CHAPTER 1

INTRODUCTION

1.1 Overview

Ferroelectric materials with perovskite structure have been extensively studied because of their technological importance and unique electromechanical properties. Perovskite lead zirconate titanate (PZT) ferroelectric materials are prototypical example of these materials due to attracting a wide interest of their potential for exploiting ferroelectric, pyroelectric and piezoelectric properties. A diversity of PZT ceramics are currently used in electronic devices ranging from multilayer capacitors to piezoelectric transducers. PZT ceramics are generally used in the form of monoliths connected to an external electronic circuit. Many devices will, therefore, be significantly reduced in size and weight if the same electrical properties are reproduced in the form of thin films [1].

A wide variety of fabrication techniques have been applied to produce ferroelectric thin films. Various aspects of vapor phase techniques are utilized for deposition of thin films. In comparison to the sol-gel process used in this work, controlling film stoichiometry and composition in vapor phase techniques requires a detailed knowledge of processing variables and tends to be largely empirical. Common problems encountered in all vapor phase techniques are compositional variations between the source and film, such as that inhomogeneous deposition of atoms results in non-uniform films [2-4]. In addition to a thermally induced reaction, high energy bombardment of substrates during sputtering may alter interfacial structures, such as the interfacial damage for RF sputtered $PbTiO_3$ on Si and the implantation of Pb into the substrate [5]. This is critical for semiconductor substrates for even low doping levels will modify electronic properties. The low deposition rates of many described processes limit their commercial value. All the vapor phase deposition routes employ expensive vacuum apparatus that limit the output rate and size of substrates. These are clearly disadvantages associated with the vapor phase deposition of thin films. The sol-gel process with the potential for a high degree of control over chemical composition and low cost processing has a capability to solve some of the described disadvantages and produce highly stoichiometric films with the commercial advantage of high output and low cost [1]. Sol–gel coating techniques have been proven as a popular means of fabricating PZT films in the submicrometer thickness range. However, film thickness that is producible with sol-gel coating techniques has limited the practicality of them as it is difficult to make crack-free films thicker than 10 μm, and many piezoelectric applications require thick films. In order to solve the thickness issue, films were fabricated by dispersing ferroelectric powder into a PZT sol-gel matrix [6]. Some have also reported that coating infiltration with a PZT sol improved both densification and surface roughness and lead to enhancement of piezoelectric coefficient (d_{33}) [7]. However, PZT films fabricated by this modified sol-gel process have a poor mechanical quality because of its porous microstructure. Therefore, with a hybrid sol-gel processing technology, further improved quality of thick films via reducing the size of PZT powders while increasing the dispersibility of nano-sized powders in matrix solution were introduced [8, 9]. Although the use of the nano-sized powder is of great benefit to the uniformity of the microstructure, too small a grain size is detrimental for ferroelectric properties of the films. This necessitates the optimization of loaded particle to balance microstructure and ferroelectric properties of the deposited PZT thick films [10].

The ferroelectric/non-ferroelectric composite films were fabricated in 1999, dispersing TiO_2 in PZT. This system reduced dielectric constant and charge storage density and increased dissipation factor in the meantime. Through this method, it was found that the dielectric behavior was thus sensitive to composition. The composition determines the formation of a specific phase field in the film and secondary phase [11]. The defects in films, including those in second phase, affect the dielectric permittivity and loss by introducing various relaxation processes which appear at different frequencies and temperatures. However, dual phase composites made by dispersing a metallic phase into a ferroelectric matrix are of great interest due to significant enhancement in the dielectric constant [12].

The development of the electronic industries or high-performance ferroelectric devices exhibiting specific function and good reliability are required [13]. One particular area that needs to be improved is fatigue property. Polarization fatigue in a ferroelectric material is defined as a systematic loss of the switchable polarization under repetitive bipolar cycling [14], and it is the main limitation for applications of ferroelectric devices such as memories, electro-optical devices and actuators.

Many investigators have attempted to modify the microstructure and properties of ferroelectric materials to gain stable electronic devices which could not be gained from a single phase. Therefore, a single phase material could no longer satisfy the demand for the high-performance and multifunctional ferroelectric devices. Then they have proposed novel ferroelectric-based composites of two or more phases. Mechanical properties of PZT ceramics were improved by some metal (Pt, Ag) [15 - 21] and metal oxides ZrO_2, MgO, Al_2O_3 [22 - 25]. In addition, some metal oxides In_2O_3 [26], NiO [27 - 29], Y_2O_3, MoO_3 [30], WO_3 [31] and ZnO [32] were reported to improve the electrical properties of PZT ceramics. Particularly, PZT/WO_3 systems using a conventional processing method showed that an addition of a certain limit of WO_3 improved electrical and mechanical properties of PZT ceramics and showed donor doping effect [31] which reduces oxygen vacancy in PZT system. Oxygen vacancy deserves the biggest attention as a subject for increasing fatigue mechanism since it is mobile in the lattice at ambient temperature and can pin at the domain walls, or make the space charge segregation at electrode interface during repeated switching [14]. One common approach for fatigue reduction is a use of metal oxide electrodes to substitute for Pt electrodes. However, this method still causes electrical leakage and makes the process more complicated and expensive [33]. The other popular approach is doping aliovalent ions which distort the electroneutrality condition. Higher-valence foreign cations (donors) are compensated by negatively charged defects, such as Pb vacancies, while lower-valence foreign cations (acceptors) create positive charged defects, such as oxygen vacancies, to maintain the overall electroneutrality. Hence, acceptor doping normally leads to an increase in the oxygen vacancy concentration [34]. Although many studies have investigated the effect of doping on fatigue in thin films, the results are contradictory [14]. For donor doping, it was reported that La showed better fatigue resistance in PZT thin films, but for Nb doping, it was found to be independent of fatigue endurance [35]. In the meantime, acceptor doping such as Mn, Sc, Na, Mg, Fe and Al were reported to have positive effects on the fatigue resistance of PZT thin films. As contradictory results in donor and acceptor remain confusing, this study was carried out to investigate the effect of donor and acceptor doping on electrical properties, especially on fatigue behaviour of PZT. Soft PZT and hard PZT thin films were prepared by adding WO_3 and CuO, respectively. Previous work found that the addition of WO_3 into PZT ceramics induced donor doping effect and improved mechanical and electrical properties [36] while the addition of CuO which is known as a sintering aid in some electroceramic materials, showed acceptor doping behaviour. The addition of CuO in some piezoelectric materials can improve dielectric and piezoelectric properties [37]. However, similar results have not yet been reported in thin-film embodiments.

1.2 Objectives of this work

The main objectives of this study are to investigate physical and electrical properties of PZT-based nanocomposite thin films by a hybrid chemical solution process. The relationship between phase evolution, dielectric properties, ferroelectric properties and fatigue endurance of the films will be investigated and discussed. The objectives of this study are as follows.

(1) To investigate new PZT-based nanocomposite thin films with better electrical performance compared to that of PZT by a hybrid chemical solution process.

(2) To study the effects of processing parameters on phase and microstructural of PZT-based nanocomposite thin films.

(3) To study the effect of type and quantity of adding materials on phase, microstructure, dielectric properties, ferroelectric properties and fatigue characteristics of PZT-based nanocomposite thin films.