Microelectronics Reliability xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Microelectronics Reliability

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

Ferroelectric of HfO_2 dielectric layer sputtered with TiN or ZrN for sandwich-like metal-insulator-metal capacitors

P.C. Juan [a], K.C. Lin [b,*], H.Y. Chu [a], Y.C. Kuo [c], H.W. Wang [c], T.Y. Shih [c]

[a] Dept. of Materials Engineering and Center for Thin Film Technologies and Applications, Ming Chi University of Technology, 84 Gungjuan Rd., Taishan Dist., New Taipei 243, Taiwan
[b] Dept. of Electronic Engineering, Ming-Chuan University, 5 De Ming Rd., Gui Shan Dist., Taoyuan 333, Taiwan
[c] Dept. of Mechatronic Technology, National Taiwan Normal University, 162, Sec. 1, Heping E. Rd., Taipei 106, Taiwan

A R T I C L E I N F O

Article history:
Received 13 January 2017
Received in revised form 29 May 2017
Accepted 13 June 2017
Available online xxxx

Keywords:
High power impulse magnetron sputtering (HIPIMS)
Ferroelectricity
HfO_2

A B S T R A C T

In this study, metal-insulator-metal (MIM) capacitors, which use HfO_2 as the intermediate insulating layer, and TiN or ZrN as the upper/lower capping layers were fabricated to form the sandwich-like structures, i.e. Al/TiN/HfO_2/TiN/Mo/p-Si and Al/ZrN/HfO_2/ZrN/Mo/p-Si. The crystallization of high-k HfO_2 thin-film is induced by high power impulse magnetron sputtering (HIPIMS) during the deposition of TiN and/or ZrN capping layers. The ferroelectric performance became better in both two structures as the thickness of metal nitride layer decreased. As the rapid thermal annealing (RTA) temperature after TiN layer deposition increased, the ferroelectric performance of the structure with TiN layer became better. On the other hand, the structure with ZrN layer exhibited opposite trends. According to X-ray diffraction (XRD) measurement, both TiN and ZrN layers offered stress and produced orthorhombic phase on HfO_2 layer. Both two layers at any thicknesses also protected Mo layer from the invasion of Hf atoms. The structure with TiN layer exhibited a higher remanent polarization (P_r) value as the roughness of TiN layer increased. However, the higher the roughness that the structure with ZrN layer had, the worse the ferroelectric performance obtained.

1. Introduction

As the memory dimension shrinks, the thickness of the tunneling dielectric layer is getting thinner than before. Due to thin tunnel oxide layer, the transition probability of charge in the polysilicon gate which goes through the tunnel oxide layer within a single point defects will increase, resulting in loss of memory function. Therefore, developing a new generation of memory will be a major research objective [1]. Traditional ferroelectric material such as $Pb(Zr,Ti)O_3$ (PZT), $SrBi_2Ta_2O_9$ (SBT), $BiFeO_3$ (BFO), etc. cannot match with the silicon substrate lattice very well, which resulting in poor ferroelectric performance. However, high-k binary materials, such as HfO_2 [2,3] and Zr-doped HfO_2 [4,5,6,7–9] were recently discovered to exhibit ferroelectricity with respect to performance and quality interface results with the silicon substrate. Other doping materials such as Si [10], Al [11], Y [12], or Gd [13] into HfO_2 thin films have been applied in order to stabilize the ferroelectric phase. The behavior of ferroelectricity is attributed to the formation of a non-centrosymmetric orthorhombic phase of space group $Pbc2_1$, which was found to be stabilized preferably by crystallization of the HfO_2-based thin films in the presence of top TiN electrode [3,14]. This is due to a mechanical confinement effect from the capping electrode which inhibited the tetragonal-monoclinic phase transformation. Thus, by applying a metal nitride material as an external stress factor to change the structure of the crystal material, it is able to produce good ferroelectricity [3,4,7–9,13]. Moreover, among those HfO_2-based ferroelectric materials, Zr-doped HfO_2 (HZO) films showed feasible ferroelectric properties that were much more resistant to degradation due to hydrogen annealing [6,7]. With the consideration of TiN capping material extensively used in binary high-k ferroelectric film stack, ZrN metal nitride can be also considered. The concept is out-diffusion of Zr atom into HfO_2 thin-film rather than the out-diffusion of Ti atom which helps to maintain the ferroelectric properties under forming gas annealing in CMOS fabrication. The later will deteriorate the ferroelectricity.

In this study, we introduce the high power impulse magnetron sputtering (HIPIMS) technology for the metal-insulator-metal (MIM) stacks. HIPIMS discharge allows a high target current and thus a production of highly energetic ions. It has been proven that both the plasma density and the ionization rate of the sputtered metallic atoms increased [15]. Energetic ion bombardment is known to increase surface diffusion and hence increase the nucleation density [16]. The metallic ions can be implanted into the film underneath to a depth of a few nm. Epitaxy or atomic registry is possible between the crystal of a metal nitride and the underlying film [17]. Most of ferroelectric binary high-k dielectrics are deposited by atomic layer deposition (ALD) for

* Corresponding author.
E-mail address: wblin@mail.mcu.edu.tw (K.C. Lin).

http://dx.doi.org/10.1016/j.microrel.2017.06.017
0026-2714/© 2017 Elsevier Ltd. All rights reserved.

the purpose of crystallization, but the process is costive. In this work, the HIPIMS technology was applied in the ultra-thin metal nitride which located on the top of RF-sputtered high-k dielectric. Two structures of Al/TiN/HfO_2/TiN/Mo/p-Si and Al/ZrN/HfO_2/ZrN/Mo/p-Si with the ferroelectric HfO_2 layer and HIPIMS-sputtered TiN or ZrN capping layer were fabricated. These stacked structures were fabricated in our previous study [18] and adopted in the current study. P_r values were measured for these two structures subsequently. In addition to the electrical measurement, XRD pattern was applied to analyze the crystallinity of ferroelectric HfO_2 film. Transmission Electron Microscopy (TEM) was also employed to observe the interfacial interactions between the HfO_2 and Mo layers. Finally, Atomic Force Microscopy (AFM) was employed to analyze the surface roughness of the device. The results can relate to ferroelectric characteristics and explain the ferroelectric problems.

2. Experimental design

In our work, two sandwich-like MIM capacitors, i.e. Al/TiN/HfO_2/TiN/Mo/p-Si and Al/ZrN/HfO_2/ZrN/Mo/p-Si, which include an intermediate HfO_2 insulating layer, and a capping TiN and/or ZrN metal nitride in upper and lower capping layer were fabricated. The stacked schematic is shown in Fig.1. Molybdenum was first deposited on p-type Si substrate and the thickness was set to be 250 nm. HfO_2 was then deposited by conventional RF sputtering. In the meantime, the metal nitride material layer sputtered by HIPIMS technique was set on and beneath the HfO_2 layer without purging the chamber. The thickness of metal nitride layer was set from 2 nm to 6 nm and varied in increments of 2 nm. Nitrogen and oxygen served as working gases in plasma while sputtering. By using the induced external stress to twist the lattice, the HfO_2 film gained orthorhombic phase and thus produced the ferroelectric phase. RTA temperature was performed at 350 °C, 450 °C and 550 °C and the process time was 3 min under N_2 ambient. Al was deposited as the top electrode. Finally, electrical properties and physical properties such as XRD, TEM, and AFM for these two structures were analyzed.

3. Results and discussion

In this section, the ferroelectric characteristics are first shown in hysteresis curves. The physical characteristics such as XRD, TEM, and AFM are then measured to illustrate the relationship between the ferroelectric and physical characteristics.

3.1. Ferroelectric characteristics

Fig. 2(a) and (b) shows the hysteresis curves of the Al/TiN/HfO_2/TiN/Mo/p-Si structure at RTA temperatures of 350 and 450 °C under the TiN thickness of 2 nm, respectively. The P_r value observed at RTA temperature of 450 °C was greater than that of 350 °C. The hysteresis curves under the TiN thickness of 4 nm at three different RTA temperatures of 350, 450 and 550 °C are shown in Fig. 3(a), (b) and (c), respectively. The P_r value observed at RTA temperature of 550 °C was obviously greater than that at RTA temperature of 350 °C but slightly greater than that at RTA temperature of 450 °C. The hysteresis curves under the TiN thickness of 6 nm at three different RTA temperatures of 350, 450, and 550 °C are shown in Fig. 4(a), (b) and (c), respectively. Similarly, the P_r value at RTA temperature of 550 °C was obviously greater than that at RTA temperatures of 350 °C, but slightly greater than that at RTA temperature of 450 °C. The results of polarization versus RTA temperatures for different thicknesses at a gate bias of 3 V are shown in Fig. 5. The highest P_r value was observed under the TiN thickness of 2 nm and at RTA temperature of 450 °C. It is a reliability issue because of the lack of P_r value at RTA temperature of 550 °C. It should be considered during the fabrication process of the insulating layer, HfO_2, sputtered by TiN.

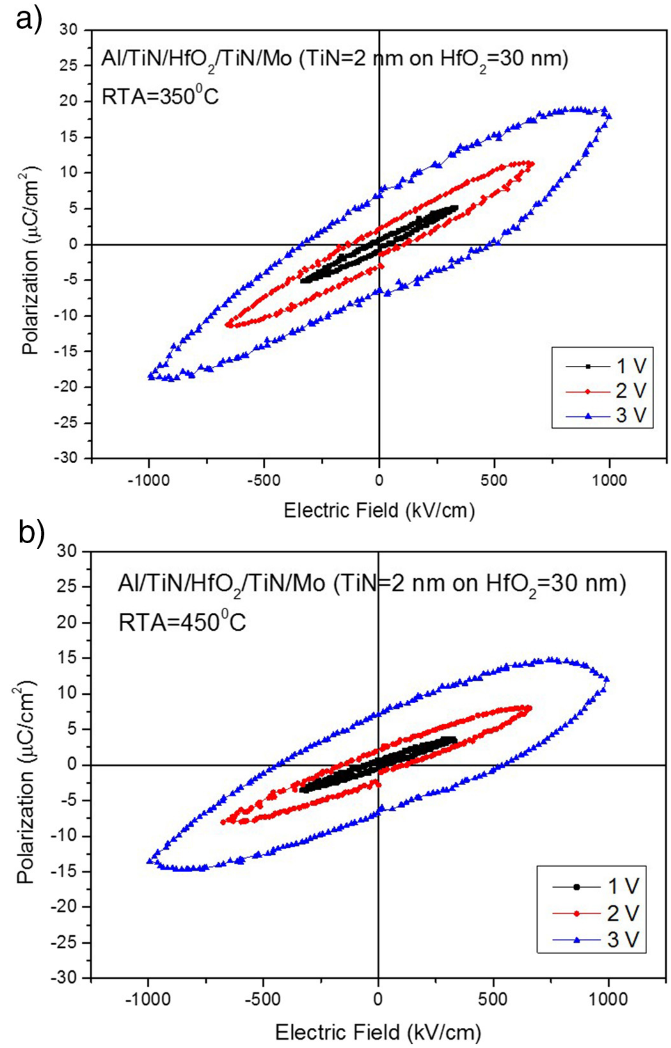

Fig. 2. The hysteresis curves of the Al/TiN/HfO_2/TiN/Mo/p-Si structure under the TiN thickness of 2 nm at RTA temperatures of (a) 350 °C and (b) 450 °C.

Fig. 6(a), (b), and (c) shows the hysteresis curves of the Al/ZrN/HfO_2/ZrN/Mo/p-Si structure at RTA temperatures of 350, 450 and 550 °C under the ZrN thickness set to 2 nm, respectively. The ferroelectric characteristics beyond gate bias of 2 V at RTA temperature of 550 °C cannot be measured any longer. The P_r value at RTA temperature of 350 °C is obviously greater than those of RTA temperatures of 450 and 550 °C. The hysteresis curves under the ZrN thickness of 4 nm at three different RTA temperatures of 350, 450 and 550 °C are shown in Fig. 7(a), (b) and

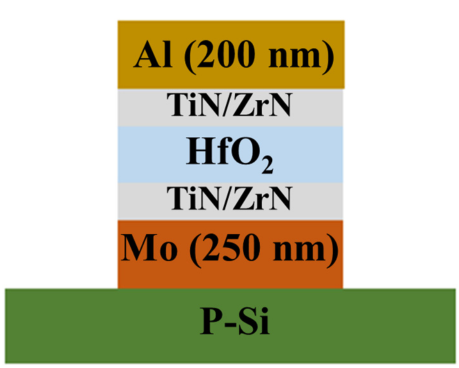

Fig. 1. The structure schematic of the sandwich-like MIM capacitor, Al/(ZrN/TiN)/HfO_2/(ZrN/TiN)/Mo/p-Si.