Microelectronic Engineering 177 (2017) 13–18

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Research paper

Process induced poling and plasma induced damage of thin film PZT

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ARTICLE INFO

Article history:
Received 14 October 2016
Received in revised form 12 January 2017
Accepted 14 January 2017
Available online 17 January 2017

Keywords:
PZT
Ar ion milling
Process induced damage
Plasma charging
Self-bias voltage
Poling
Reliability
Dielectric damage
TDDB
Capacitance-voltage measurement

ABSTRACT

This paper treats processing sequence induced changes on PZT. Two kinds of metal-PZT-metal capacitors are compared. The top surface and sidewall of PZT in one kind of capacitor is directly bombarded by energetic particles during ion milling process, whereas PZT in the other kind of capacitor is not. The polarity of plasma charging may depend on the ion milling parameters and influence the self-poling of virgin PZT capacitors. Direct ion bombardment induces a significant decrease of PZT permittivity. The PZT reliability (both RVS and TDDB) at positive voltage worsens because of bombardments of energetic particles; whereas the PZT reliability at negative voltage is not influenced. It indicates that the process induced positively charged defects present in the upper part of the capacitor structure initiate the dielectric breakdown.

1. Introduction

$PbZr_{1-x}Ti_xO_3$ (PZT) material is widely used in piezoelectric MEMS (Micro Electro Mechanical Systems). Its applications include ultrasound medical imaging, robotic insects, inkjet printing, mechanically based logic, and energy harvesting [1]. Further improvement of piezoelectric MEMS requires an increased integration density and a decreased feature size [1,2]. Dry etching is more widely used than wet etching because of its anisotropic and accurate pattern transfer for PZT, especially for a small feature size [3]. Plasma induced damage of PZT during dry etching has been reported by several authors [4–13]. Notwithstanding the benefits of integration, plasma etching induced dielectric damage may become a more prominent issue with increasing integration density [14–19]. Therefore, it is important to study the effects and mechanisms that cause plasma induced damage in PZT based devices.

Both physical and chemical effects contribute to the detected PZT damage/degradation during plasma etching [4,7,9–11]. The physical effect stems from the bombardment of energetic ions; the chemical effect comes from the contamination of impurities in the plasma. Pan et al. think that the physical effect of ion bombardment is the main reason of the PZT degradation [4]. Stanishevsky et al. find that the impurity in etching gas contribute to the change of PZT chemical composition [7]. Lim et al. propose that residues like ZrCl and ZrF might worsen electrical properties [9]. Jung et al. detect the generation of H—O dipoles due to hydrogen reduction during plasma exposure [10]. Soyer et al. show a surface layer developed during plasma etching which contains fluorine and has poor electrical properties [11].

In case of pure ion etching, the chemical effect on PZT degradation during etching could be eliminated. In addition, the particle bombardment is assumed to be primarily responsible for the etching [6]. By using ion milling, it is possible to etch a global structure including several materials without having to change the etching gas, which is beneficial for MEMS applications [6]. Therefore, Ar ion milling is chosen for patterning of PZT capacitors for this study.

The PZT damage/degradation caused by physical effect of ion bombardments can manifest itself by the increase of surface roughness, shift of the hysteresis loop, decrease of permittivity, decrease of remnant polarization, and increase of coercive fields [6,8,13]. Soyer et al. study the PZT damage as a function of ion milling parameters [6]. The PZT grain boundaries contain more Pb than PZT bulk. The etching rate of Pb oxide is higher than Ti/Zr oxide. Thus PZT grain boundaries are preferentially etched and the PZT surface roughness increases [6]. The shift of the hysteresis loop indicates the generation of an internal electric field, which may correspond to the charge accumulation and releasing at the top electrode-PZT interface [6]. A damaged layer at the PZT surface (or sidewall) becomes non-ferroelectric due to the ion bombardments. The total capacitance is then the remained ferroelectric capacitance connecting in series (or in parallel) with the non-ferroelectric capacitance. Since the non-ferroelectric layer has much smaller

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http://dx.doi.org/10.1016/j.mee.2017.01.016

permittivity than ferroelectric PZT, the total capacitance (thus the equivalent permittivity) decreases during the ion milling process [6,8, 13]. The formation of a non-ferroelectric layer causes a reduction of the ferroelectric zone; thus it also explains the reduction of the remnant polarization. The pinning between the damaged layer and the undamaged PZT layer contributes to a loss of mobility of domain walls, resulting in an increase of coercive fields [6,13].

Besides the change of PZT properties mentioned above, the physical ion bombardments also influence the aging performance of PZT. Yang et al. also find that the clamping from the substrate is reduced by etching. The clamping from the substrate produces deep potential wells which prevent part of the spontaneous polarization to switch. The damaged PZT sidewall/surface produces shallow potential wells. The domains can be exited out of the shallow potential wells at high electric field, which increases polarization and worsen aging performance [13]. An increase of leakage current because of plasma etching is also detected in [9,12]. Some people find that the plasma etching induced PZT damage can be partly recovered by annealing [6,9].

However, the dielectric breakdown of PZT damaged by plasma etching is not studied in detail. To this purpose, in this paper, we compare two kinds of PZT capacitors processed in parallel, only one of them being directly damaged by ion bombardment. Except for ion bombardments, we also study the influence of plasma charging on the virgin PZT capacitors, which is similar to the antenna effect in industrial IC processes [19]. The ramped voltage stress (RVS) breakdown and time dependent dielectric breakdown (TDDB) of these two kinds of PZT capacitors are compared.

2. Materials and methods

In the present work, we simultaneously fabricate two kinds of metal-insulator-metal (MIM) PZT capacitors on TiO_2 terminated (001) oriented $SrTiO_3$ (STO) substrates. The schematic cross-section of the two kinds of PZT capacitors is shown in Fig. 1. Both kinds of capacitors have 80 nm thick of $SrRuO_3$ (SRO) bottom electrodes, and 800-nm-thick epitaxial $PbZr_{0.37}Ti_{0.63}O_3$ (PZT) thin films with (001) orientation. The PZT layer is deposited by pulsed laser deposition using a KrF Excimer laser (Lambda Physik, 248 nm wavelength) at a laser fluency of 2.5 J/cm^2, substrate temperature of 600 °C, pure oxygen pressure of 0.1 mbar, target-substrate distance of 6 cm, and 10 Hz repetition rate. The SRO electrode is deposited as in [21]. More fabrication detailed are found in [28].

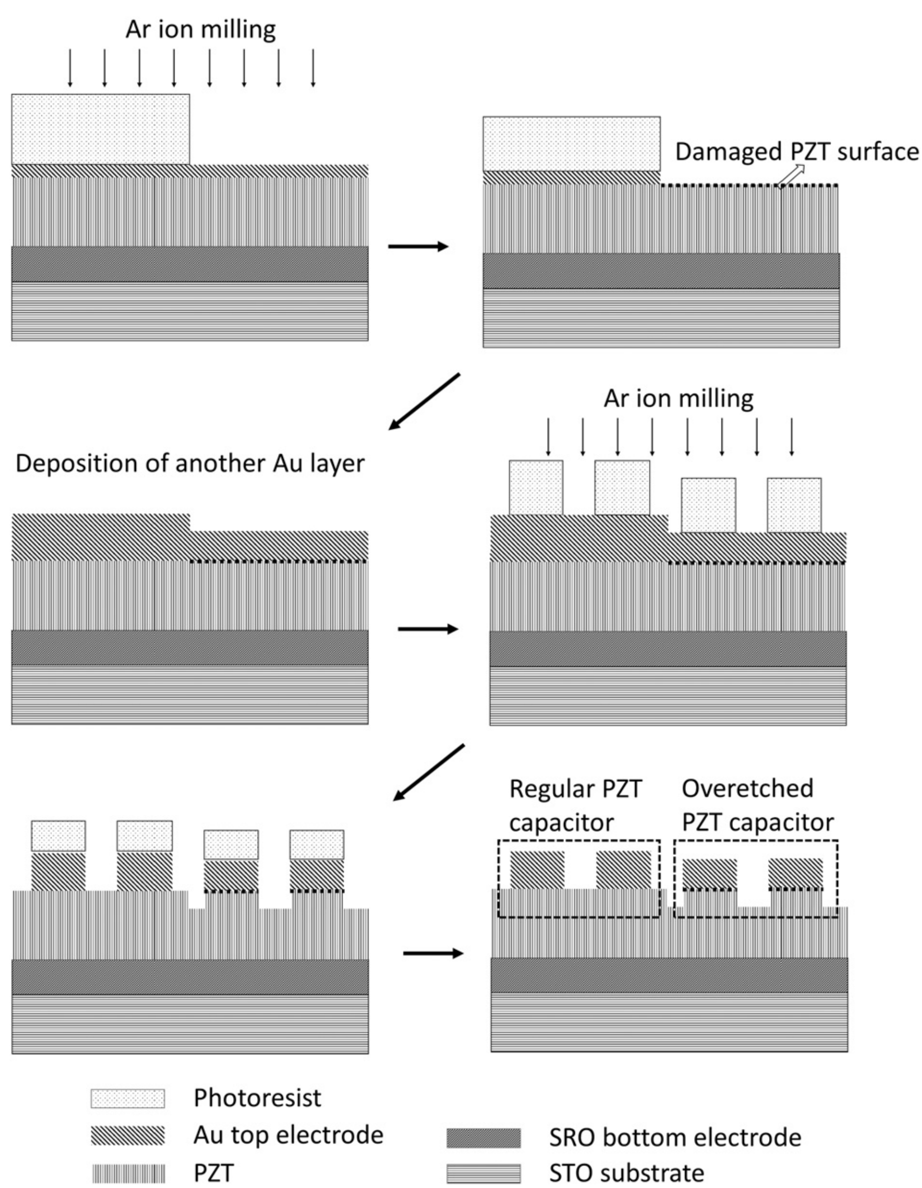

Fig. 1. Schematic cross-section of two kinds of PZT capacitors in main process steps.