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In situ atomic layer nitridation on the top and down regions of the amorphous and crystalline high-*K* gate dielectrics

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ABSTRACT

Amorphous and crystalline ZrO_2 gate dielectrics treated with *in situ* atomic layer nitridation on the top and down regions (top and down nitridation, abbreviated as TN and DN) were investigated. In a comparison between the as-deposited amorphous DN and TN samples, the DN sample has a lower leakage current density (J_g) of $\sim 7 \times 10^{-4}$ A/cm^2 with a similar capacitance equivalent thickness (CET) of ~1.53 nm, attributed to the formation of SiO_xN_y in the interfacial layer (IL). The post-metallization annealing (PMA) leads to the transformation of ZrO_2 from the amorphous to the crystalline tetragonal/cubic phase, resulting in an increment of the dielectric constant. The PMA-treated TN sample exhibits a lower CET of 1.22 nm along with a similar J_g of $\sim 1.4 \times 10^{-5}$ A/cm^2 as compared with the PMA-treated DN sample, which can be ascribed to the suppression of IL regrowth. The result reveals that the nitrogen engineering in the top and down regions has a significant impact on the electrical characteristics of amorphous and crystalline ZrO_2 gate dielectrics, and the nitrogen incorporation at the top of crystalline ZrO_2 is an effective approach to scale the CET and J_g, as well as to improve the reliability.

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1. Introduction

In order to fulfill the scaling rule in the roadmap of International Technology Roadmap for Semiconductors (ITRS), a variety of high-*K* materials, such as HfO_2, ZrO_2, La_2O_3, and their silicates have been proposed to substitute for the conventional SiO_2 gate oxide [1]. Considering these high-*K* materials, ZrO_2 has been considered as a promising gate dielectric thanks to its high dielectric constant, large band gap, and relatively high thermal stability in contact with Si [2]. However, the nanoscale ZrO_2 thin films have a low crystallization temperature of ~450 °C [3], leading to the tetragonal or cubic crystalline phase with a high dielectric constants (K = 25–47) [4,5]. Actually, it had been demonstrated that a *K* value as high as 45 can be achieved in tetragonal ZrO_2 [6]. This high dielectric constant of crystalline ZrO_2 is favorable for further equivalent oxide thickness (EOT) scaling [6]. In addition, oxygen diffusion during the deposition and thermal processes in crystalline high-*K* dielectrics leads to the formation of low-*K* silicate in the interfacial layer (IL), resulting a scaling limit of EOT [7].

On the other hand, it has been reported that nitrogen incorporation in the high-*K* gate dielectrics can effectively suppress the IL growth, EOT, and leakage current density (J_g) [8–10]. Our previous research result has demonstrated that nitrogen incorporation into HfO_2 gate dielectrics using remote NH_3 plasma can effectively deactivate the oxygen vacancies and suppress the IL growth, giving rise to the decrease of J_g and EOT [11]. It has also been reported that the nitrogen distribution in high-*K* layer contributes to significant impact on its electrical characteristics [12,13]. Accordingly, the precise control of the nitrogen distribution in the high-*K* gate dielectrics is of crucial importance [10,14]. However, the effects on the nitrogen distribution in amorphous and crystalline high-*K* gate dielectrics are not investigated extensively and well understood.

In order to figure out the effect of nitrogen distribution in high-*K* dielectrics, *in situ* atomic layer nitridation on the top and down regions (top and down nitridation, abbreviated as TN and DN) of both the amorphous and crystalline ZrO_2 high-*K* gate dielectrics were carried out in this study, using the remote plasma atomic layer deposition (RP-ALD) technique. Because of layer-by-layer (or "digital") growth, the ALD technique has the *in situ* capability of precise atomic layer control of the doping process [14,15]. By comparing between the electrical and structural characteristics of the TN and DN samples, we can get a clear picture of the impacts of the different nitridation distribution on the amorphous and crystalline high-*K* gate dielectrics. The result indicates that top nitridation on

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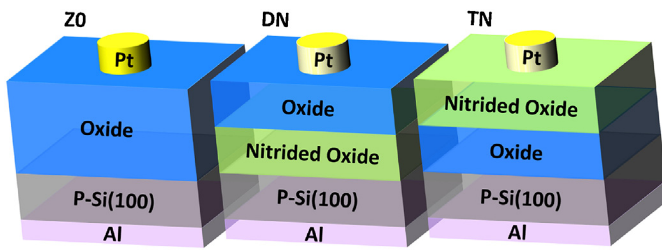

Fig. 1. Schematic structures of the (a) Z0, (b) DN, and (c) TN samples.

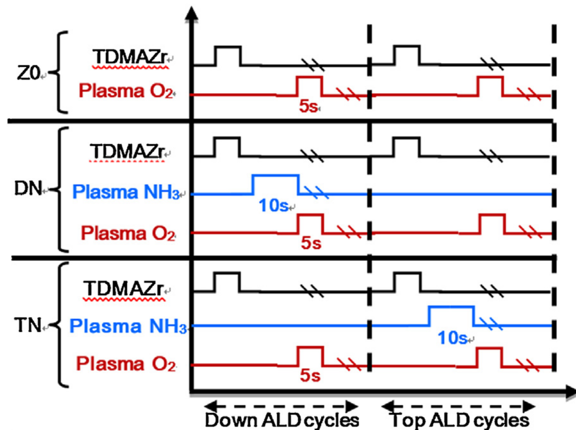

Fig. 2. Schematic diagram of the RP-ALD process of the Z0, DN, and TN samples.

the crystalline ZrO_2 is a well-suited approach to scale down the EOT and J_g of the high-*K* gate dielectrics.

2. Experimental

The schematic diagram of the metal-oxide-semiconductor (MOS) capacitors in this study are plotted in Fig. 1. *P*-type Si (100) substrates with 1–10 Ω-cm resistivity were cleaned in a dilute HF (2%) solution to remove native oxide. The pure ZrO_2 thin film without any nitrogen incorporation (designed as the Z0 sample), and in situ TN the DN ZrO_2 thin films were deposited at a temperature of 250 °C by RP-ALD (Ultratech, Fiji). Tetrakis-(dimethylamino)-zirconium (TDMAZ, $Zr[N(CH_3)_2]_4$) and O_2 plasma were used as the precursors for zirconium and oxygen, respectively. Remote NH_3 plasma was used as the reactants for nitrogen incorporation into the TN and DN samples. Fig. 2 schematically shows the ALD cycling processes for the preparation of Z0, TN, and DN samples. The processes were composed of two kinds of ALD cycles: the first one contained the following sequence: TDMAZ → Ar purge → O_2 plasma → Ar purge for the deposition of ZrO_2, and the second one comprised TDMAZ → Ar purge → remote NH_3 plasma → Ar purge → O_2 plasma → Ar purge for the *in situ* atomic layer nitridation on the ZrO_2 films. In the TN and DN samples, nitrogen was *in situ* incorporated into the top and down regions of ZrO_2, as shown schematically in Fig. 1. The thickness of all the samples was ~4 nm, which was controlled precisely by the ALD cycles and confirmed by spectroscopic ellipsometry. Then the platinum metal gate was deposited upon the high-*K* layer through a shadow mask with an area of 3×10^{-4} cm^2 by sputtering. Aluminum was coated as the back contact electrode by thermal evaporator. Finally, post-metallization annealing (PMA) was carried out in the 5% H_2/95% N_2 forming gas atmosphere at 450 °C for 30 minutes. The crystalline structure of the Z0, TN, and DN samples was probed by the grazing incident angle X-ray diffraction (GIXRD) with Cu Kα radiation at an incident angle of 0.5°. High-resolution transmission electron microscopy (HRTEM) was used to characterize the thickness of the high-*K* thin film and interfacial layer (IL). The chemical states and compositions of the oxides were analyzed by the X-ray photoelectron spectroscopy (XPS) using monochromatic Al Kα as the X-ray source. The capacitance–voltage (*C-V*) and current–voltage (*I-V*) of the Z0, TN, and DN samples were extracted using the Agilent B1500A to analyze the effects of *in situ* atomic layer nitridation on the ZrO_2 high-*K* gate dielectrics.

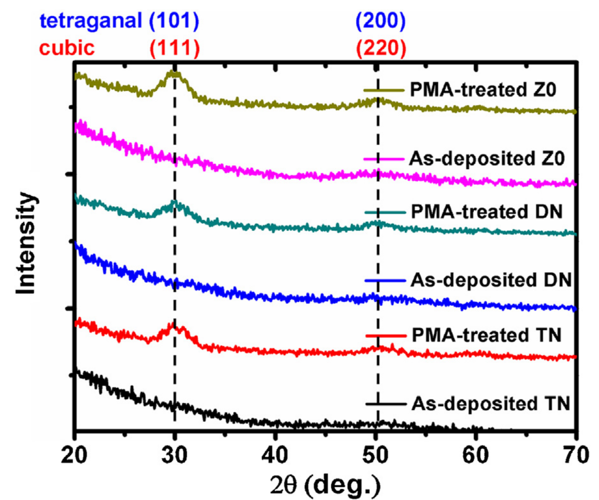

Fig. 3. GIXRD patterns of the as-deposited and PMA-treated Z0, DN and TN samples.

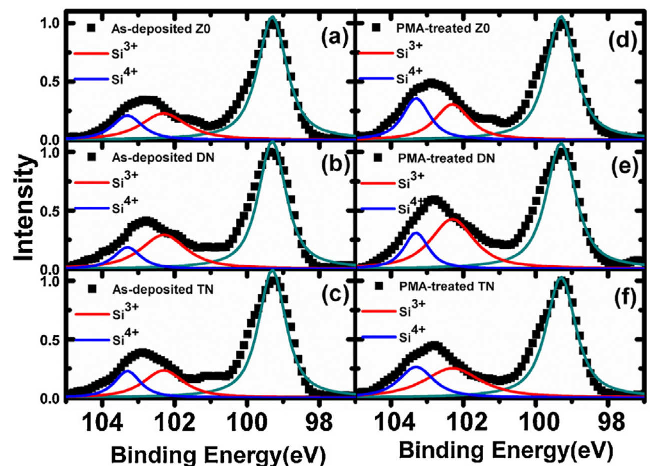

Fig. 4. Si 2p XPS spectra of the as-deposited (a) Z0, (b) DN, and (c) TN samples and PMA-treated (d) Z0, (e) DN, and (f) TN samples.

3. Results and discussion

The GIXRD patterns of the Z0, DN, and TN samples are shown in Fig. 3. The amorphous structure (i.e., those without any diffraction peaks) appears in all of the as-deposited samples. After the PMA treatment, the diffraction peaks at 2θ=30.4° and 50.6° were observed in the Z0, TN, and DN samples, corresponding to the ZrO_2 tetragonal (101) and (200) phase (88–1007 JCPDS) or the cubic (111) and (220) phase (49–1642 JCPDS). The dielectric constant of the tetragonal and cubic crystalline phase in ZrO_2 is as high as ~37 and 47, which is eminently beneficial to sub-nm EOT scaling [4,5]. The GIXRD patterns indicate the crystallization of nanoscale ZrO_2 thin films after the PMA treatment at a low temperature of 450 °C.

Fig. 4 shows Si 2p XPS spectra of the as-deposited (left column) and PMA-treated (right column) Z0, TN, and DN samples, where the intensity of the Si^0 oxidation state from the Si substrate at 99.3 eV

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