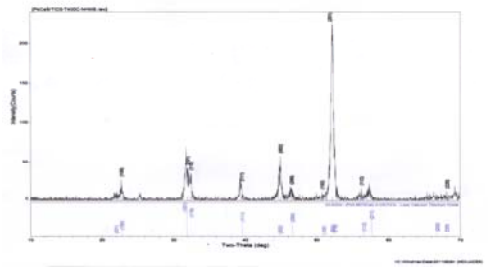

Fig 3 (b)XRD pattern of Pb(Ca) Sr TiO_3 film annealed at 400 ºC

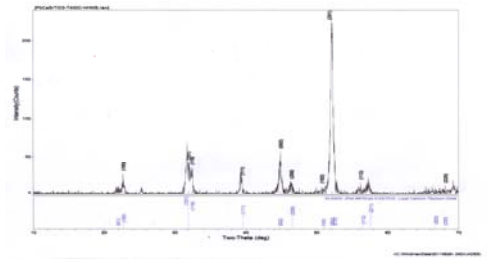

Fig. 3 (c)XRD pattern of Pb(Ca)$SrTiO_3$ film annealed at 500 ºC

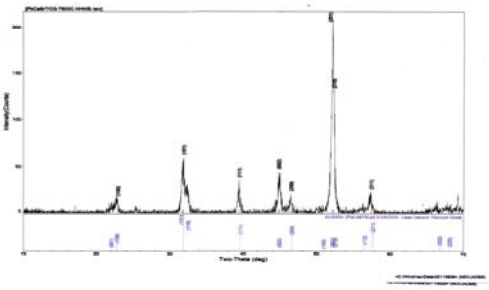

Fig. 3 (d)XRD pattern of Pb (Ca) Sr TiO_3 film annealed at 600 ºC

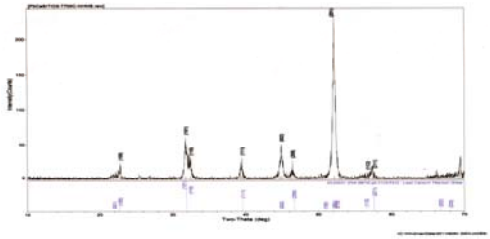

Fig 3 (e)XRD pattern of Pb (Ca) Sr TiO3 film annealed at 700 ºC

SEM was employed to study the surface morphology and microstructural properties of PCST film. As the detail analysis of SEM photomicrographs, the surface morphology of the film became rough after annealing at 500°C. SEM studies on the film showed non-cracking but grain growth pattern was clearly found. Some grains were in continuity but some were separated by pin holes. The grain distributions were found on all SEM images. The density of the films looked fair, except the film at 600°C. It looked dense. The calculated grain sizes were 0.63 μm, 0.38μm, 0.45 μm, 0.30 μm and 0.76 μm respectively. The grain orientation of the films was towards left, except the films at 500°C and 600°C. The microstructural properties of PCST film were shown in Table 3. The

variation of grain-size and process temperature wasindicated. Figure 5 (a - e) gave the SEM images of our fabricated film as the cross sectional point of view. The observed thickness were 4.6 µm, 5.9 µm, 4.6 µm, 3.9 µm and 6.5 µm. The grain sizes and thickness of fabricated films were shown in Table 3. The microstructural properties of PCST thin films with different annealing temperature were studied by SEM. Fig. 4 (a - e) showed the SEM images of PCST film at different annealing temperatures.

TABLE III

GRAIN SIZE AND THICKNESS MEASUREMENT OF FABRICATED FILMS AT PROCESS TEMPERATURE

Temperature (°C)	Grain Size (µm)	Thickness (µm)
300	0.63	4.6
400	0.38	5.9
500	0.45	4.6
600	0.30	3.9
700	0.76	6.5

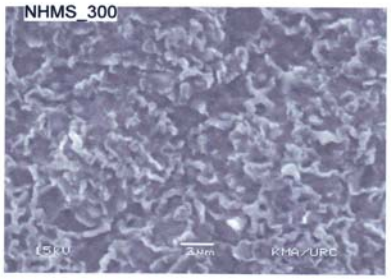

Fig 4 (a) SEM image of PCST film at 300 ºC

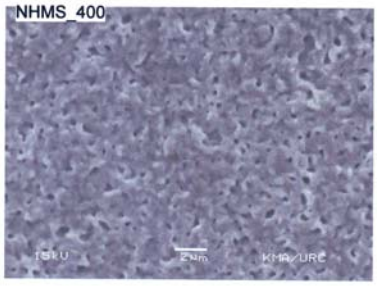

Fig 4 (b) SEM image of PCST film at 400 ºC

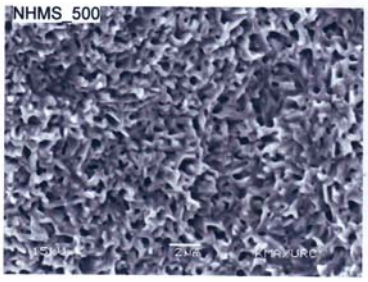

Fig 4 (c) SEM image of PCST film at 500 ºC

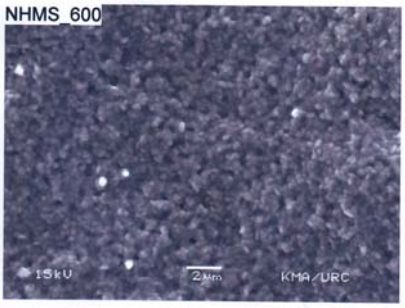

Fig 4 (d) SEM image of PCST film at 600 ºC

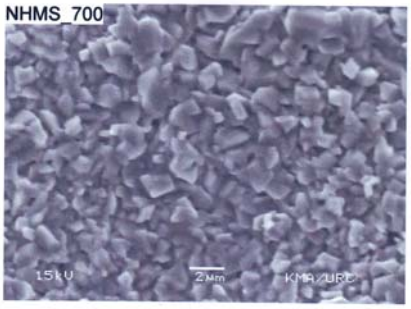

Fig 4 (e) SEM image of PCST film at 700 ºC

The film thickness of PCST thin films with different annealing temperature were studied by SEM. Fig. 5 (a- e) showed the SEM images of PCST film at different annealing temperatures. The observed thickness were 4.6 µm, 5.9µm, 4.6 µm, 3.9µm and 6.5 µm. From the figure, it was obvious that the minimum film thickness was found at 600 ºC.

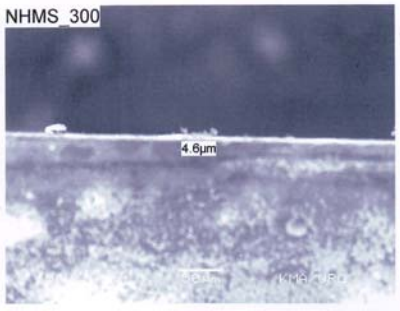

Fig 5 (a) SEM image of PCST film at 300 ºC

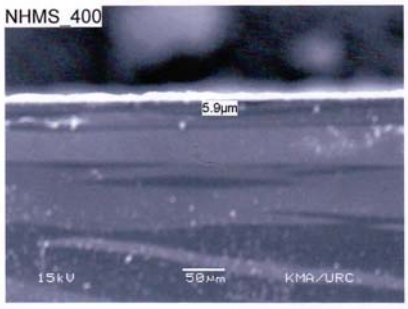

Fig 5 (b) SEM image of PCST film at 400 ºC

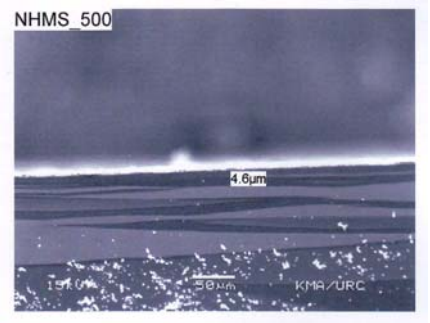

Fig 5 (c) SEM image of PCST film at 500 ºC

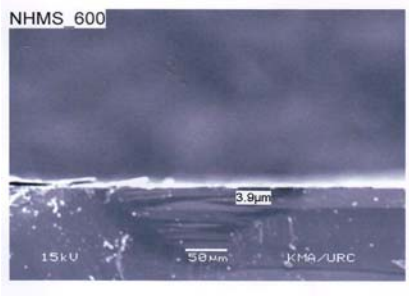

Fig 5 (d) SEM image of PCST film at 600 ºC

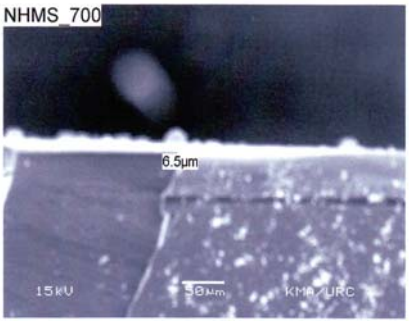

Fig 5 (e) SEM image of PCST film at 700 ºC

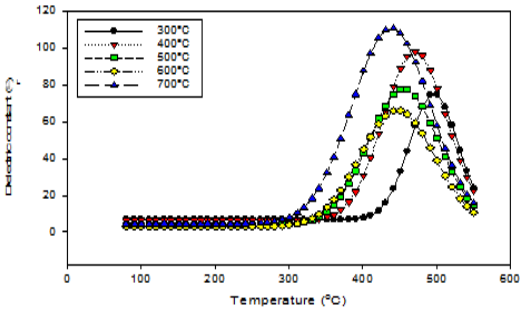

Fig 6 Phase Transition of PCST film

According to Fig 6, a shift to higher angel is observed, indicating the lower lattice constant of PCST thin films due to the smaller atoms radius of Ca and Sr in the single -phase compositions. The measurement of capacitance (C) as a function of reverse bias could be used to determine the built-in-voltage (V_{bi}) and the dopant concentration near the junction. The graph of $\frac{1}{C^2}$ as a function of V was linear relationship whose intercept on the voltage axis gave V_{bi} and the slope could be used to determine the dopant concentration. Fig. 7 (a) to Fig 7 (e) showed the $\frac{1}{C^2}$-V variation at 100 kHz for the fabrication film at various process temperatures. From the graphs, the value of built-in-voltage (V_{bi}), acceptor concentration (N_a), affective doping concentration (N_i),donor concentration (Nd) barrier height (ϕ_b) and depletion layer with (W) with different process temperature were determined and described in Table 4.

TABLE IV
ELECTRICAL PARAMETERS DERIVED FROM THE ANALYSIS OF $\frac{1}{C^2}$-V CHARACTERISTICS

$PbCaTiO_3$ Films	V_{bi} (V)	$N_a(cm^{-3})$	$N_i(cm^{-3})$	$N_d(cm^{-3})$	ϕ_b(eV)	W (cm)
300ºC	7.96×10^{-1}	1.90×10^{17}	2.38×10^{16}	4.92×10^{20}	1.02×10^{0}	2.98555×10^{-5}
400 ºC	6.50×10^{-1}	1.7×10^{17}	1.08×10^{14}	4.92×10^{20}	8.82×10^{-1}	3.13412×10^{-5}
500°C	1.00×10^{0}	1.63×10^{17}	1.63×10^{17}	4.92×10^{20}	1.24×10^{0}	3.22285×10^{-5}
600 ºC	1.14×10^{0}	1.79×10^{17}	1.79×10^{17}	4.92×10^{20}	1.37×100	3.20677×10^{-5}
700 ºC	6.64×10^{-1}	1.70×10^{17}	1.87×10^{14}	4.92×10^{20}	8.96×10^{-1}	3.14522×10^{-5}

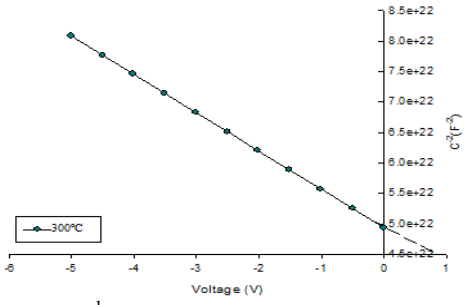

Fig 7 (a) $\frac{1}{C^2}$-V Characteristic of PCST Film at 300 ºC

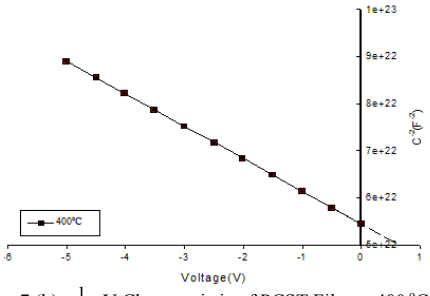

Fig. 7 (b) $\frac{1}{C^2}$-V Characteristic of PCST Film at 400 ºC

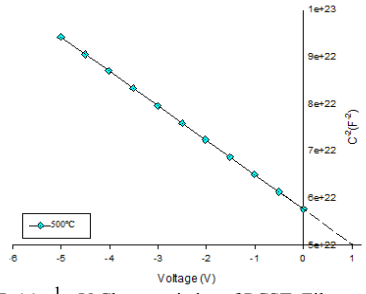

Fig. 7 (c) $\frac{1}{C^2}$-V Characteristics of PCST Film at 500°C

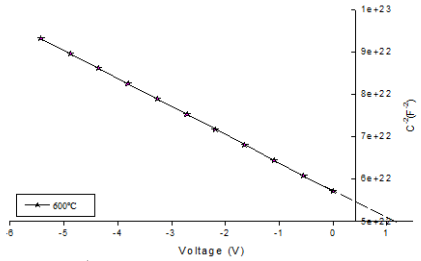

Fig. 7 (d) $\frac{1}{C^2}$-V Characteristic of PCST Film at 600 °C

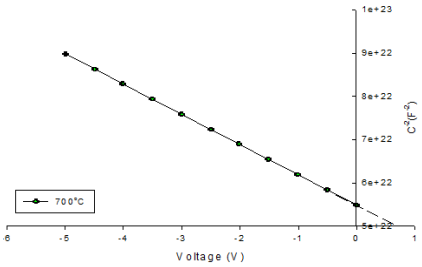

Fig. 7 (e) $\frac{1}{C^2}$- V Characteristic of PCST Film at 700 °C

IV. CONCLUSION

As the detail analysis of SEM photomicrographs, the surface morphology of the film became rough after annealing at 500°C. SEM studies on the film showed non-cracking but grain growth pattern was clearly found. Some grains were in continuity but some were separated by pin holes. The grain distributions were found on all SEM images. The density of the films looked fair, except the film at 600ºC. It looked dense. The calculated grain sizes were 0.63 μm, 0.38μm, 0.45μm, 0.30 μm and 0.76 μm respectively. The grain orientation of the films was towards left, except the films at 500ºC and 600ºC. All film thicknesses and grain sizes obtained from SEM information were range in micrometre. The minimum film thickness was found at 600ºC. From the ε_r-T characteristics, the phase transition temperatures of PCST films were observed between 440ºC and 500ºC. It might be attributed to the substrate induced effect. According to the $\frac{1}{C^2}$- V Characteristic curves, it was found that all fabricated films were uniform and chemical homogeneity.

ACKNOWLEDGEMENT

One of the authors, Naw Hla Myat San would like to thank Pro- Rector Dr Po Kaung ,Director of Universities' Research Centre for his kind permission to use facilities.

REFERENCES

[1] Chopra S et al 2004 Appl Surface Sci 230 207

[2] Chopra S et al 2003 Mat Sci and Eng 100 180

[3] Pontes D S L et al 2008 J Phys and Chem of solid 69 1951

[4] Naw Hla Myat S et al 2010, Proceeding of ICSE 1 605