Influence of Nitrogen/argon Flow Ratio on the Crystallization of Hafnium Oxynitride Films

Dae Han Choi, Jong In Choi, Hwan Jin Park, Joo Hyun Chae, and Daeil Kim[a]
School of Materials Science and Engineering, University of Ulsan,
Mugeo 2-dong, Nam-gu, Ulsan 680-749, Korea

[a]E-mail : dkim84@mail.ulsan.ac.kr

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Hafnium oxynitride films have been deposited onto a silicon substrate by means of radio frequency (RF) reactive sputtering using a hafnium dioxide (HfO_2) target with a variety of nitrogen/ argon (N_2/Ar) gas flow ratios. Auger electron spectroscopy (AES) results confirm that N_2 was successfully incorporated into the HfON films. An increase in the N_2/Ar gas flow ratio resulted in metal oxynitride formation. The films prepared with a N_2/Ar flow ratio of 20/20 sccm show (222), (530), and (611) directions of HfO_2N_2, and the (-111), (311) directions of HfO_2. From X-ray reflectometry measurements, it can be concluded that with N_2 incorporated into the HfON films, the film density increases. The density increases from 9.8 to 10.1 g/cm^3. XRR also reveals that the surface roughness is related to the N_2/Ar flow ratio.

Keywords : Hafnium oxynitride, Nitrogen, Reactive sputtering, XRD, XRR

1. INTRODUCTION

Several metal oxides have been considered as alternative gate dielectric materials to replace conventional SiO_2 in metal oxide semiconductor field effect transistors (MOSFET)[1]. Among these materials, hafnium dioxide (HfO_2) is recommended as one of the superior gate dielectric materials, due to its high dielectric constant, high density, and wide band gap[2]. However, chemical reaction between the Si substrate and the reactive oxygen gas leads to poor electrical properties of high dielectric constant thin films. Thus, several reports have appeared concerning a nitrogen incorporation technique that simultaneously suppresses the penetration of impurities and improves electrical reliability of the films[1,3,4].

Many deposition techniques have been used to deposit Hafnium oxynitride (HfON) films such as plasma enhanced chemical vapor deposition[3], metal organic chemical vapor deposition[5], and reactive magnetron sputtering[6]. For the case of reactive magnetron sputtering, the focus has been to optimize the reactive sputtering of Hf metal target with a mixture of N_2/O_2/Ar ambient[6,7].

The discussion in this paper describes the HfON films that were deposited by radio frequency (RF) magnetron sputtering utilizing an HfO_2 target (4N) with a constant Ar gas flow rate of 20 sccm and variable N_2 flow ratio conditions. After deposition, the effect of the N_2/Ar flow ratio on the depth profile, surface roughness, crystalline phase, surface morphology, and optical transmittance of the films were evaluated using Auger electron spectroscopy (AES), X-ray reflectometry (XRR), X-ray diffraction (XRD), scanning electron microscope (SEM), and a UV- Visible spectrometer, respectively.

2. EXPERIMENTAL DETAILS

The HfON films were deposited with a variety of Ar/N_2 gas flow rate ratios using the radio frequency (RF) magnetron sputtering system. The 100 mm diameter Si (100) wafers were pre-cleaned ultrasonically in acetone and alcohol. Prior to deposition the system was evacuated to 5×10^{-5} Pa at which point a gas mixture of Ar and N_2 gases were injected into the chamber. The Ar gas flow rate was kept constant at 20 sccm, while the N_2 gas flow rate was varied from 0 to 20 sccm. The typical target thickness is 6 mm and the diameter is 150 mm.

During deposition, the substrate temperature and the pressure of work chamber were kept to 60 °C and 8×10^{-2} Pa, respectively. The distance between the HfO_2 target and Si substrate was 70 mm. The substrate was rotated at 4 rpm for the purpose of creating a deposited film with uniform thickness. The deposition power was kept at 2.5 W/cm^2. The target was sputter cleaned in a pure Ar atmosphere for 10 min and the deposition rate was 15 nm/min. The thickness is controlled using the deposition time. All the films are kept to a thickness of about 100 nm.

The film's crystal phase was examined by XRD using Cu Kα radiation at 40 KV and 150 mA. The optical transmittance was observed by a UV-Visible spectrophotometer (Lambda 12). The density of the films, thickness and surface roughness were observed by XRR measurements. The density, thickness and surface roughness of the films were derived by performing theoretical simulations using the simulation software package WINGIXA, which is supplied by Phillips. In this software, the thickness of the films is determined from the period of the intensity oscillations and the density is determined from the total reflection edge. The decay of the oscillation amplitude and overall intensity is related to the surface roughness of the films.

After deposition, Auger electron spectroscopy (AES) depth profile measurements were also conducted, in order to observe the presence of nitrogen in the film. AES were performed on a VG Scientific spectrometer. The primary beam energy was 10 keV. The step energy and Ar ion energy were 1 eV and 3 keV, respectively.

3. RESULTS AND DISCUSSION

Figures 1 and 2 show AES depth profiles of the HfON films deposited with a N_2/Ar flow ratio of 10/20 and 20/20 sccm, respectively. AES results confirm that nitrogen was successfully incorporated into the film. Unfortunately, the VG firm software does not contain data for Hf sensitivity factors, which is necessary to calculate the composition of the films. However, a comparison of data for different HfON films provides a change in the relative concentrations. The films deposited with a N_2/Ar flow ratio of 5/20 sccm show a relative composition of O:Hf:N = 0.67:0.27 : 0.06, while the films deposited with a N_2/Ar flow ratio of 20/20 sccm show a relative composition of O:Hf:N = 0.6: 0.25:0.15, respectively.

Figure 3 shows XRR results obtained from the films deposited with a N_2/Ar flow ratio of 20/20 sccm and Figure 4 shows the density of the films prepared for different N_2 /Ar flow ratios. As the N_2/Ar flow ratio increases from 5/20 to 20/20 sccm, the density of the film increases from 9.8 to 10.1 g/cm^3. The increase in density of the films has been observed by S. Venkataraj et al., with an increase of N_2 flow rates[6]. In this study, the effect of the N_2/Ar flow ratio on the effective dielectric constant of the films was not investigated directly.

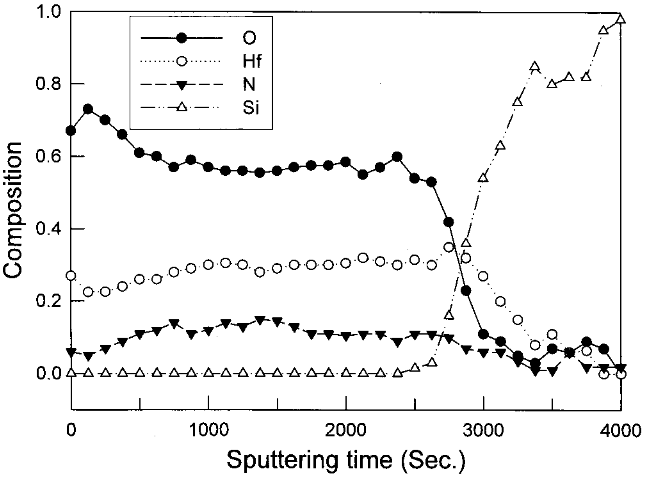

Fig. 1. AES depth profiles of HfON films deposited on the Si with a N_2 / Ar flow ratio of 10/20 sccm.

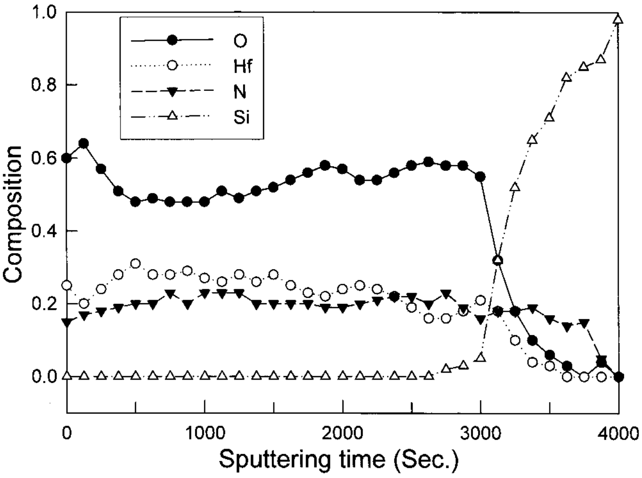

Fig. 2. AES depth profiles of HfON films deposited on the Si with a N_2 / Ar gas flow ratio of 20/20 sccm.

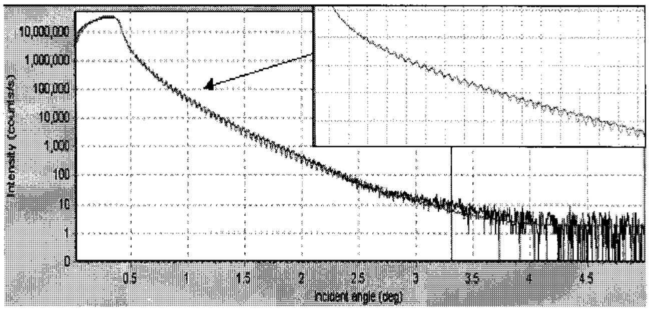

Fig. 3. XRR spectra obtained from HfON films deposited with a N_2 / Ar flow ratio of 20/20 sccm.

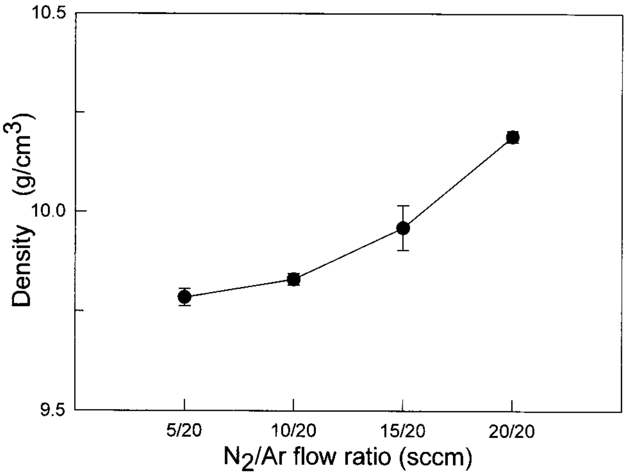

Fig. 4. The density of HfON films deposited with various N_2 / Ar flow ratios.

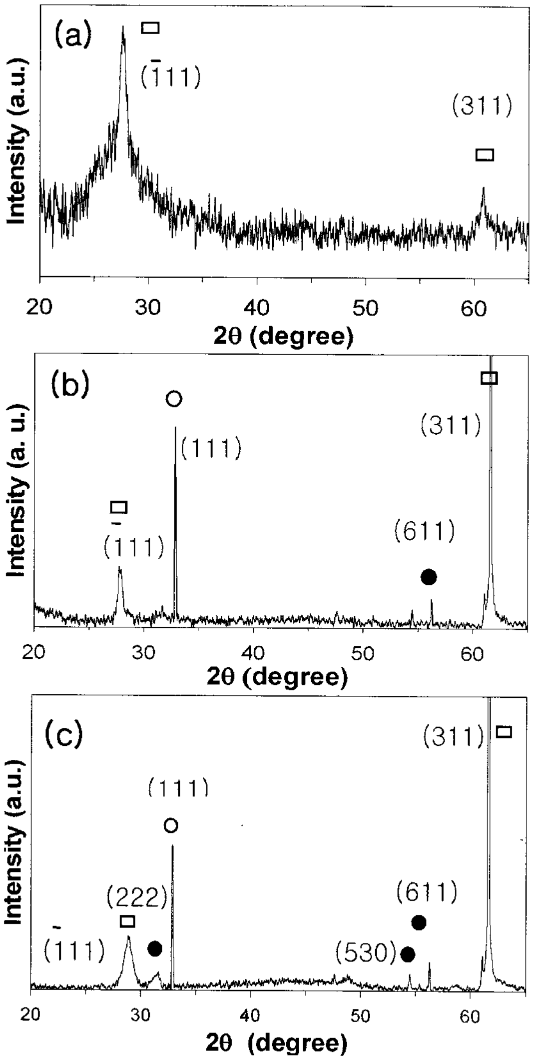

Fig. 5. XRD spectra of HfON films deposited with various N_2/Ar flow ratios(□:HfO_2, ○:HfN, ●: Hf_2ON_2).

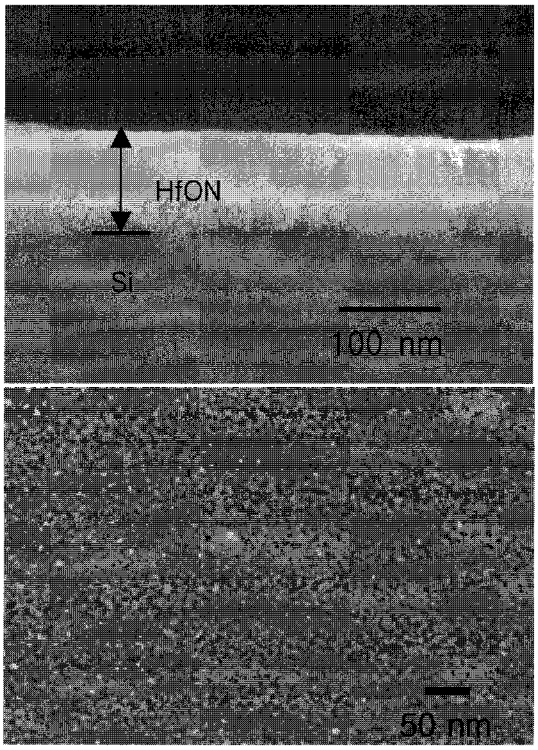

Fig. 6. SEM images of HfON films deposited with a N_2/Ar flow ratio of 20/20 sccm. (a) Cross-sectional image, (b) Surface image.

Thin film XRD, utilizing a glancing angle of 3 °, was used to investigate the effect of N_2/Ar flow ratio on the crystalline structure of HfON films. Figure 5 shows XRD spectra of the films deposited with a N_2/Ar gas flow ratio of 0/20 (a), 10/20 (b) and 20/20 sccm (c), respectively.

Although some papers report that HfO_2 films prepared by reactive DC magnetron sputtering is amorphous, all the films deposited in this study with RF magnetron sputtering are polycrystalline in regardless of the N_2 /Ar flow ratio.

The films deposited with a pure Ar gas atmosphere (a) were polycrystalline with an orientation in the (-111) and (311) directions, which correspond to the HfO_2 films. The films deposited with a N_2 /Ar flow ratio of 20/20 resulted in the metal oxynitride formation. The films prepared with a N_2/Ar flow ratio of 20/20 sccm, as shown in Fig. 5(c), reveal the (222), (530), and (611) directions that correspond to HfO_2N_2 and the (-111), (311) directions of HfO_2, simultaneously.

Figure 6 shows SEM images of a HfON film, while Fig. 7 reveals the surface RMS roughness obtained from XRR measurements for the same film. The surface rms roughness of the films was decreased by increasing the N_2 flow rate. Similar results are reported by M. Liu et al.[4].

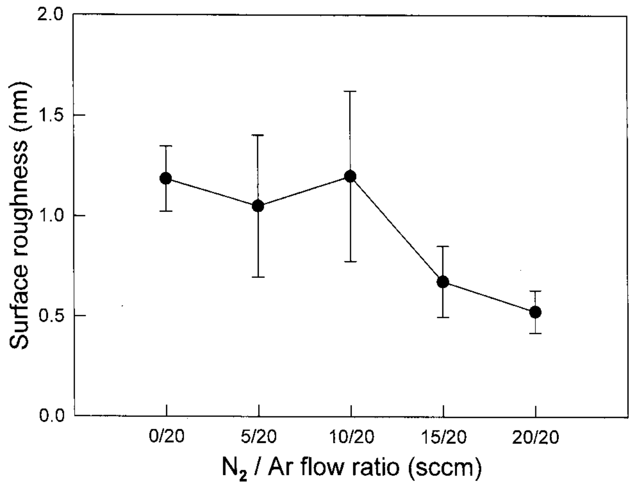

Fig. 7. Surface RMS roughness of HfON films deposited with various N_2/Ar flow ratios.

The highest surface roughness of 1.04 nm was obtained from the film deposited with a N_2/Ar gas flow ratio of 0/20 sccm, while the lowest surface roughness of 0.45 nm was obtained from the film prepared with a N_2/Ar gas flow ratio of 20/20 sccm.

4. CONCLUSION

Hafnium oxynitride (HfON) films were deposited onto a silicon (100) substrate by radio frequency (RF) reactive sputtering using an HfO_2 target utilizing different N_2/Ar flow ratios. The films deposited with a N_2/Ar flow ratio of 5/20 sccm and 20/20 sccm show a relative composition of O:Hf:N = 0.67:0.27:0.06 and 0.6:0.25:0.15, respectively. The films deposited with a pure Ar gas atmosphere were polycrystalline with an orientation in the (-111) and (311) directions that correspond to the HfO_2 films. The films prepared with a N_2/Ar flow ratio of 20/20 sccm show (222), (530), and (611) directions that correspond to HfO_2N_2 and (-111), (311) directions of HfO_2. XRR measurement results reveal that the surface roughness and the thin film density are also affected by the N_2/Ar flow ratio. A film deposited with a N_2/Ar flow ratio of 20/20 sccm provides a low surface roughness of 0.45 nm and a high density of 10.1 g/cm^3.

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