



## Improved electrical characteristics high-*k* gated MOS devices with in-situ remote plasma treatment in atomic layer deposition

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### ABSTRACT

Metal oxide semiconductor (MOS) devices with in situ remote plasma treatment during high-*k* dielectric deposition are studied in this work. The EOT value and leakage current of the MOS device with in situ NH<sub>3</sub> plasma treated high-*k* dielectrics can be significantly reduced to 0.83 nm and  $1.7 \times 10^{-3}$  A/cm<sup>2</sup>, respectively. The stress-induced flat-band voltage shifts and leakage current are obviously reduced as well. In-situ remote plasma treatment also provides a good approach of nitridation for high-*k* dielectrics. The oxygen vacancy can be passivated by nitrogen, which suppresses further oxygen diffusion and the formation of the oxygen vacancies. The in situ NH<sub>3</sub> plasma treatment is useful for high performance MOS devices with good reliability.

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### 1. Introduction

High-*k* gate dielectrics such as HfO<sub>2</sub>, ZrO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> have been proposed to reduce the gate leakage current in MOS devices with a low equivalent oxide thickness (EOT) value. Among these high-*k* materials, HfO<sub>2</sub> has a high dielectric constant, large band gap and is compatible with complementary metal oxide semiconductor (CMOS) processes. As EOT value below 0.8 nm, the dielectric constant (*k*) value of 18–20 for HfO<sub>2</sub> with amorphous or monoclinic structure is not enough for the MOS devices [1]. To further increase the *k* value of Hf-based dielectric without the degradation of leakage or reliability, the tetragonal and cubic phase HfO<sub>2</sub> are good candidates [2]. It was reported that the tetragonal phase of ALD-formed HfO<sub>2</sub> is obtained by post-deposition annealing in NH<sub>3</sub> or N<sub>2</sub> ambient, and nitrogen incorporation into the high-*k* gate dielectrics can also reduce crystallization and leakage current [3]. Besides, the density of interface traps (Dit) and bias-temperature-instability (BTI) reliability of high-*k* gate dielectrics are still issues. The electrical characteristics are affected by nitrogen incorporation, which is clearly regarded as the critical factor when nitrogen atoms diffuse to the Si interface and form Si–N bonds during the deposition of nitrided high-*k* dielectrics or nitridation processes [4]. In this work, a tetragonal phase HfO<sub>2</sub> dielectric in MOS devices was obtained by in situ NH<sub>3</sub> and N<sub>2</sub> plasma treatments during ALD processes. The electrical characteristics of high-*k* gated MOS devices with various in situ plasma treatments

were also investigated. The EOT value and leakage current of MOS device can be significantly reduced with NH<sub>3</sub> plasma treated high-*k* dielectrics. The reliability is obviously improved as well.

### 2. Experiment

A chemical oxide interfacial layer (IL) was formed by H<sub>2</sub>O<sub>2</sub> solution at 75 °C on (100)-oriented 6-inch p-type Si wafer with resistivity of 15–25 Ω-cm. A 3 nm thick HfO<sub>2</sub> was deposited by an atomic layer deposition (ALD), and the precursors are Hf(NCH<sub>3</sub>C<sub>2</sub>H<sub>5</sub>)<sub>4</sub> (TE-MAH) and H<sub>2</sub>O. Simultaneously, in situ NH<sub>3</sub> or N<sub>2</sub> or H<sub>2</sub> remote plasma treatments were performed after every three deposition cycles in ALD. A brief cycling process of in situ remote plasma treatment is shown in Fig. 1. Then, a post deposition annealing (PDA) was performed at 650 °C in N<sub>2</sub> ambient for 30 s. Subsequently, a 50 nm thick TaN film was deposited by a sputtering to serve as the metal gate, and a post metallization annealing was carried out at 600 °C in N<sub>2</sub> ambient for 30 s. After a 300 nm Al deposition, the pattern was then defined by helicon-wave plasma etching. A 500 nm thick Al film was deposited on the backside of all samples. Finally, a sintering was conducted in a N<sub>2</sub>/H<sub>2</sub> ambient at 400 °C for 30 min.

The electrical measurement was performed on MOS capacitors with a gate area of 100 × 100 μm<sup>2</sup> in this work. The HP4145B instrument was used to measure the current–voltage (*I*–*V*) characteristics, and the high-frequency capacitance–voltage (*C*–*V*) measurements were carried out at 100 kHz by using HP4284A. The equivalent oxide thickness (EOT) and flat-band voltage (*V*<sub>fb</sub>) were extracted from the simulation program considering quantum effect

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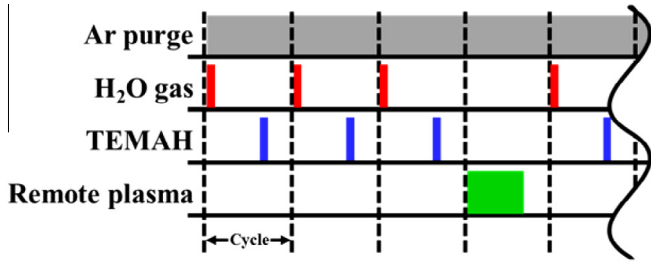


Fig. 1. Process of in situ remote plasma treatment in ALD.

[5]. Besides, stress-induced leakage current (SILC) and stress-induced Vfb shift were measured to investigate the reliability of MOS capacitors.

### 3. Results and discussion

Fig. 2 shows the X-ray diffraction (XRD) spectra at the diffraction angle ( $2\theta$ ) for (a) 20–40° and (b) 40–60° and a PDA at 650 °C of samples with different in situ plasma treatments. Since there is no obvious peak for the sample with H<sub>2</sub> plasma treatment, its data are not shown. As shown in Fig. 2(a), the angles of tetragonal and monoclinic HfO<sub>2</sub> are about 30.7 and 28.3°, respectively [6,7]. It is found that the diffraction angles for samples with in situ NH<sub>3</sub>

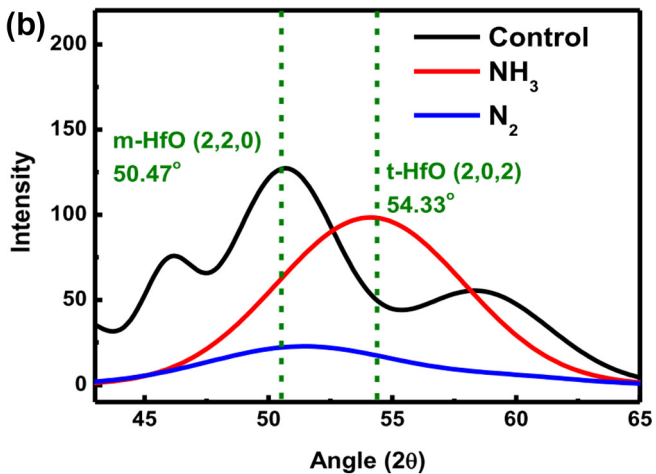
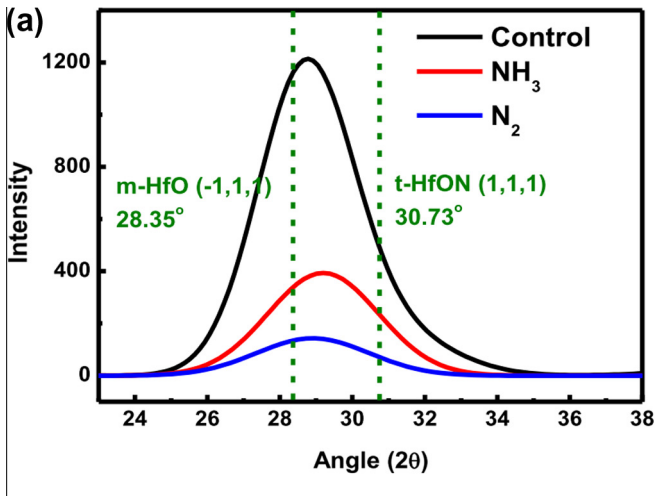


Fig. 2. XRD spectra of HfO<sub>2</sub> films with different plasma treatments at  $2\theta$  (a) for 20–40° (b) for 40–60°.

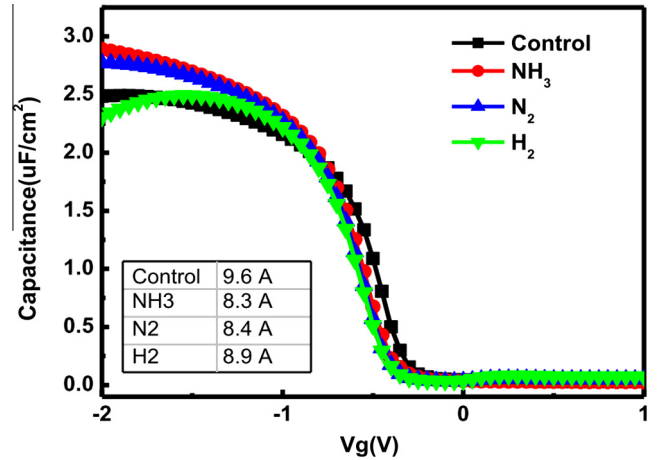


Fig. 3. C–V curves for MOS devices with different plasma treatments.

and N<sub>2</sub> plasma treatments are close to that of tetragonal HfO<sub>2</sub> (t-HfO<sub>2</sub>). It indicates that the crystallization phase of HfO<sub>2</sub> is composed of both t-HfO<sub>2</sub> and m-HfO<sub>2</sub>, and more t-HfO<sub>2</sub> could be formed by in situ NH<sub>3</sub> and N<sub>2</sub> plasma treatments. For the sample with NH<sub>3</sub> plasma treatment, an obvious tetragonal peak can also be observed at about 54.33° as shown in Fig. 2(b) [6,8], suggesting more t-HfO<sub>2</sub> is obtained by NH<sub>3</sub> plasma than N<sub>2</sub> one.

Fig. 3 shows the curves of capacitance versus applied voltage (C–V) for samples with different in situ plasma treatments. It is observed that the sample with in situ NH<sub>3</sub> plasma treatment shows a higher capacitance than the others. When the EOT data are correlated with XRD peaks in Fig. 2, the reduction on EOT can be attributed to the t-HfO<sub>2</sub> formation. More composition of t-HfO<sub>2</sub> in crystal HfO<sub>2</sub> can be obtained for the sample with in situ NH<sub>3</sub> plasma treatment in ALD. The  $k$  values of high- $k$  dielectrics for samples with in situ NH<sub>3</sub> and N<sub>2</sub> plasma treatments estimated with IL having a fixed  $k$  value of 6 are about 29.4 and 28.5, respectively. However, the  $k$  value of the sample without any in situ plasma treatment is about 21.6. The  $k$  value of HfO<sub>2</sub> with more t-HfO<sub>2</sub> by in situ plasma treatment is indeed increased about 24%. The data of leakage current ( $J_g$ ) versus EOT for the all samples are shown in Fig. 4. The EOT can be further scaled without increasing leakage current by in situ NH<sub>3</sub> plasma treatment, which is much below the dashed trend line of the sample without one.

Fig. 5 shows X-ray photoelectron spectroscopy (XPS) of (a) Si 2p and (b) N 1s for samples with different in situ plasma treatments.

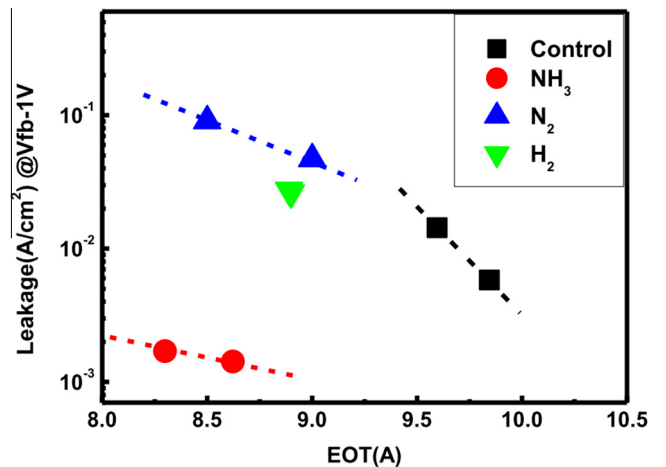


Fig. 4.  $J_g$  vs. EOT for MOS devices with different plasma treatments.

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