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Characterization of HfO_xN_y thin film formation by *in-situ* plasma enhanced atomic layer deposition using NH_3 and N_2 plasmas

Young Bok Lee [1], Il-Kwon Oh [1], Edward Namkyu Cho, Pyung Moon, Hyungjun Kim, Ilgu Yun *

Department of Electrical and Electronic Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

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ABSTRACT

The structural and electrical characteristics of *in-situ* nitrogen-incorporated plasma enhanced atomic layer deposition (PE-ALD) HfO_xN_y thin films using NH_3 and N_2 plasmas as reactants were comparatively studied. The HfO_xN_y test structures prepared using NH_3 and N_2 plasmas were analyzed by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), and high resolution transmission electron microscopy (HR-TEM) to investigate the chemical composition, crystallinity, and cross-sectional layers including the interfacial layer, respectively. By utilizing NH_3 and N_2 plasmas, the nitrogen-incorporated HfO_xN_y thin films fabricated by *in-situ* PE-ALD showed a high dielectric constant and thermal stability, which suppresses the interfacial layer and increases the crystallization temperature. The high leakage current densities of the HfO_xN_y thin film test structures fabricated using NH_3 and N_2 plasmas caused by lowering the energy bandgap and band offset are related to the Hf—N bond ratio and dielectric constant.

1. Introduction

HfO_2 dielectric thin films have been considered to be one of the most promising high-k materials to replace conventional SiO_2 thin films in complementary metal-oxide-semiconductor (CMOS) technology applications due to their high dielectric constant resulting in a decrease in the equivalent oxide thickness (EOT) [1–4]. However, problems associated with the technology include formation of an interfacial layer with a low dielectric constant, low crystallization temperature, and the threshold voltage shift caused by the fixed charge [5–8]. Thus, incorporation of nitrogen into HfO_2 films has been researched to supplement the disadvantages of HfO_2 dielectric thin films. It was reported that the incorporation of nitrogen into HfO_2 films is useful to increase the crystallization temperature, can inhibit the formation of the interfacial layer, and improve the electrical properties of devices [9–11]. However, the incorporation of nitrogen into hafnium-based thin films is generally carried out by high temperature annealing or plasma nitridation in nitrogen ambient. Thus, these methods require a high temperature and multiple steps [12,13]. Furthermore, it is difficult to control the nitrogen profile with atomic accuracy. The degradation of electrical characteristics can be induced by incorporating nitrogen at the interface between dielectric thin films and the Si substrate [14,15]. Generally, there are several nitridation methods including chemical vapor deposition (CVD) [16], re-oxidation of HfN films formed by physical vapor deposition (PVD) [17], and thermal annealing with NH_3 [18] for HfO_xN_y thin films that have a high dielectric constant and thermal stability [9–11].

In this study, nitrogen-incorporated HfO_xN_y thin films prepared by using *in-situ* plasma enhanced atomic deposition (PE-ALD) at a low processing temperature were investigated. The *in-situ* PE-ALD process can uniformly control a higher nitrogen profile with atomic accuracy. In addition, the process does not require a high temperature or multiple steps. The structural and electrical characteristics of the *in-situ* PE-ALD HfO_xN_y thin films fabricated using NH_3 and N_2 plasmas as reactants were also evaluated.

2. Experiments

The p-type Si(1 0 0) substrates were pre-cleaned at 80 °C for 10 min in a standard Radio Corporation of America (RCA) solution [1:1:5 (v/v/v) $NH_4OH/H_2O_2/H_2O$]. The HfO_xN_y films were subsequently deposited by PE-ALD using TDMAH [tetrakis(dimethylamino)hafnium] as the Hf precursor, which was evaporated at 50 °C in stainless-steel bubbler to obtain sufficient vapor pressure at a temperature of 250 °C. Two types of counter reactants were used for comparison: NH_3 and N_2 plasmas. ALD

* Corresponding author. Tel.: +82 2 2123 4619; fax: +82 2 313 2879.
E-mail address: iyun@yonsei.ac.kr (I. Yun).
[1] These authors contributed equally to this work.

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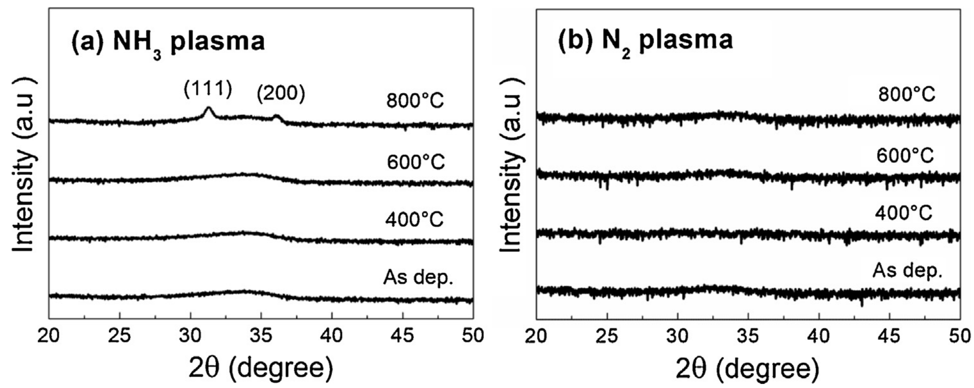

Fig. 1. XRD spectra of the as-deposited HfO_xN_y films on Si substrates fabricated using (a) NH_3 and (b) N_2 plasma at various annealing temperatures.

processes were developed based on optimized process conditions such as the precursor and the reactant exposure time, the purging time and the substrate temperature. The saturation conditions of PE-ALD HfO_xN_y using NH_3 plasma are 2 s of the precursor exposure time, 1 s of the reactant exposure time, and 5 s of the purging time at the temperature of 250 °C, which is the same process as PE-ALD HfO_xN_y using N_2 plasma except for 1.5 s of the reactant exposure time. After deposition, post-deposition annealing (PDA) was carried out in N_2 ambient at temperatures varying from 400 to 800 °C for 60 s by applying a rapid thermal annealing (RTA) process for the X-ray diffraction (XRD) analysis. The chemical bonding structures of the HfO_xN_y films were investigated by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al *K*α X-ray source. High resolution transmission electron microscopy (HR-TEM) was additionally performed to investigate the thicknesses of the HfO_xN_y films and interfacial layers. For electrical characterization, MOS capacitor structures were fabricated and Ru was deposited on the HfO_xN_y films by magnetron sputtering through a shadow mask with an area of 3.14×10^{-4} cm^2 as a gate electrode in order to evaluate the electrical properties. The capacitance–voltage (*C*–*V*) measurements were performed using a Keithley 590 *C*–*V* analyzer at 1 MHz and the leakage current density–electric field (*J*–*E*) characteristics were calculated from the current–voltage (*I*–*V*) characteristics measured by a Keithley 236 source measure unit.

3. Results and discussion

Fig. 1 shows the XRD patterns of the HfO_xN_y films on Si substrates fabricated using NH_3 and N_2 plasmas at various annealing temperatures. As seen in Fig. 1(a), no diffraction peaks were observed up to an annealing temperature of 600 °C for the HfO_xN_y films using NH_3 plasma indicating that the film consists of an amorphous phase [19]. However, at a temperature of 800 °C, the film exhibits some weak crystallization peaks, which can be attributed to the monoclinic HfO_xN_y (1 1 1) and (2 0 0) planes [20,21]. As observed in Fig. 1(b), the amorphous structure of the HfO_xN_y film produced using N_2 plasma remains at annealing temperatures up to 800 °C, resulting in a higher crystallization temperature than that of the HfO_xN_y films fabricated using NH_3 plasma. Compared to the HfO_2 films, the crystallization temperature of the nitrogen-incorporated HfO_xN_y films using NH_3 and N_2 plasmas increased by over 200 °C, indicating enhanced thermal stability for crystallization [20].

In order to evaluate the nitrogen concentration and chemical bonding states of the HfO_xN_y films deposited by *in-situ* PE-ALD using NH_3 and N_2 plasmas, XPS depth profile measurements were performed. The shift of the whole spectrum was calibrated by the Si 2p peak at 99.3 eV.

Fig. 2 shows the depth profiles of the atomic concentrations of Hf, N, O, and Si in the films. A large amount of nitrogen is mainly distributed in the bulk films and not at the Si/HfO_xN_y interface. From the XPS depth profiles, the nitrogen concentrations are approximately 40 atomic conc. %, indicating that the *in-situ* PE-ALD process can uniformly control the higher nitrogen profile without requiring a high temperature or multiple steps. Thus, it is found from the results of the electrical characteristics shown in the below that the nitrogen-rich HfO_xN_y film shows high dielectric constant and electrically insulating characteristics.

As shown in Fig. 3(a), the XPS spectra of Hf 4f shows a doublet shape according to the spin-orbit splitting into Hf $4f_{5/2}$ and Hf $4f_{7/2}$ [13,22]. The fitted data of the Hf 4f peaks of the HfO_xN_y films appear

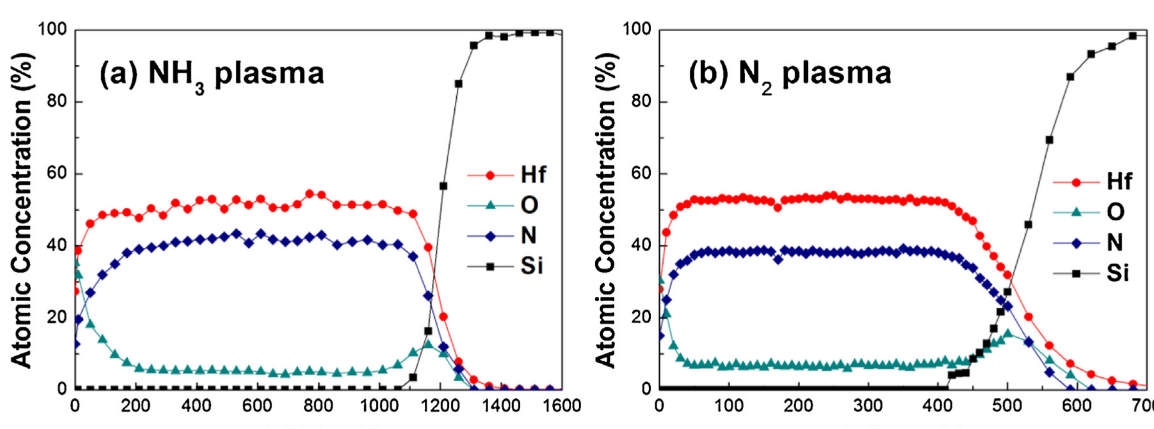

Fig. 2. XPS depth profiles of the atomic concentrations of Hf, N, O, and Si in the HfO_xN_y films produced by using (a) NH_3 and (b) N_2 plasma.