Characterization of HfO$_x$N$_y$ thin film formation by in-situ plasma enhanced atomic layer deposition using NH$_3$ and N$_2$ plasmas

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The structural and electrical characteristics of in-situ nitrogen-incorporated plasma enhanced atomic layer deposition (PE-ALD) HfO$_x$N$_y$ thin films using NH$_3$ and N$_2$ plasmas as reactants were comparatively studied. The HfO$_x$N$_y$ 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$_x$N$_y$ 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$_x$N$_y$ 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. © 2015 Elsevier B.V. All rights reserved.

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$_x$N$_y$ thin films that have a high dielectric constant and thermal stability [9–11].

In this study, nitrogen-incorporated HfO$_x$N$_y$ 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$_x$N$_y$ thin films fabricated using NH$_3$ and N$_2$ plasmas as reactants were also evaluated.

2. Experiments

The p-type Si(100) 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$_4$OH/H$_2$O$_2$/H$_2$O]. The HfO$_x$N$_y$ films were subsequently deposited by PE-ALD using TDMAC [tetraakis(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...
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\(_N\) 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\(_N\) 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\(_N\) films were investigated by X-ray photoelectron spectroscopy (XPS) with a monochromatic Al K\(_{\alpha}\) X-ray. High resolution transmission electron microscopy (HR-TEM) was additionally performed to investigate the thicknesses of the HfO\(_N\) films and interfacial layers. For electrical characterization, MOS capacitor structures were fabricated and Ru was deposited on the HfO\(_N\) films by magnetron sputtering through a shadow mask with an area of 3.14 \times 10^{-4} \text{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\(_N\) 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\(_N\) 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\(_N\) (1 1 1) and (2 0 0) planes [20,21]. As observed in Fig. 1(b), the amorphous structure of the HfO\(_N\) 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\(_N\) films fabricated using NH\(_3\) plasma. Compared to the HfO\(_2\) films, the crystallization temperature of the nitrogen-incorporated HfO\(_N\) 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\(_N\) 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\(_N\) 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\(_N\) 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\(_N\) films appear
to consist of two sub-peaks corresponding to Hf–N and Hf–O–N bonds \[13,22\]. For the HfO\(_x\)N\(_y\) film produced using NH\(_3\) plasma, the Hf–N bond-related binding energy peaks corresponding to Hf 4f\(_{5/2}\) and Hf 4f\(_{7/2}\) are located at 16.8 and 14.8 eV, respectively. The Hf–N bond-related binding energy peaks for the HfO\(_x\)N\(_y\) film using N\(_2\) plasma corresponding to Hf 4f\(_{5/2}\) and Hf 4f\(_{7/2}\) are also located at 16.7 and 14.7 eV, respectively. It has been reported that the binding energies of Hf–O bonds for HfO\(_2\) films corresponding to Hf 4f\(_{5/2}\) and Hf 4f\(_{7/2}\) are located at ~19.2 and 17.5 eV \[22,25\], respectively.

The shift to lower binding energies compared to HfO\(_2\) films and the different shape of the Hf 4f spectral peaks observed for the HfO\(_x\)N\(_y\) films indicate the presence of Hf–N \[22,25\]. Fig. 3(b) shows the XPS spectra of the N 1s peaks for the HfO\(_x\)N\(_y\) films produced using NH\(_3\) and N\(_2\) plasmas. The binding energies for the Hf–N bonds of the HfO\(_x\)N\(_y\) films made using NH\(_3\) and N\(_2\) plasmas corresponding to N 1s are located at 396.4 and 396.0 eV, respectively, which are in good agreement with the reported values for HfO\(_x\)N\(_y\) films \[22,25\]. The deconvolution results suggest that the shapes of the Hf 4f and N 1s peaks compared to the HfO\(_2\) films made using NH\(_3\) and N\(_2\) plasmas are slightly distorted due to a small difference of the nitrogen concentration. The relative Hf–N bond ratios for the Hf 4f state level are 49.4 and 44.8% for the HfO\(_x\)N\(_y\) films fabricated using NH\(_3\) and N\(_2\) plasmas, respectively. Since the ionization rates for N\(_2\) plasma is smaller than those of NH\(_3\) plasma, it can be concluded that NH\(_3\) plasma process is more effective than the N\(_2\) plasma process.

Fig. 4 shows cross-sectional HR-TEM images of the as-deposited HfO\(_x\)N\(_y\) films produced using NH\(_3\) and N\(_2\) plasmas and HfO\(_2\) film using O\(_2\) plasma (as a reference) on the Si substrate to investigate the interfacial layer thickness and microstructure. The thickness of the interfacial layer (IL) for the HfO\(_x\)N\(_y\) film generated using NH\(_3\) plasma is about 1.3 nm whereas the IL thickness for the HfO\(_2\) film produced using N\(_2\) plasma is about 1.7 nm. The thicknesses of the IL for the HfO\(_x\)N\(_y\) films fabricated using NH\(_3\) and N\(_2\) plasmas are reduced compared to separately prepared Al\(_2\)O\(_3\) (4.7 nm) and HfO\(_2\) (2.6 nm) films because nitrogen incorporation suppresses oxygen diffusion and inhibits interfacial reactions with the Si substrate \[11\].

The microstructures of the as-grown HfO\(_x\)N\(_y\) films produced using NH\(_3\) and N\(_2\) plasmas were confirmed to be an amorphous phase, which are well matched with the results of the XRD analyses.

A Ru/HfO\(_x\)N\(_y\)/p-Si(1 0 0) MOS capacitor test structure was fabricated to evaluate the electrical characteristics of the in-situ PE-ALD HfO\(_x\)N\(_y\) thin films grown using NH\(_3\) and N\(_2\) plasmas. Fig. 5(a) shows the C–V curves of the HfO\(_x\)N\(_y\) MOS capacitor test structures using NH\(_3\) and N\(_2\) plasmas, which were normalized to calibrate for the thickness difference. The dielectric constants of the HfO\(_x\)N\(_y\) films fabricated using NH\(_3\) and N\(_2\) plasmas extracted from the 1 MHz C–V measurements are 34.2 and 25.8, respectively. The EOT of the HfO\(_x\)N\(_y\) films produced using NH\(_3\) and N\(_2\) plasmas are lower than that of HfO\(_2\) due to the higher dielectric constant. It was reported that the higher nitrogen concentration in the deposited HfO\(_x\)N\(_y\) films results in the higher dielectric constant \[9\]. The C–V hysteresis of the HfO\(_x\)N\(_y\) MOS capacitor test structures containing films produced using NH\(_3\) and N\(_2\) plasmas were extracted using conductance method and they were determined to be 14.4 \(\times\) 10\(^{11}\) and 9.65 \(\times\) 10\(^{11}\) (cm\(^2\)) eV, respectively. The differences of the C–V hysteresis and \(D_{it}\) values between the NH\(_3\) and N\(_2\) plasma processed HfO\(_x\)N\(_y\) films are related to the incorporated nitrogen concentration difference in the bulk of the HfO\(_x\)N\(_y\) films and the interface with the Si substrate \[21\]. The results indicates that the nitrogen will stabilize the incomplete bonding in the HfO\(_x\)N\(_y\) interface layer fabricated using N\(_2\) plasma even it contains slightly more the trapped oxide charges.

Fig. 5(b) shows the \(J–E\) characteristics of the HfO\(_x\)N\(_y\) MOS capacitor test structures containing films produced using NH\(_3\) and N\(_2\) plasmas. The leakage current densities of the test structures with films fabricated using NH\(_3\) and N\(_2\) plasmas at −1 MV/cm were 4.87 \(\times\) 10\(^{−3}\) and 1.13 \(\times\) 10\(^{−3}\) A/cm\(^2\), respectively. These high leakage current densities of both the NH\(_3\) and N\(_2\) plasma-processed HfO\(_x\)N\(_y\) films can be primarily attributed to the decrease of the energy bandgap and band offset as a result of the high nitrogen.
incorporation in the HfO$_x$N$_y$ films [22,23]. The difference of leakage current densities for the NH$_3$ and N$_2$ plasma processed HfO$_x$N$_y$ films are correlated with the Hf–N bond ratio for the Hf 4f state level, as demonstrated in the XPS and dielectric constant results. The electrical properties of the HfO$_x$N$_y$ MOS capacitor test structure containing films fabricated using NH$_3$ and N$_2$ plasmas are summarized and compared in Table 1.

However, the results shown in the above exhibit a different trend with the previous report [11]. Previous report presented remote plasma nitridation (RPN) of HfO$_x$N$_y$ film, which is the initial HfO$_2$ film formation followed by ex-situ RPN process using N$_2$ and NH$_3$ plasmas [11]. In our work, the in-situ HfO$_x$N$_y$ film formation using N$_2$ and NH$_3$ plasmas was presented, which is a different process for film formation. As a result, the nitrogen concentrations are different, i.e. the N concentration of previous result is in the range of 10–15%, which is much smaller than that of our work (~40%).

The originality of our work is the in-situ HfO$_x$N$_y$ film formation using N$_2$ and NH$_3$ plasmas to obtain high N concentration. Since the previous report explained that for N$_2$–RPN case, the nitrogen can suppress the oxygen diffusion resulting in the reduction of the interface layer (IL) of 1.0 nm whereas, for NH$_3$–RPN case, by the reaction of NH$_3$ and NH with Si and HfO$_x$N$_y$, the Hf-silicate of HSfO$_x$N$_y$ layer was formed in the interface layer resulting in the increase of IL (~1.9 nm). In addition, EOT of NH$_3$–RPN (1.45 nm) is smaller than EOT of N$_2$–RPN (1.75 nm) and the capacitance of NH$_3$–RPN is larger than that of N$_2$–RPN. However, the leakage current of NH$_3$–RPN is better than that of N$_2$–RPN, which was explained by the increase of interface layer. In our work, the interface layer

![Figure 4](image1.png)

**Fig. 4.** Cross-sectional HR-TEM images of the Si/HfO$_x$N$_y$ films produced using (a) NH$_3$ and (b) N$_2$ plasma and (c) HfO$_2$ film using O$_2$ plasma (as a reference).

![Figure 5](image2.png)

**Fig. 5.** (a) C–V and (b) J–E characteristics of the Ru/HfO$_x$N$_y$/p-Si(100) containing films produced using NH$_3$ and N$_2$ plasmas.

<table>
<thead>
<tr>
<th>Plasma type</th>
<th>Dielectric constant</th>
<th>$D_n$ (cm$^{-2}$ eV$^{-1}$)</th>
<th>Hysteresis (mV)</th>
<th>Leakage current density at $-1$ MV/cm (A/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$ plasma</td>
<td>34.2</td>
<td>$1.44 \times 10^{11}$</td>
<td>200</td>
<td>$4.87 \times 10^{-5}$</td>
</tr>
<tr>
<td>N$_2$ plasma</td>
<td>25.8</td>
<td>$9.7 \times 10^{11}$</td>
<td>300</td>
<td>$1.13 \times 10^{-5}$</td>
</tr>
</tbody>
</table>
of N₂-plasma (1.7 nm) is larger than that of NH₃ plasma (1.3 nm), which shows a different result with previous report [11].

For the C–V characteristics in our work, higher k values compared with the previous report [11] were obtained. Although they did not mention the dielectric constant of HfO₂:N films in the report, all of calculated values from accumulation capacitance are below 15, which are much smaller than our results (larger than 25). In addition, the C–V hump effect was not observed in our work, indicating that the HfO₂:N films has less damage for the interface layer compared with the previous report [11]. For the I–V characteristics, N can be replaced with the replacement of oxygen or vacancy of oxygen (Vo), which can remove the trap state resulting in the reduction of leakage current by hopping mechanism. In our work, the leakage current of the film using N₂ plasma is smaller than that of NH₃ plasma due to the larger Hf–O–N ratio verified by XPS. Since HfO₂:N films show insulator characteristic, the film using N₂ plasma is more effective to form Hf–O–N bonding than that of NH₃ plasma.

Based on the previous studies for crystallization of HfO₂:N film formation, the crystallization processes for N₂ and NH₃ plasmas were different depending on the nitrogen and oxygen concentrations. Contrary to the previous work, the nitrogen concentration of our work is much larger (~40%) than those of previous studies (10–15%).

It was reported that when the N concentration of HfO₂:N film was increased, the crystallization of HfO₂:N was suppressed [24]. It was also reported that the crystallization temperatures of HfO₂ and HfN films are relatively higher than that of HfO₂:N film [25]. When the O concentration is increased and N concentration is decreased in HfN film, the crystallization of the film is also suppressed [26]. In our work, the deposited HfO₂:N film contains high N concentration around 40% and small O concentration around 10%. In other words, the deposited film in our work is HfN film doped with oxygen, rather than HfO₂ film doped with nitrogen. Thus, the crystallization is suppressed as N concentration is decreased. Since the film using N₂ plasma contains relatively smaller N concentration and larger O concentration than the film using NH₃ plasma (see Fig. 2), the crystallization of the film using N₂ plasma was more suppressed than that of NH₃ plasma, resulting in lower leakage current and larger hysteresis.

In addition, from the XPS results shown in Fig. 3, the area of de-convoluted peaks are different and the area of Hf–O–N peak for N₂ plasma is larger than that for NH₃ plasma. It is explained that the film using N₂ plasma has larger nitrogen ratio bonded with Hf–O than that using NH₃ plasma, which shows deficiency of the phase separation. For the case of NH₃ plasma, even though N concentration is relatively larger than that of N₂ plasma, the bonding is dominantly formed with Hf–N bonding indicating that the phase separation is easier than the case of N₂ plasma. This indicates another evidence of the suppression of the crystallization of the film.

Finally, it is observed that the growth rate of the film using NH₃ plasma is much larger than that using N₂ plasma. This is due to the hydrogen ion and radical separated from NH₃ plasma, which increases the plasma density. As the plasma density is increased, more numbers of the radicals and ions chemically react on the film surface resulting in the increase of growth rate. In general, for the film deposition using N₂ plasma, H₂ plasma is also utilized for the deposition process to promote the film growth characteristics since H radical can promote Hf–N bonding by the reduction of precursor ligand easily [27]. In our work, since the N₂ plasma is solely utilized for the comparison of the case for using NH₃ plasma, the growth rate using N₂ plasma is lower than that of using NH₃ plasma.

Therefore, it can be concluded that N₂ plasma process is preferred for leakage current suppression and NH₃ plasma process is preferred for dielectric constant enhancement.

4. Conclusion

In this study, nitrogen-incorporated HfO₂:N thin films deposited using NH₃ and N₂ plasmas as a reactant during in-situ PE-ALD were structurally and electrically investigated. The XPS analyses showed that a large amount of nitrogen was mainly distributed in the bulk films and not at the Si/HfO₂:N interface. The interfacial layer thicknesses of the HfO₂:N films fabricated using NH₃ and N₂ plasmas were about 1.3 nm and 1.7 nm, respectively. As observed in the cross-sectional HR-TEM images, the nitrogen-incorporated HfO₂:N films had reduced IL thicknesses compared to Al₂O₃ and HfO₂. The electrical characteristics of the MOS capacitor test structures showed that the in-situ PE-ALD nitrogen-incorporated HfO₂:N thin films fabricated using NH₃ and N₂ plasmas exhibited high dielectric constants. In addition, the leakage current densities for both test structures caused by the lower energy bandgap and band offset were correlated with the Hf–N bond ratio and dielectric constant.

References


