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Lead zirconate titanate films prepared by liquid source misted chemical deposition

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Abstract

In this study, lead zirconate titanate (PZT) thin films were prepared by liquid source misted chemical deposition (LSMCD) method and their structural and electrical properties were investigated. The LSMCD technique utilizes micron-sized droplets of an organic based liquid precursor to produce high quality thin films with good conformality and uniformity. PZT films, annealed at temperature of 750 ℃ for 1 min in oxygen ambient, were polycrystalline and exhibited good phase purity with a (111)-preferred crystallographic orientation. The capacitance voltage (C-V) and polarization electric field (P-E) hysteresis measurements in wide frequency range showed that mist deposited PZT films exhibited the electrical properties comparable with those of other processing methods.

K e y w o r d s: ferroelectric, thin film, PZT, misted deposition, dielectric properties

1. Introduction

Ferroelectric thin films are of intensive research mostly due to their potential applications in nonvolatile ferroelectric random access memories (FeRAMs) [1] and micro-electro-mechanical systems (MEMSs) [2, 3], such as micro-motors, membrane-type micropumps, atomic force microscopy cantilevers, accelerometers, micro-scanning mirror devices, etc. Among the ferroelectric compositions, lead zirconate titanate $Pb(Zr,Ti)O_3$ (PZT) thin films have been widely studied and found to be very attractive for such applications because of their excellent electrical properties [4]. It has been shown that the electromechanical response of PZT films is strongly dependent on many parameters, including compositions [4], crystallographic orientation [5], microstructure, and properties of a substrate [6]. Though, a variety of techniques has been proposed to fabricate PZT films, such as pulsed laser ablation (PLD) [7], metalorganic chemical vapor deposition (MOCVD) [8], chemical solution deposition (CSD) [9], and sol-gel method [10], at present there does not appear to be a strong correlation between factors like deposition method and substantial enhancement of electrical properties of thin films. On the other hand, issues of the flexibility and yields of processing methods become important in terms of enhancing the quality and minimizing the production costs of PZT thin films. Recently, liquid source misted chemical deposition (LSMCD) has been reported as a suitable low cost method for depositing high quality ferroelectric PZT films [11]. The technique of mist deposition was invented by McMillan and Paz de Araujo in 1992 [12]. Since then, the method has been successfully used besides the PZT films in fabrication of high-k dielectrics for storage capacitors [13] and barium strontium titanate (SBT) thin films for memory applications [14]. The LSMCD employs liquid metal-organic precursors as a source just like spin-on processes, but in contrast to spin-on processes, misted deposition allows controlled deposition of thin films as thin as 4 nm and as thick as 100 nm. It also uses amount of liquid significantly lower than spin-on technology (reduced chemical usage by up 50 %) to obtain required coverage, which reduces overall capital cost and environmental concerns related to the disposal of organic waste [15]. The small size of the liquid droplets (a misted aerosol) promotes a highly

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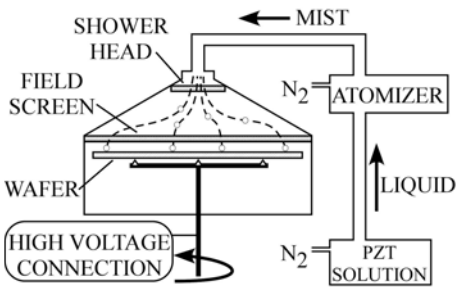

Fig. 1. Schematic diagram of LSMCD reactor.

uniform coating of the wafer submicron architecture and, in general, results in denser films than those prepared by the spin-on method. Besides the precise stoichiometric ratio and homogeneous composition distribution, LSMCD assures also a high conformality of the films, and thus it can be used to deposit thin films onto substrates that are totally incompatible with spin-on deposition, including very large diameter, flexible and heavy wafers. In order to improve the quality and properties of PZT ferroelectric thin films, Kawasaki's group has developed an advanced LSMCD system with a modified atomizer and an ultrasonic--vibration-based refiner that produces mist droplets with a diameter of 0.2 μm [16]. More recently, the LSMCD processing method has been further modified with heating mist and substrate and allows to process three-dimensional PZT nano-ferroelectrics for ultrahigh density FeRAMs [17]. Losego and Trolier--McKinstry [18] have reported on processing piezoelectric actuators based on PZT thick films for MEMS devices. They proposed that increasing the temperature of the deposition chamber enables a 1-μm-thick PZT film to be deposited readily by LSMCD technique. Moreover, the total process time of micron--thick PZT films can be significantly reduced by optimizing the showerhead geometry. As an extension of the research on PZT thick films, we present here results of the study of the structural and electrical properties of 770-nm-thick PZT films prepared by conventional LSMCD method.

2. Experimental

A commercial spin-coat solution of Pb/Zr/Ti = 1.1/0.52/0.48 (Nippon Ferro Technology Co., Ltd.) was used in this study as a precursor. Film deposition was carried out in the PRIMAXX-2F Lab Deposition system as shown in Fig. 1. The system is a standalone LSMCD process tool consisting of an LSMCD process module, a control tower and a manual substrate loading platform which is equipped with a stepper motor operated loading arm end effector capable loading substrates of up to 200 mm size into the process chamber. In a mono-disperse aerosol generator (atomizer), a controlled amount of liquid PZT precursor is converted into submicron droplets with average particle diameters less than 0.25 μm and subsequently the aerosol is carried to the reactor chamber by nitrogen flow. Inside the reactor the aerosol mist passes through a showerhead, then through a metal field screen, and into an electric field created between the substrate, which has a high voltage applied to it, and the grounded field screen. Electrostatic forces attract the droplets to the wafer surface and into the wafer boundary layer, where diffusive forces are sufficient to form a uniform and conformal coating. A high--field electrostatic field of 8 kV is used in this investigation to control the deposition rate in between 12–15 nm min^{-1}. Platinized p-type Si [100] single crystal wafers were used as bottom-electroded substrates. Prior to the film deposition the surface of substrates was treated thermally by annealing at 700 ℃ in oxygen to eliminate moisture and layers of organics. During deposition the wafer was rotated slowly (≈ 10 rpm) in the deposition chamber to promote uniform deposition while minimizing centrifugal action on the PZT film. The entire process of misted deposition was carried out in nitrogen ambient at a sub-atmospheric pressure (≈ 650 Torr) maintained in the reactor chamber. After the deposition of 10 min, the samples were pyrolyzed at 275 ℃ for 2 min on a hot plate. Each deposition/pyrolysis sequence produced a layer approximately 120 nm in thickness and the sequence was repeated to obtain the desired film thickness. Typically, a 700–800 nm thick PZT films were achieved in 6–7 deposition cycles. PZT films were crystallized in oxygen at temperature of 750 ℃ for 1 min using a rapid thermal annealer (RTA, Tsunami series RTP--600S). Film thickness was measured by profilometry (Tencor, a surface profiler Alpha Step 500) after acid--etching a corner of the film. The crystal structure of the PZT films and their crystallographic orientation were examined via X-ray diffraction (XRD; Scintag, Sunnyvale, CA) using Cu Kα radiation for 2Θ angular scans ranging from 20° to 60° with a 0.025° step size. Scanning electron microscopy was used to observe the surface morphology and cross-sections of the films.

For dielectric and ferroelectric measurements reported here, upper electrodes of the PZT films were fabricated by RF sputtering of Pt through a metal foil shadow mask. Electrodes were circular with a diameter of 200, 400, 600 and 1000 μm and a thickness of approximately 1200 Å. Resultant metal/ferroelectric/metal (M/F/M) structure was annealed at 500 ℃ for 20 min in RTA for making a good electrical contact between the top electrode and PZT layer. In order to make a pressure electrical contact with MFM structures, a micro probe station equipped with micro-positioners (Signatone, Gilroy, CA) was used in electrical experiments. The capacit-

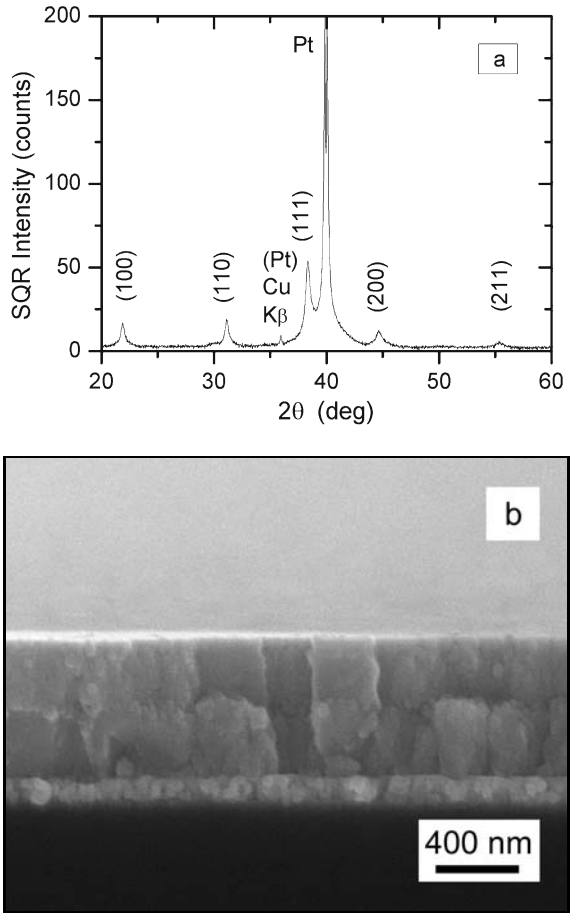

Fig. 2. Cross-sectional scanning electron microscopy image (a), and X-ray diffraction (b) of mist deposited PZT thin film of 770 nm thickness on platinized silicone wafer and annealed at 750 °C for 1 min.

ance voltage (C-V) measurements were made using a 4192A LF impedance analyzer (Hewlett-Packard, Palo Alto, CA) at a frequency of 100 kHz and a 15 V maximum amplitude dc bias. Polarization vs. electric field (P-E) hysteresis behavior of the PZT films was measured at 1 kHz using a TF 2000 analyzer (aixACCT, Aachen, Germany) in dynamic mode.

3. Results and discussion

Figures 2a and 2b show, respectively, the SEM of the cross section and corresponding X-ray diffraction pattern of the 770-nm-thick PZT film mist deposited on platinized Si substrate and subsequently annealed in oxygen at 750 °C for 1 min. The XRD pattern reveals well crystallized, nearly phase-pure perovskite, highly oriented film along (111) direction. All peak indexing for the perovskite PZT film is done on the basis of the pseudocubic unit cell. As can be seen from the cross-sectional SEM image in Fig. 2b, the PZT film

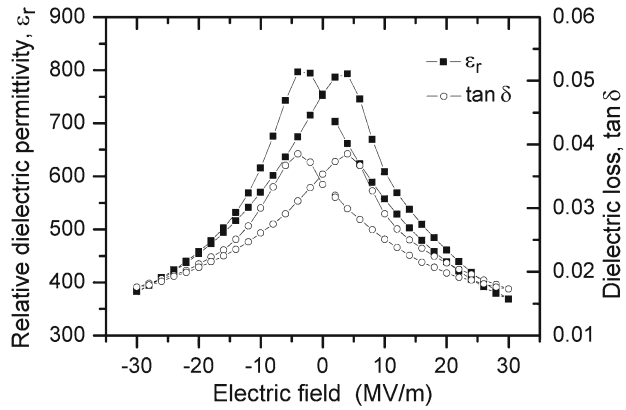

Fig. 3. C-V characteristics of the 770 nm thick PZT film prepared by LSMCD. Measuring frequency is 100 kHz and dc bias varies between +15 V and –15 V.

deposited from the misted precursor has a polycrystalline columnar microstructure similar to the films prepared by conventional spin-on processes. The nucleation of the perovskite phase is considered to occur at the PZT film/Pt bottom electrode interface. It has been demonstrated that the nucleation and preferred orientation of the thin films are strongly influenced by the orientation of the underlying Pt substrate [6]. The C-V curve of the PZT film prepared by LSMCD technique is presented in Fig. 3. Small-signal capacitance was measured at 100 kHz while the dc bias voltage swept slowly between +15 V and –15 V. The film response has a typical "butterfly" shape, with two asymmetrically placed maxima, which should correspond to the coercive field values [5]. For the 770-nm-thick PZT film, the calculation of the effective coercive field gives a value of about 40 kV cm^{-1}. As the dc bias voltage is reversed, the number of movable, preferentially oriented, domains contributing to the dielectric response decreases and subsequently the capacitance decreases. The dielectric permittivity and dielectric loss tangent, as measured on different diameter top electrodes at 1 kHz using an LCR meter (Hewlett-Packard, HP 4284A), were 800 and 0.04, respectively. These values are better than those reported by Nunes et al. [19] and Pontes et al. [20] for 350-nm-thick PZT films of the same composition but processed by dip-coating (dielectric constant of 436 and dielectric loss of 0.07) and spin-coating process (646 and 0.09), respectively, on $Pt/Ti/SiO_2/Si$ substrates. Unlike a weak asymmetry of the capacitance along zero bias voltage observed in Fig. 3 for the LSMCD-derived films, the C-V curves of the spin- and dip-coated films [19, 20] displayed symmetry in the maximum capacitance values in the vicinity of the spontaneous polarization switching.

Although, spin-coating and dip-coating are currently, owing to their simplicity and rapidity, the most

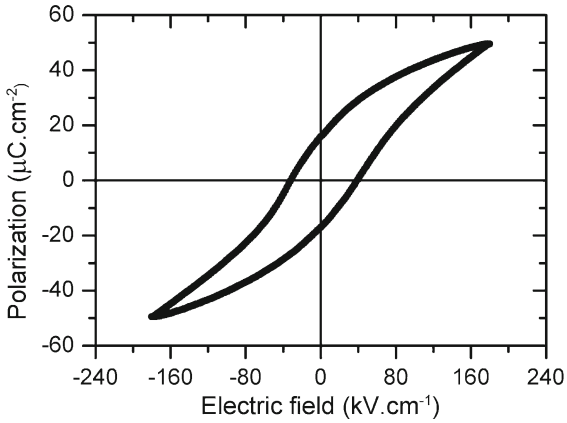

Fig. 4. Ferroelectric (P-E) hysteresis loop of the PZT film fabricated by LSMCD technique. Polarization switching is traced with a 15 V-peak drive voltage with a 1 kHz triangular waveform using a TF 2000 analyzer in dynamic mode.

commonly used methods for depositing ferroelectric thin films from liquid precursors, an inherent inability to cover surface features conformally, poor film quality across the wafer, and significant chemical waste make these techniques unusable for the fabrication of thicker films (between 0.5 μm and 5 μm), which are necessary for high-performance piezoelectric applications. On the other hand, misted deposition used in our work combines successfully the precise stoichiometric control of a chemical solution deposition process with superior step coverage [21], enabling thus cost-effective production of ferroelectric thick films with improved properties.

The ferroelectricity of the films was investigated by observing the P-E hysteresis loop (Fig. 4) using a triangular waveform. From the figure, it can be found that a driving voltage of 15 V-amplitude is not enough to saturate the ferroelectric polarization of the PZT films with a thickness of 770 nm. It relates with the charge accumulation due to the leakage of ferroelectric capacitor [22]. The P-E loop is shifted along the field axis toward the positive voltages and the average coercive field of the film, as calculated from the negative (E_c–)and positive (E_c+) coercive field, is about 40 kV cm^{-1}. This value may be compared with similar one obtained from C-V measurements. On the contrary, the remanent polarization is smaller than the values reported in literature for PZT films prepared by other processing techniques [4–6]. It is suggested that the electrical contact between the upper electrode and PZT layer can be improved by optimizing the sputtering of Pt electrodes which should result in more effective collecting the charge produced by polarization switching and higher values of the remanent polarization. Voltage shift phenomena of the hysteresis loop in ferroelectric thin films (e.g., $|E_c-| \neq |E_c+|$ in Fig. 4) are attributed to the defect-built-up internal field. A conspicuous voltage shift was observed in as-grown heteroepitaxial thin films as well as in sol-gel derived PZT films deposited by conventional spin-on technology [23]. A number of phenomenological scenarios and microscopic models, such as asymmetric dc conduction approach [24], space-charge region model [25], or nonswitching "dead" layer mechanism [26] have been proposed in the literature to explain anomalous hysteresis behavior and asymmetric switching of ferroelectric thin films. However, there is no agreement on a definitive physical mechanism controlling the internal field yet. It is very possible that the voltage shift phenomena may possibly arise from multiple sources. For instance, large internal stresses developed in the films during their fabrication may considerably influence the switching characteristics and hysteresis behavior of PZT films due to a strong electro-mechanical coupling in the perovskite structure [23]. The other possible mechanism, contributing to the voltage shift phenomena in ferroelectric PZT films, might be related to the defects. It is commonly understood and generally accepted that the defects are predominantly accumulated at the electrode-film interface. An asymmetric distribution of trapped charge has been suggested to be responsible for imprint phenomena in ferroelectric thin film capacitors [24].

Within the context, it should be noted that the capacitance peaks and butterfly-like shape of the C-V curves (shown in Fig. 3) could be related to the irreversible switching of the ferroelectric non-180° domain walls. A qualitative indication suggesting the link between the polarization switching processes and the C-V characteristics is that the switching asymmetry observed in the hysteresis P-E loops can also be found in the C-V curves in Fig. 3 where the slopes toward the switching peaks and their broadness are clearly different for the two branches.

4. Conclusions

In summary, the LSMCD method was investigated as a way to deposit high quality ferroelectric thin films at minimized production costs. Polycrystalline $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) thin films of various thicknesses were produced on $Pt/Ti/SiO_2/Si$ substrates using a standalone laboratory deposition process tool. In this study, fundamental electrical and material characteristics are presented for the 770-nm-thick PZT films. The films of a nearly pure perovskite phase were well-crystallized with a high (111)-preferred orientation at a temperature of 750 °C for 1 min in oxygen atmosphere. They showed a columnar microstructure with the grains growing from the film/bottom electrode interface. The relative dielectric permittivity and loss value are 800 and 0.04, respectively, at room tem-

perature. The average coercive field, as obtained from asymmetrically shifted C-V curves and P-E hysteresis loops, is about 40 kV cm^{-1}. It can be concluded that mist deposited PZT thin films show very adequate electrical characteristics and material properties and the LSMCD technique offers new possibilities in low--cost processing of high-quality ferroelectric films.

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