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X-ray reflectivity studies of ferroelectric and dielectric multilayer structures

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Abstract

Dielectric and ferroelectric thin-film capacitors are of great importance as dynamic random-access memories (DRAM) and non-volatile random-access memories (NVRAM) for storage technology applications. Further improvements of the electrical performance of these devices require particularly a better control of thin-film engineering, since nanoscale layers of complex stoichiometry are subjected to relatively high-thermal budgets during the integration process. X-ray specular and diffuse reflectivity can provide valuable insight into current material problems of this field, e.g. structural changes and the possibility of interfacial reactions. An example is given for the annealing of thin $Pb(Zr_{0.3}Ti_{0.7})O_3$ (PZT) films on Pt/Ti-based layered electrodes. The correlation of electrical function and structural changes subsequent to electrical stress requires in situ investigations under applied electric fields. We report first experiments on Pt/PZT/Pt/Ti-films and discuss the setup of electrical in situ measurements under grazing incidence.

Keywords: Ferroelectrics; Electrode; X-ray reflectivity; Multilayer

1. Introduction

After 40 years of significant development and successful expansion, the Si semiconductor industry is facing serious challenges owing to the rapid approaching of the SiO_2 thickness to the physical limit beyond which the leakage current due to the electron tunneling through the dielectrics becomes unacceptable [1,2]. The fundamental aspect of Si industry is that Si can be reacted with oxygen or nitrogen to form stable Si–O or Si–O–N dielectrics. The dielectric layer is the most important part of the complementary metal–oxide–semiconductor (CMOS) field-effect-transistors (FET) and metal–insulator–semiconductor (MIS) DRAM. One of the opportunities is the potential application of ferroelectric materials as NVRAM [3]. As compared to magnetic storage media and DRAM, ferroelectric memories have the advantages of high speed and nonvolatility, respectively. However,

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there are still several reliability problems hindering the full commercialization such as ferroelectric fatigue under external AC electric field and imprint, i.e. the horizontal shift of the hysteresis loop of a polarized capacitor with time [4]. In the search to find suitable alternative dielectrics and the ongoing endeavor to realize ferroelectric memories, the quality of the multilayered structure, interface engineering, process compatibility and reliability must be considered carefully and optimized.

Here, we report our recent studies using X-ray reflectivity on the structural changes of the Pt/Ti electrode stack for NVRAM and DRAM integration during the thin-film fabrication. A first in situ study on the piezoelectric response of PZT capacitors to applied electric fields is also reported.

2. Samples

Samples with structures of $Pt/TiO_2/SiO_2$ and $PZT/Pt/TiO_2/SiO_2$ were used for the structural study of the electrode stack during the film fabrication. Firstly, the silicon wafer was thermally oxidized to form a SiO_2 surface layer with a thickness of about 470 nm. Secondly, a Ti layer was sputtered as an adhesion layer and oxidized at 700 °C creating a pre-oxidized barrier layer. Hereafter, unless otherwise stated, all the annealing was performed in oxygen by using rapid thermal annealing (RTA). Thirdly, a 120 nm thick Pt bottom electrode was sputtered onto the TiO_2 layer and annealed at 700 °C for 5 min. Here, one sample was taken from the batch and used for X-ray reflectivity measurement of the bottom electrode alone while on another sample, a PZT film was deposited by a chemical solution deposition process through three spin-coatings and crystallized at 700 °C for 5 min. Then after a post-annealing at 700 °C for 5 min the sample with a PZT layer of 106 nm was used for the comparison reflectivity measurement.

The capacitor for converse piezoelectric response studies contained six coatings of PZT that were deposited in two separate runs each consisting of three spin-coatings of PZT and a crystallization treatment at 700 °C for 5 min. Then a top Pt of about 70 nm was sputtered thereon and the capacitor was post-annealed at 700 °C for 5 min.

3. Experimental

X-ray reflectivity measurements were performed at HASYLAB (DESY) beam line E2 using an X-ray energy of 11 keV. For in situ studies the X-ray reflectivity measurements were combined with an electrical setup. A reproducible and stable electrical contact was established by two commercial soft needles, which were each positioned by a micromanipulator. The bottom electrode was exposed by etching the ceramics with diluted hydrofluoric acid.

The ferroelectric properties were measured by a computer-controlled modified Sawyer-Tower circuit [5] as shown in Fig. 1, where a linear capacitance C_{ref} is connected in series with the ferroelectric capacitor C. Because C_{ref} is approximately 100 times larger than C, nearly the entire voltage supplied by the signal generator drops across C. Since the charges Q on capacitors in series are equal, the polarization is given by $P = Q/A = C_{ref}U_{ref}/A$.

Within the time scale of the experiments, no changes of the electrical properties of the capacitors were observed, indicating no observable X-ray radiation damage here.

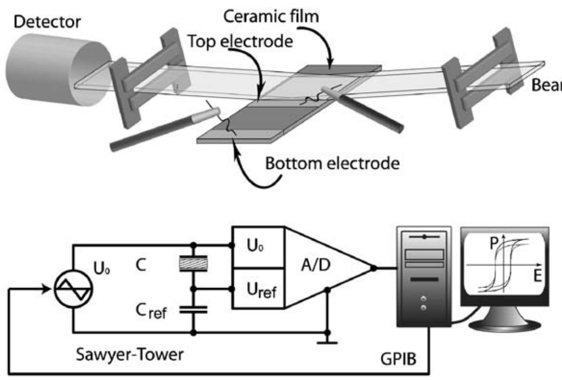

Fig. 1. Schematic of the in situ X-ray reflectivity combined with a Sawyer–Tower circuit for electrical polarization measurement.