Synthesis and ferroelectric properties of SrBi$_2$Ta$_2$O$_9$/Bi$_4$Ti$_3$O$_{12}$/p-Si multilayer thin films by Sol-Gel

H. Wang · M. F. Ren

Abstract SrBi$_2$Ta$_2$O$_9$(SBT)/Bi$_4$Ti$_3$O$_{12}$(BIT) multilayer thin films were prepared on p-Si substrates by Sol-Gel method, the effect of thickness of SBT and annealing temperature on structure, morphology, ferroelectric and fatigue properties of SBT/BIT ferroelectric films were investigated. The SBT/BIT multilayer films annealed at above 600°C were uniform and crack free as well as exhibited no pyrochlore phase. The remanent polarization and the coercive field of SBT/BIT multilayer films both increases with the increase of annealing temperature due to better crystallization and larger grain size. The SBT/BIT multilayer thin films consisting of 1 layer of SBT and 3 layers of BIT annealed above 650°C obtained its best ferroelectric properties with a $P_r$ of 8.1 μC/cm$^2$ and an $E_c$ of 130 kV/cm which is comparable to that of pure BIT films and had a fatigue-free property up to $10^{11}$ switching cycles, but $P_{nv}$ appeared under the cycle field of 175 kV/cm and increased with the decrease of cycle field.

1. Introduction

Considerable attention has been focused in developments of ferroelectric field effect transistor (FFET) memories based on ferroelectric materials for several decades [1, 2]. Many ferroelectric materials have been studied as candidates for FFET applications. Among them, Pb (ZrxTi$_{1-x}$)O$_3$ (PZT) thin films with various compositions are the most promising and the most intensively investigated. Although PZT has advantages of large $P_r$ values (typically 20–70 μC/cm$^2$) and low processing temperature, PZT thin film suffer severe fatigue after repetitive read/write cycles with Pt electrodes, the serious interaction and interdiffusion between PZT ferroelectric films and Si substrate lead to low retention and large leakage current.

Recently, bismuth layered structure ferroelectrics (BLSF) thin films have been widely investigated aimed at applications in FFET. In the last decade, studies to solve the problem of fatigue have been concentrated on replacing PZT thin films with SrBi$_2$Ta$_2$O$_9$ (SBT) thin films as the memory media. SBT has a bismuth-layered perovskite structure with two connected TaO$_6$ octahedra in perovskite-like layers separated by Bi$_2$O$_2$ layers and it has been found to show little polarization reduction up to $10^{12}$ switching cycles with Pt electrodes [3, 4]. However, the SBT films have some serious drawbacks, such as high processing temperatures (above 750°C) and low remanent polarization of 4-10 μC/cm$^2$, which is insufficient for the high-density integration of FFET [3, 5]. Bi$_4$Ti$_3$O$_{12}$ (BIT) is a kind of the BLSF materials with lattice parameters of $a = 0.541$ nm, $b = 0.545$ nm, $c = 3.28$ nm [6]. An a-axis-orientation BIT thin film has a large spontaneous polarization of 15-45 μC/cm$^2$, which is 3-4 times higher than that of SBT. Due to the high polarization and the good matching in lattice parameters with Si (100), BIT is also suitable as a ferroelectric insulator in the MFS-FET [7], but it is more fatigued with Pt electrodes than SBT. High annealing temperature is another problem of ferroelectric thin films applied in Si integration devices (for example, in FFET). However, in previous works, several researches reported that the temperature of 750°C or higher is required to produce perovskite layered SBT thin films [8, 9].

In the present paper, the synthesis of SBT/BIT multilayer thin films annealed at lower temperature, microstructure and
ferroelectric properties of SBT/BIT multilayer thin films deposited on p-Si are reported.

2. Experimental procedure

2.1. Fabrication of SBT/BIT multilayer thin films

SBT/BIT multilayer thin films were prepared on p-Si (100) substrates by Sol-Gel method. This processing was selected due to its low cost, easy control of stoichiometry, simplicity, and the potential of commercial application to deposit uniform films over large areas. Moreover, this processing has previously been successfully applied to deposit BLSF thin films.

Bismuth nitrate, titanium isopropoxide, strontium 2-ethylhexanate and tantalum ethoxide were selected as precursors. Excess 5% Bi and 2% Sr precursor were added to compensate Bi and Sr evaporation during annealing. Acetic acid and 2-methoxyethanol were used as solvent. Bismuth nitrate and strontium 2-ethylhexanate were initially dissolved in glacial acetic acid, respectively. Titanium isopropoxide and tantalum ethoxide were added to these mixtures with constant stirring, respectively. Finally, the SBT and BIT solutions thus formed were diluted with 2-methoxyethanol to adjust the viscosity and concentration of the solution. (100) p-type silicon wafers with a resistivity of 6–9 Ω·cm were cleaned by a standard process. The spin-on technique was employed to deposit solution on silicon substrates. After spinning onto substrates, wet films were kept on a hot plate in air at 300 °C for 10 minutes to remove solvents and other organics. The desired thickness of SBT/BIT multilayer thin films was achieved by multiple spin-bake processes. The dry multilayer films were annealed for 30 minutes at various temperatures in oxygen atmosphere. In this work, all the films prepared were about 400 nm thick, which can be obtained by depositing 1–4 layers of BIT and 3–0 layers of SBT.

2.2. Characterization of the samples

The structure and the surface morphology of the films were analyzed by x-ray diffraction (XRD) and examined by atom force microscope (AFM), respectively. Ferroelectric properties and fatigue characteristics of the SBT/BIT multilayer thin films were measured using a RT66A standardized ferroelectric tester (Radiant Technologies, USA). Before electrical measurements, the Pt electrode, with a thickness of 50 nm and a diameter of 0.4 mm, was patterned by a shadow-mask-process.

3. Results and discussion

3.1. Structure and surface morphology of SBT/BIT multilayer thin films

The structure of SBT/BIT multilayer thin films was analyzed by x-ray diffraction. Figure 1 shows the XRD patterns of SBT/BIT multilayer thin films annealed at 550 °C, 650 °C, 650 °C and 700 °C in oxygen, while the annealing time is kept of 30 minutes. The SBT/BIT multilayer thin films were polycrystalline annealed at above 550 °C and their X-ray diffraction patterns exhibited the peaks corresponding to the (004), (006), (008), (115), (117) and (020) reflections of BIT and the (103) and (115) reflections of SBT, but the characteristic peaks shown in 550 °C patterns are weak and broad. As the annealing temperature increases, annealing results in sharp peaks with high intensity, indicating better crystallinity and an increase in grain size. The patterns of XRD also exhibited that there were not any pyrochlore phase or other second phase in SBT/BIT multilayer thin films deposited on p-Si substrates and they all exhibit a polycrystalline structure. The higher and sharper peaks of XRD patterns of BIT compared with those of SBT illustrated that the BIT films had better crystallinity and larger grain size, which indicated that SBT thin films require higher annealing temperature than BIT thin films at the same processing conditions.

Figure 2(a)–(d) show the typical AFM surface morphology of SBT/BIT multilayer thin films annealed at 550 °C,