Low-temperature processing of sol-gel derived Pb(Zr,Ti)O₃ thick films using CO₂ laser annealing

Chen-Chia Chou · Shen-Da Tsai · Wen-Hsiang Tu · Yu-En Yeh-Liu · Hsien-Lung Tsai

Published online: 7 March 2007
© Springer Science + Business Media, LLC 2007

Abstract Fabrication of ferroelectric Pb(Zr₀.₅₂Ti₀.₄₈)O₃ (PZT) thick films on a Pt/Ti/SiO₂/Si substrate using powder-mixing sol-gel spin coating and continuous wave CO₂ laser annealing technique to treat the specimens with at a relatively low temperature was investigated in the present work. PZT fine powders were prepared by drying and pyrolysis of sol-gel solutions and calcined at temperatures from 400 to 750°C. After fine powder-containing sol-gel solutions were spin-coated on a substrate and pyrolyzed, CO₂ laser annealing was carried out to heat treat the specimens. The results show that laser annealing provides an extremely efficient way to crystallize the materials, but an amorphous phase may also form in the case of overheating. Thicker films absorb laser energy more effectively and therefore melt at shorter periods, implying a significant volume effect. A film with thickness of 1 µm shows cracks and rough surface morphology and it was difficult to obtain acceptable electrical properties, indicating importance of controlling interfacial stress and choosing appropriate size of the mixing powders. On the other hand, a thick film of 5 µm annealed at 100 W/cm² for 15 s exhibits excellent properties (Pₑ = 36.1 µC/cm², Eₑ = 19.66 kV/cm). Films of 10 µm form a melting zone at the surface and a non-crystallized bottom layer easily at an energy density of 100 W/cm², showing poor electrical properties. Besides, porosity and electrical properties of thick films can be controlled using appropriate processing parameters, suggesting that CO₂ laser annealing of modified sol-gel films is suitable for fabricating films of low dielectric constants and high crystallinity.

Keywords Laser annealing · Sol-gel · Ferroelectric · PbZrTiO₃ · Thick films

1 Introduction

Pb(Zr₀.₅₂Ti₀.₄₈)O₃ (PZT) is one of the most promising ferroelectric materials for nonvolatile memory devices, sensors, actuators and microelectromechanical systems due to its high remanent polarization and high piezoelectric constants [1–3]. Most device developments have centered on silicon micro-machined structures. Combining micromachined silicon with ferroelectric films has resulted in several novel microdevices, such as membrane sensors [4] and accelerometers [5]. These devices are generally based upon thin film materials with thickness less than 1 µm. However, the application of devices using PZT films is not limited to the microdevices. Many applications require film thickness of 1 to 30 µm and geometries of µm² to cm², such as optical fiber modulator [6], ultrasonic high frequency transducer for eye examination [7], self-controlled vibrational damping systems [8] etc. The film thickness and device geometry required for those applications is difficult to be achieved by conventional thin film preparation processes, such as sputtering, sol-gel, or chemical vapor depositions.

Fabrication of a PZT thin film of 1 µm has however been achieved in conventional sol-gel method, but the spin coating cycle has to be repeated many times to attain desired thickness in order to produce thick films [8, 9]. This fabrication procedure is clearly time-consuming and other problems, such as crack development after films was grown over a critical thickness, ordinarily less than 1 µm, due to mechanical
stress building up during processing. Philips et al. [10] introduced a novel diol-based sol-gel method to fabricate thicker films up to 5 μm with a single deposition of about 1 μm. Several methods have been proposed by different research groups [11–16] to fabricate PZT films with thickness to several 10 μm. Akedo and Lebedev [11, 12] fabricated thick PZT films with high density at high deposition rate by using aerosol deposition method at low processing temperatures. Yasuda et al. [13] have prepared PZT films that have good crystallinity as to that of thin films by using Arc-Discharged Reactive Ion-plating method. However, these kinds of gas deposition methods generally require complicated set-up and expensive apparatus. Alternatively, modified sol-gel coating techniques are relatively simple [14–16]. Trurumi et al. [14] have prepared PZT films of 10–50 μm using an interfacial polymerization technique. Sayer and Barrow et al. [15] have introduced a 0-3 composite process in which a piezoelectric coating is produced by spin coating a suspension of PZT powder in a PZT sol-gel solution. Wu et al. [16] have introduced different seeding techniques which used a seeding layer of PbTiO3 before coating PZT on substrate. Wang et al. [17] adopted sol-gel based nano-composite process to fabricate dense PZT thick films at a sintering temperature of 700 to 800 °C and the ferroelectric properties are comparable to that of bulk PZT ceramics.

The atomic inter-diffusions among the heterostructures and deterioration of electrical properties might occur when the growth condition of PZT films is at a substrate temperature of 600 °C or above under an oxygen reaction atmosphere. From this viewpoint, a low-temperature process for growth of PZT films is therefore required for yielding a reliable integrated device with superior performance. Calzada et al. [18] employed UV irradiation assisted RTP process to develop a low temperature processing method for ferroelectric thin films, compatible with silicon integrated circuit technology. Park et al. [19] introduced the low-temperature processing of PZT thin films and they uses RF and microwave oxygen-plasma treatment successfully to anneal PZT films. Kwok and Desu was the first group to use seeding particles in the sol (sols containing powders) for decreasing the crystallisation temperature of the films, and they employed seeding layers of PbTiO3 produced by a sol-gel method to reduce the pyrochlore-to-perovskie transformation temperature [20]. However, the thick films prepared by this technique showed poor mechanical properties due to their porous or cracked microstructure [21]. Electrical properties of PZT thin films grown by sol-gel and PLD techniques using a seeding layer were also reported and compared [22].

Donohue et al. [23] have shown a low temperature process using a pulse-extended excimer laser to treat the ferroelectric thin film on a low thermal budget substrate. However, properties of the films were not revealed. Lai et al. employed extended-pulse excimer laser annealing to PZT films on a LaNiO3 electrode, and a 50% improvement in remanent polarization was observed. However, the value is still low compared to properties of bulk PZT [24]. We have reported that the laser annealing processes may be an alternative low-temperature process for fabricating high quality PZT thin films [25, 26]. The continuous CO2 laser can be successfully applied to anneal PZT thin films with much better electrical properties than those processed by an excimer laser for a specimen with thickness higher than 0.4 μm [25–27]. Homogenous microstructures, good ferroelectric properties and well crystallinity of PZT thin films could be obtained after CO2 laser irradiation at room temperatures. But an amorphous layer can be observed at the bottom part of a specimen treated by an excimer laser [28]. Kholkin et al. [26] fabricate thick PZT films using sedimentation of the PZT powder onto Pt-coated Si substrates with a subsequent multiple infiltration of powder coatings with PZT sol-gel solution. PZT films with a thickness range of 1–20 μm can be fabricated at a temperature as low as 550 °C.

In this work, a modified sol-gel route with fine-grain containing sol-gel solutions were employed to prepare PZT thick films. The spin-coated PZT thick films were sequentially irradiated by the CO2 laser for crystallization and sintering. Change of surface morphology, crystal structure and microstructural evolution and electrical properties of the laser annealed PZT thick films were investigated to evaluate CO2 laser annealing process for PZT thick film fabrication, which was carried out at temperatures less than 400 °C.

2 Experiments

Flow chart of preparing the stock solution of Pb(Zr0.52Ti0.48)O3 is shown in Fig. 1. The lead acetate [Pb(CH3COO)2·3H2O], zirconium n-butoxide [Zr(OC4H9)4], and titanium n-butoxide [Ti(OC4H9)4] were used as the starting materials for synthesis of Pb(Zr0.52Ti0.48)O3 precursor solution. Lead acetate was firstly dissolved in 1.2-propanediol and then a stoichiometric amount of titanium n-butoxide and zirconium n-butoxide was added under a steady-state stirring to produce a 0.3 M-PZT complex solution. 10 mol% excess lead acetate for the precursor was added to the PZT solution, in order to compensate PbO evaporation, and 10 vol% formamide was also added to control the wetting angle. PZT powder was prepared by drying PZT precursor at 200 °C for 30 min and pyrolyzed at 400 °C for 24 h and calcined at a temperature from 400 to 750 °C for 30 min. The dried sol-gel pyrolyzed powders were ball-milled using methanol as media to a particle size at around 0.4 μm and powders using an oxide-mixing method calcined at 870 °C 4 h and ball-milled were also prepared for comparison.