Raman, FT-IR and dielectric studies of PZT 40/60 films deposited by MOD technology

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Ferroelectric Pb(Zr₀.₄Ti₀.₆)O₃ (PZT 40/60) thin films with uniform composition have been fabricated using the metallo-organic precursor compounds lead di-ethylhexanoate Pb(C₁₇H₃₅COO)₂, titanium di-methoxy-di-neodecanoate Ti(OCH₃)₂(C₁₇H₃₉COO)₂ and zirconium octoate Zr(C₁₇H₃₅COO)₄. These metallo-organic precursors were stored for more than four years and are very stable in ambient conditions, compared to sol–gel solutions. The structural development of these films under different annealing temperatures was systematically studied using X-ray diffraction, FT-IR spectroscopy and Raman scattering. The results show that the overlapping of (h00) and (00l) peaks of the PZT 40/60 films in X-ray diffraction patterns, mainly due to the small grain sizes in films, makes it very difficult to distinguish individual diffraction peaks and to identify the phases. In FT-IR measurements, the intensity of Zr/TiO₆ metal–oxygen octahedral vibrational modes becomes stronger with increasing annealing temperatures, while the FT–IR spectral peaks of vibrations of the residual carbon ligands (COO⁻) finally disappear at high temperatures, showing that FT–IR spectroscopy is a good way to monitor the growth of the perovskite phase in PZT 40/60 films. Raman measurements undoubtedly reveal the Raman spectra of these PZT 40/60 films in the tetragonal phase field, demonstrating that Raman spectroscopy is an effective tool to identify structures, especially in the case of thin films having small grains. The values of high dielectric constant and the total remanent polarization obtained by ferroelectric pulse measurements show that the PZT film is a suitable material for non-volatile random access memory and dynamic random access memory applications.

1. Introduction

The renewed interest in ferroelectric materials for non-volatile random access memory (NV-RAM) and dynamic random access memory (DRAM) has received great attention in the electronic industry. Extensive research and development work in this area has been carried out in recent years [1–7]. Below the Curie temperature, ferroelectric materials have a directional spontaneous electrical polarization due to a non-centrosymmetric atomic unit cell. This polarization, caused by the displacement of ions in the cell, can be electrically switched. Thus the two stable electrically switchable polarization states make ferroelectric materials very suitable for non-volatile binary data storage. The most recent approach to ferroelectric memories has been to integrate the ferroelectric memory capacitor into a random access memory (RAM) circuit on an integrated circuit to convert semiconductor RAMs to a non-volatile form. Lead zirconate titanate (PZT) thin films have been extensively investigated for such applications. The PZT ferroelectric memory has many advantages such as high density, retention of charge over long periods of time (order of decades) without any supplied voltage, and radiation immunity. Since these PZT/PLZT materials have high dielectric constants [8], their application as dielectric layers in extreme high density, new generation DRAMs looks promising. The potential of combining the ferroelectric non-volatility with the fast read and write characteristics of a DRAM has also been realized in the fabrication of non-volatile DRAMs [9].

PZT thin films have been fabricated by various techniques such as evaporation [10], RF sputtering [11], laser ablation [12], metallo-organic chemical vapour deposition (MOCVD) [13], the sol–gel process [14] and metallo-organic decomposition (MOD) [15]. Low-temperature processes for the production of ferroelectric thin films are needed to integrate these thin films with state-of-the-art silicon integrated circuit technology. The interfacial reactions of substrates and ferroelectric thin films at elevated temperatures are of major concern during device fabrication since they may degrade stored charge, fatigue and long-term reliability characteristics of the films. Control of the material composition is difficult in films made by RF sputtering. In the sol–gel process, precursor solutions are usually water-sensitive and tend to gel quickly, which imposes stability problems if these solutions
are to be kept for a reasonably long time. Of all the deposition methods, MOD is one of the simplest techniques available to prepare pure stoichiometric thin films of multi-component ceramics. Since the MOD technique is a non-gelling chemistry process in which molecular homogeneity is attained in the liquid phase, solutions can be prepared under ambient conditions without solution gelling and at a lower processing temperature. MOD technology and its wide applications in electronic devices has been reviewed by Kuo [16] and Vest [17].

In this paper, we report some experimental results of a systematic study of PZT 40/60 films using X-ray diffraction, FT-IR spectroscopy, Raman scattering and ferroelectric characterization. Also included is a discussion of the structural development of films under different conditions and we demonstrate that FT-IR and Raman spectra are effective tools for monitoring the growth of tetragonal perovskite phase in the PZT 40/60 thin films of small grains.

2. Experimental procedure

2.1. Thin film preparation

The metallo-organic precursor compounds used for Pb(Zr_{0.4}Ti_{0.6})O_3 (PZT 40/60) films were lead di-ethyl-hexanoate Pb(CTH15COO)_2, titanium di-methoxy-didecanoate Ti(OCH3)2(C9H19COO)2 and zirconium octoate Zr(C15H15 COO)4, all in xylene solution [18]. The thermal decomposition behaviour of the compounds was studied using thermogravimetric analysis (TGA, Perkin-Elmer 7 series TA system). From the TGA profiles, the temperatures at which the metallo-organic compounds converted to oxides were determined, as were the weight percentages of oxides produced. The weight percentages of the oxides for the metallo-organic compounds were also determined by firing the compounds in a furnace, the yields being consistent with those of the TGA. Fig. 1 shows a thermogram of the Pb(Zr_{0.4}Ti_{0.6})O_3 formulation solution at a heating rate of 2°C min^{-1} in air. At temperatures below 120°C, the weight loss of the sample was due to evaporation of the xylene solution. The precursor compounds began to decompose at about 280°C and the decomposition was completed by 380°C. The Pb(Zr_{0.4}Ti_{0.6}) O_3 formulation solution was spun onto (001) single-crystal silicon substrates, which were coated with a 500nm thick SiO_2 layer, a 100nm thick Ti layer, and a 100nm thick Pt layer was then sputtered on the top surface by Silicon Sense Inc., USA. The wet film was then pyrolysed in a fused quartz tube furnace at 400°C for 12 min in flowing oxygen of 0.5 slm (standard litres per minute). This procedure was repeated four times to produce PZT 40/60 films with the thickness of about 500 nm.

2.2. Measurements

The film thickness was measured using an Veeco Dektak 3ST surface profilometer. A corner of the film was removed using 10:1 diluted HF acid after annealing to produce the step. A Philips PW 1830 X-ray diffractometer with CuKα radiation was used to analyse the crystalline phases in the films. A Perkin Elmer 2000 FT-IR spectrometer was used to measure the vibrational modes in the PZT 40/60 films. Raman measurements were performed using a Spex 1403 Raman spectroscope with a 514.5 nm line of an argon laser. The incident light was strongly reflected by the platinum layer on the silicon substrate. As shown in Fig. 2, a right-angle scattering geometry was used in Raman measurements in order to remove the directly reflected light. The incident angle φ was about 75°. The scattered light was focussed into a Spex double monochromator and was detected by a standard photon-counting technique. Both the top and bottom electrodes were sputterd platinum; the bottom electrode covered the entire substrate, while the top electrodes were in a square-matrix pattern of 100 µm x 100 µm size for each. Ferroelectric hysteresis loop, pulse polarizations and dielectric constant were measured using an RT 66A ferroelectric test system made by Radiant Technologies, Inc.

3. Results and discussion

3.1. X-ray diffraction

40/60 lead zirconate titanate has a tetragonal structure with lattice constants of a = 0.40045 nm and