CHAPTER II
LITERATURE SURVEY

Dage *et al.* (1997) synthesized PZT nanocrystalline powder with a composition near the morphotropic phase boundary Zr/Ti = 52/48 by the sol-gel method. Lead acetate trihydrate, zirconium oxynitrate and tetra-n-butyltitanate were dissolved in ethylene glycol to obtain PZT sol. During the dissolving process, electromagnetic agitating was required and the temperature was controlled at about 80°C until a completely dissolved and transparent solution formed. The sol was kept at 120°C to obtain a transparent gel which was then annealed at 450°C for 2 h to get the perovskite structure.

Paik *et al.* (1997) reported ferroelectric lead titanate and lead zirconate titanate, anti-ferroelectric lead zirconate, and alternatively deposited lead titanate-lead zirconate films fabricated by the sol-gel method. In a stock solution, lead zirconate titanate was prepared with lead acetate in acetate by boiling at 110°C and keeping Pb-to-acetic acid ratio at 1:5. In a separate flask, stoichiometric amounts of titanium isopropoxide and zirconium n-propoxide were mixed in 1:1 molar ratio of alkoxide and acetic acid and in a 1:5 molar ratio of alkoxide and n-propanol. Under constant stirring, the above two solutions were then mixed and 2 M water and 1 M ethylene glycol were added. The resulting solution was found to be clear and stable when stored in a closed container. PZT solution was used for coating onto platinum-coated silicon substrates. Rapid pyrolysis of gel film was achieved by placing the films on hot plate at 350°C for 10 min. Films were crystallized into perovskite structure by annealing at 650° or 700°C for 30 min. Properties of the films coated onto platinized silicon substrate were examined using XRD and SEM.

Laubersheimer *et al.* (1997) developed piezoceramic micro-parts produced directly using liquid metal-organic lead-zirconnate-titanate (PZT) precursor. Stoichiometric amounts of zirconium-n-propoxide and titanium-ethoxide were mixed at 90°-95°C under nitrogen-atmosphere and stirred. The complexion agent was then added to form a complex with Zr and Ti for retarding hydrolysis. Lead-

hydroxyacetate was then slowly added to the mixture until it was completely dissolved. Partial gelatin was performed by adding less than the stoichiometric amount of water to avoid a complete transformation into a solid gel. The calcination temperature of dried gel above 700°C was used to form the pure perovskite structure as analyzed and confirmed by XRD patterns.

Caruso *et al.* (1999) synthesized PZT by the sol-gel process from lead acetate trihydrate, 95% titanium ethoxide in ethanol and 70% zirconium n-propoxide in propanol and methoxyethanol (very toxic solvent). Lead precursors were prepared by dehydration and alcoholsis in methoxyethanol for 10 h at 124°C, titanium and zirconium precursors were prepared by alcoholic exchange in methoxyethanol for 4 h and 5 h, respectively, at 124°C. All three precursors were mixed at 124°C for 3 h to form a PZT precursor solution followed by preparing the PZT gel powders, with no water addition, by evaporating the solvents from the precursor solutions in an open flask at 120°C under a normal atmosphere (40% of relative humidity) for 24 h. From FTIR results, the PZT precursor before calcination showed O-H bonds at 3400-2800 cm^{-1}, C-H bonds at 2850 cm^{-1}, 1300-1400 cm^{-1}, metal-O bonds at 1000-450 cm^{-1}, and calcined PZT precursor at 400°-550°C showed only metal-O peaks

Bac *et al.* (2000) reported the preference of orientation using lead acetate trihydrate and zirconium n-butoxide as the starting materials for making PZ precursor. 2-Methoxyethanol (ROH), having a high boiling point of 124°C and a low vapor pressure, was used as the solvent. HNO_3 was used as catalyst, and ethylene glycol was used to protect cracking developed during the thermal process for the crystallization. The alkoxides, used as the precursor, are very sensitive to moisture in the air; therefore, each process was carried out inside a glove box filled with nitrogen. The 5 % by mole of excess lead acetate was added to prevent Pb deficiency during the thermal treatment. Annealing temperature was also found to be an important factor. No significant difference was found for the thermal treatment methods, viz. normal furnace and rapid thermal annealing (RTA). The results of X-ray diffraction and rocking curve analysis confirmed the result of atomic force microscopy (AFM) on morphologies of the films.

Zeng *et al.* (2002) reported nanocrystalline lead titanate prepared by accelerating the sol-gel process. The reactive system contained $Pb(AC)_2 \cdot 3H_2O$, $Ti(OC_4H_9)_4$ and isopropanol. The mechanism of gel formation and the $PbTiO_3$ formation were studied thoroughly using Fourier Transform Infrared spectroscopy (FT-IR) showing peaks of C-H, O-H, Pb-O-C and Ti-O-C before calcination. After calcinations, organic groups disappeared, and FTIR showed Pb-O and Ti-O peaks. X-ray Diffraction (XRD) showed the perovskite structure at high temperature and tetragonal perovskite structure $PbTiO_3$ was prepared at 550°C.

Lee *et al.* (2002) synthesized PZT derived from the sol-gel route. They studied the formation temperature for the perovskite PZT by seeding particle. The precursor materials used were lead acetate trihydrate, titanium isopropoxide and zirconium propoxide. Ti and Zr were dissolved in 2-methoxyethanol and heated at 110°C to reflux for 4 h. The lead acetate powder was dissolved in 2-methoxyethanol and then refluxed at 120°C for 4 h prior to removal of water by distillation. A PZT reaction was performed by mixing these two solutions and heating the mixture at 120°C under reflux for 8 h. The resulting sol was allowed to gel in an oven at 100°C for 3 days followed by calcination at various temperatures ranging from 400° to 700°C for 1 h of unseeded and seeded PZT. The characterization from XRD pattern of unseed PZT calcined at 650°C provided pure perovskite PZT.

Zhang *et al.* (2003) synthesized PZT fibers prepared by the sol-gel method using acetic acid and methacrylic acid to control the pH of the PZT precursor sol. The sol was then kept at 100°C to obtain condensed gel. The proper pH using acetic acid was 2.5 and 3.0 for methacrylic acid. Characterization of XRD pattern showed the pure perovskite after calcined condensed gel using acetic acid solvent at 700°C and methacrylic acid solvent at 550°C. The micro-structure was investigated using SEM showing that PZT fibers prepared with acetic acid were round, dense, homogeneous with a smooth surface. Fiber prepared with methacrylic acid was round with smaller

amount. Micro-cracks were detected at the surface prepared with methacrylic acid.