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Annealing effect of platinum-based electrodes on physical properties of PZT thin films

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Abstract

This study examined the crystal structure and surface morphology, including the Ti segregation mechanism on the surface due to the inter-diffusion between Pt, Ti and TiO_x as a glue layer, according to the annealing temperature and growth orientation of a Pt film. In addition, the fatigue mechanism of ferroelectric PZT thin films deposited on a Pt-based electrode was also investigated. The nano-structure, orientation mapping, and micro-morphologies of the triangular Pt hillocks were investigated by scanning electron microscopy with an electron backscatter diffraction (EBSD) function. The *D*–*E* hysteresis loop of the ferroelectric films was measured using a Sawyer–Tower circuit at 1 kHz to obtain the remanent polarization and coercive field.

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1. Introduction

There has been increasing interest in thin film high permittivity metal oxide capacitors for use in integrated circuit (IC) memory [1]. Integrated ferroelectrics have attracted considerable attention for their wide applications in memory devices. There have been many studies on Pt/Ti bilayers as a bottom electrode for ferroelectric films [2]. Platinum (Pt) has been selected primarily due to its stability in a high temperature oxygen environment, which is essential for crystallizing ferroelectric oxide films, and its high Schottky barrier height, which gives rise to a low leakage current. Pt has an FCC (Face Centered Cubic) structure, and tends to grow with a columnar structure [3]. Therefore, high priority has been placed on depositing platinum in its preferred growth orientation (111). Solid state diffusion occurs through the grain boundaries. The utilization of Pt as a diffusion barrier layer is poor during the thermal annealing due to its columnar structure. Ferroelectric materials deposited on Pt are believed to have a good orientation due to it adopting the orientation of Pt. However, the adhesion of Pt to a substrate such as silicon dioxide (SiO_x) is poor [2]. Therefore, a Ti glue layer has been used to improve the adhesion of Pt to SiO_x. The surface of the Pt/TiO_x electrode, which was substituted for a Ti or TiO_2 glue layer, is flat and uniform, even after the high temperature annealing process is complete [1]. Usually, the Pt/Ti electrode is deposited by sputtering. However, this method tends to have major instability problems, such as Pt hillock formation [4,5]. Pt hillocks are a major concern because they can lead to capacitor failure [6]. In addition, there is also a possibility that inter-diffusion between each layer

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creates a Pt–Ti compound, which can alter the crystal structure of the bottom electrode, affecting the orientation and crystal structure of the ferroelectric materials [7,8].

This study investigated the surface of the Pt layer and inter-diffusion properties due to the post-annealing process. Moreover, the annealing effects of Pt/Ti electrodes, hillock formation, inter-diffusion through each layer, and the formation of an ultra thin oxide layer on the surface were studied systematically. The ferroelectric properties of PZT thin film deposited on the annealed electrodes were also examined.

2. Experimental

Silicon-based Pt/TiO_x, such as Pt(1 1 1)/Ti, Pt(1 1 1)/TiO_2, and Pt(poly)/TiO_2 were selected as the bottom electrodes. Pt and Ti were deposited on substrate with temperature of 300 °C by sputtering, and SiO_2 was formed by thermal oxidation. Silicon was oriented in an n-type (1 0 0) direction. The thickness of the Pt, Ti, and SiO_2 layers were 150 nm, 10 nm, and 300 nm, respectively. Thermal treatment was performed in a conventional furnace (CFA) at temperatures of 600, 700, 800, and 900 °C for 1 h, respectively. For all samples, the temperature was increased at a rate of 10 °C/min.

The PZT films were prepared using a sol–gel method. The starting solution was prepared from lead acetate trihydrate, zirconium propoxide, and titanium iso-propoxide preferentially dissolved in 2-methoxyethanol. These were mixed at a molar ratio of Pb:Zr:Ti = 1.1:0.52:0.48. The resulting solution was diluted to 0.35 M. The film was deposited onto the substrate by spin coating followed by annealing at 700 °C for 30 min.

The nanostructure, crystal orientation mapping, and micro-morphology of the Pt hillock were obtained by scanning electron microscopy (SEM; Hitachi-S900) with electron backscatter diffraction (EBSD). The *D–E* hysteresis loop of the ferroelectric films was measured using a Sawyer–Tower circuit at 1 kHz to obtain the remanent polarization and coercive field. A Radiant Technologies RT66A ferroelectric tester was used to measure the fatigue.

3. Results and discussion

X-ray diffraction (XRD) was used to investigate the structural orientation of the annealed Pt/Ti stacks. Fig. 1 shows the XRD patterns according to the annealing temperature of the films deposited on various substrates. Chason et al. [7] reported the detection of Pt–Ti compounds due to the annealing process. However, the XRD data did not reveal any other secondary phases in the sample. The (1 1 1)-oriented Pt films only showed the (1 1 1) direction with annealing temperature of 600–900 °C. However, the (1 1 1)-preferred orientation of the Pt (poly)/TiO_2 films changed to a (2 0 0)-preferred orientation at annealing temperature of above 600 °C.

Fig. 2 shows the surface morphology of the Pt/TiO_x electrodes. Their surface morphology was influenced by the formation condition of the electrodes. By considering the crystallization temperature of ferroelectric materials

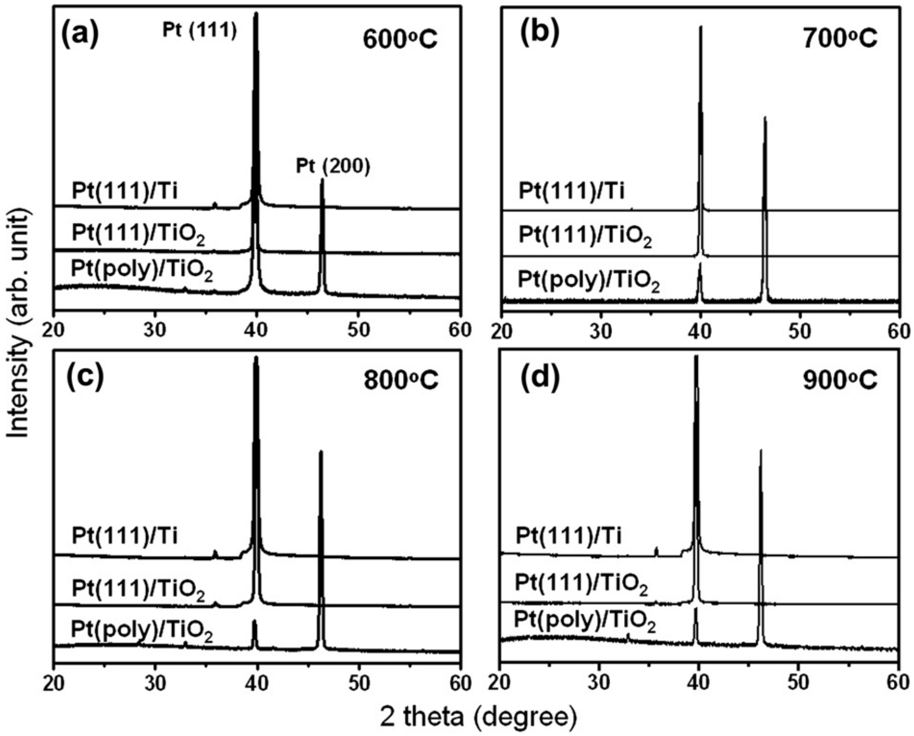

Fig. 1. XRD patterns of the Pt/TiO_x electrodes annealed at (a) 600 °C (b) 700 °C (c) 800 °C, and (d) 900 °C, respectively.