# Effect of Carbon Nanotubes Incorporation on Characteristics of Sol-gel Derived PZT Film

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## ABSTRACT

***Sol-gel derived lead-zirconate-titanate (PZT) thin films with Zr/Ti ratio of 52/48 homogeneously mixed with multiwalled carbon nanotubes (MWNTs) of different weight concentrations. The mixtures were deposited on platinised silicon substrates. The as-deposited films were investigated using various techniques: X-ray diffraction, scanning electron microscopy, polarization versus electric field and frequency-dependent capacitance. The porous films annealed at 650°C showed perovskite phase with randomly oriented polycrystalline. The surface indicated microcracks in the porous films while the cross sectional views did not show any porous traces. It was found that electrical properties such as remnent polarization and capacitance were degraded in the porous films.***

**Key words:** Sol-gel; PZT; MWNTs; Porous

## INTRODUCTION

Influence of porosity on ferroelectric film has been studied not only for bulk and film PZT but also for other ferroelectric materials (Zeng et al., 2007; Seifert et al., 1999; Suyal et al., 2002). Some researchers (Stancu et al., 2007; Suyal and Setter, 2004) recently reported strong impact of porosity conducted by polymer on dielectric constant of PZT films which were suit for good pyroelectric applications. Furthermore, Shaw et al., (2007) synthesized porous PZT layer by adding starch as volatile phase in graded bimorph/trimorph pyroelectric materials. The MWNTs exhibit dissoluble behavior against organic compounds compared with raw polymer powder and have exact shape. Then, the present study aims to study the influence of porosity on electrical properties of the PZT thin films in which the precursor solution was added by the MWNTs varied from 0.2 to 1.0 wt% and then subsequently burnt out to create porosity. Electrical and microstructure characterizations were carried out and reported.

## MATERIALS AND METHODS

PZT thin films were prepared by sol-gel method. The preparation of the sol was based on previous report (Khaenamkaew et al., 2007). $Pb(Zr_{0.52},Ti_{0.48})O_3$ (PZT 52/48) solutions were prepared using lead acetate trihydrate, zirconium n-propoxide and titanium iso-propoxide in 2-methoxyethanol solvent. Formamide with 4 vol% was added to the solution in order to improve drying behavior (Suyal and Setter, 2004). The light yellowish solution was adjusted to the concentration of 0.6 M. Approximately 20% excess lead acetate was added to the solution in order to compensate lead loss during thermal annealing.

Purified MWNTs at compositions of 0.2, 0.4, 0.6, 0.8 and 1.0 wt% were mixed in the solution and dispersed using sonic tip (Ultrasonic Homogenizer 150VT) for 30 min to form a uniform suspension. The PZT 52/48 solutions with and without MWNTs suspension were dropped onto commercial Pt(111)/Ti/TiO/$SiO_2$/Si(200) substrates using a conventional spin coater with a spinning speed of 3000 rpm for 30 s and then dried on a hot plate at 200°C for 1 min and finally pyrolyzing at 400°C for 2 min to decompose organic compounds. The coating-drying-pyrolysis was performed repeatedly 4 times. The final films were annealed in furnace tube in air at 650°C for 30 min.

The crystalline texture of the PZT thin films were examined by X-ray diffraction (XRD) in Philips X-Pert diffractometer at a scan speed of 2°/min. The film thickness and surface morphologies were investigated using scanning electron microscopy (SEM) by JEOL, JSM-5800 LV. To evaluate electrical properties, a top electrode of gold dot (diameter 1 mm, thickness 0.1 µm) was sputtered onto the surface of the films and platinum layer was used as a bottom electrode. Frequency-dependent capacitances were measured by HP 4192A LF impedance analyzer under room temperature and polarization versus electric filed hysteresis loops were carried out through a Radiant Technologies RT66A under the frequency of 1 kHz.

## RESULTS AND DISCUSSION

The crystal structures of PZT films fabricated with 1 wt% and without MWNTs are shown in Figure 1. The XRD patterns revealed perovskite phase with random orientation but mostly favored the peak of (120). The peak at 40° and 46.5° indicated the Pt(111) and (200), respectively, and at 33° belonged to Si(200). Nevertheless, the broadening of 29° peak may be matched meta-stable pyrochlore (Ma et al., 2005). The annealing temperature was increased to be 700°C (not shown in the present result) in order to recheck; this peak still appeared at the same intensity. It suggested that Si (111) (Miyazaki et al., 2007; Xia et al., 2001) should be claimed rather than the pyrochlore phase. For the XRD result, the PZT film with 1 wt% MWNTs showed no significant difference compared to that of the pure PZT film due to the small amount of added MWNTs.

The surface morphology of the PZT films (0, 0.2 and 1 wt% MWNTs) illustrates in Figure 2. The film with 0 wt% MWNTs showed dense morphology whereas the increment in MWNTs affects more microcracks. Lattice mismatch during thermal process between MWNTs and PZT film made stretch stress, thus resulting the microcracks. Details explained the nature of microcracks as discussed by Wang et al., (2002) that new coating layer could fill up the previous ones on the underlayer but new microcracks occurred on the next layer. It seemed that microcracks did not penetrate through underlayer. The SEM-cross sectional profile in Figure 3 (a) shows well columnar structure of PZT dense film without an incorporation of MWNTs. It is expected to find the porosity in Figure 3 (b) & (c), however, no trace of porosity existed due to MWNT addition. It was because the well uniform and extremely small size of MWNT including low magnification of which the SEM can reach to this purpose. All the films had a thickness of approximately 600 nm or the thickness of each film layer was about 150 nm.

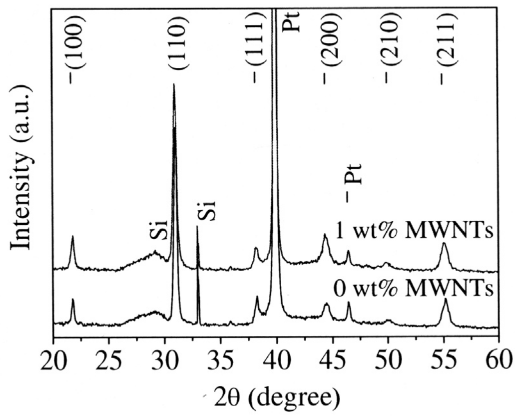



**Figure 1.** XRD patterns of films with and without an addition of MWNTs.

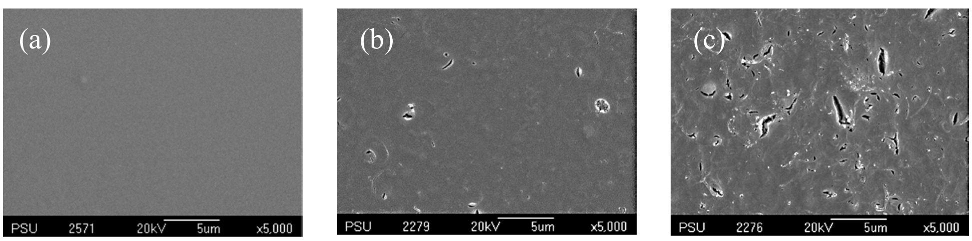



**Figure 2.** SEM planar images of the PZT films with (a) 0, (b) 0.2 and (c) 1 wt% MWNTs.

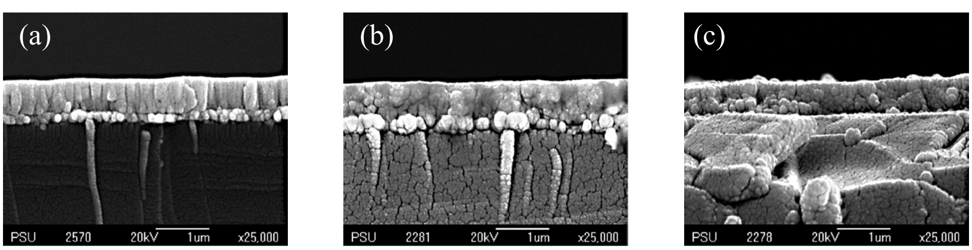



**Figure 3.** SEM cross-sectional images of the PZT films with (a) 0, (b) 0.2 and (c) 1 wt % MWNTs.

Depositing the gold electrode on PZT film (with and without MWNTs)/Pt was to resemble the structure like metal-insulator-metal capacitor prior to electrical investigation. The ferroelectric properties of the films derived from several weight concentrations of MWNTs were compared in Figure 4. The ferroelectric results can be obtained in the film samples doped with 0, 0.4 and 0.6 wt% MWNTs. The rest of the films was unable to observe the P-E response due to their surfaces were very rough and failed to be electrically connected. In Figure 4, the films showed bigger P-E response with increase in electric field. The films also exhibited asymmetric on both voltage and polarization axes for which it should be attributed to internal bias related to the electrode asymmetry posing different work function and by either movable ions or charges accumulated at the interface between the film and the electrode (Fan and Kim, 2002; Zhu et al., 2006). In case of the dense film, the loop behaved typical saturation in agreement with general ferroelectric PZT film with Zr/Ti ratio of 52/48 (Khaenamkaew et al., 2007) but, in turn, the porous films did not saturate at increasing voltage due to high leakage currents adding parasitic contribution to charges detected by the ferroelectric analyzer (Stancu et al., 2007). Furthermore, the porous films showed obviously lower remnent polarization values than that of the dense film; the more porous the films, the lower the remnent polarization.

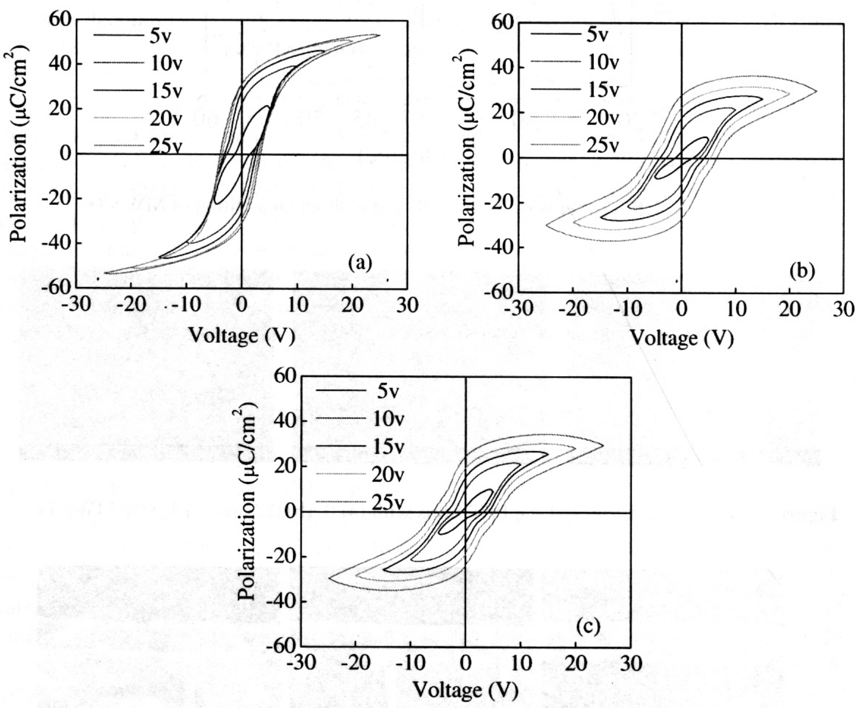
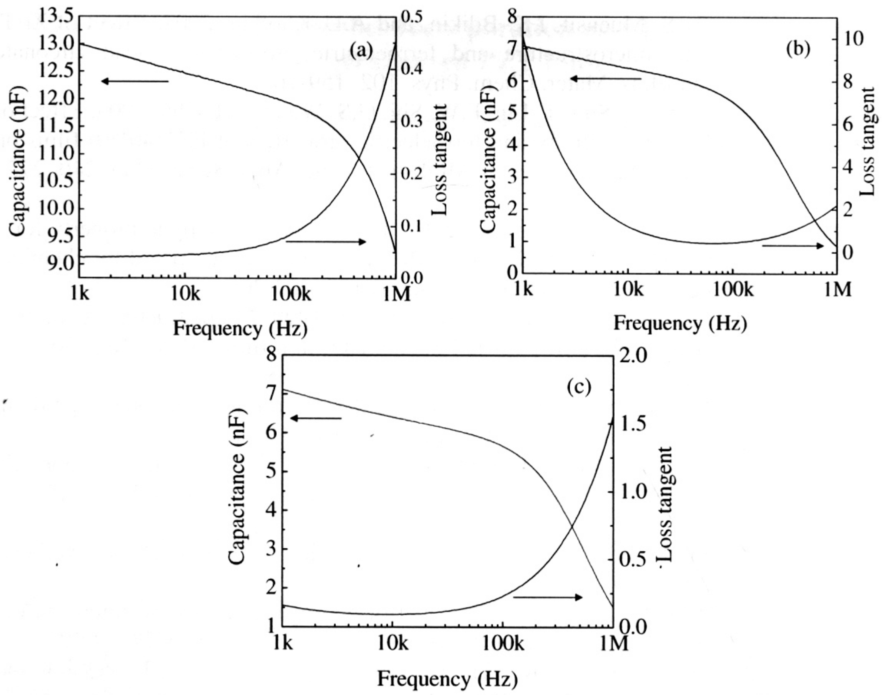



**Figure 4.** Ferroelectric hysteresis loops of PZT films with (a) 0, (b) 0.4 and (c) 0.6 wt% MWNTs.

We were not able to evaluate the exact thickness of the porous films in Figure 3 (b) & (c) then capacitance was presented in stead of dielectric constant. Figure 5 shows frequency-dependent capacitances and dissipation factor. In typical, the nature of voids or porosities within the films were a space mostly consisting of air so that the dielectric constant was verified to be 1 lower than that of value in a PZT film. Thus, this led in lower capacitance in case of the porous films.




## CONCLUSION

The PZT thin films derived from sol-gel method deposited on platinised silicon substrate were successfully fabricated. The porous films could be made by the introduction of MWNTs into the PZT precursor solution. Degradation in electrical properties favored the porous films, especially, for a lower dielectric constant.


## ACKNOWLEDGEMENTS

This work has been funded by Prince of Songkla University Grant and the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program under Grant No.PHD/0205/2548. Thanks to Prof.Wu Xiaoqing at Xi'an Jiaotong University for observation of P-E hysteresis loops and frequency-dependent capacitances.

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