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Hafnium-nitride gate insulator formed by electron-cyclotron-resonance plasma sputtering

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Abstract: We investigated nitrogen-rich HfN insulator on p-Si(100) substrate to prevent to form an interface layer with low dielectric constant by electron-cyclotron-resonance plasma sputtering method for the first time. The nitrogen concentration in the deposited HfN film was confirmed as approximately Hf:N = 1:1.2. Furthermore, the electrical properties of Al/HfN/p-Si(100) gate stack were improved by hydrogen anneal compared to nitrogen (N_2) anneal. The EOT of 0.64 nm with low leakage current of 6.2×10^{-4} A/cm^2 (@ V_{FB} -1 V) was obtained. The results suggest that the effect of hydrogen anneal attributed to improve the electrical properties of HfN gate dielectric.

Keywords: hafnium nitride, hydrogen anneal, ECR plasma sputtering
Classification: Electron devices, circuits, and systems

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1 Introduction

Recently, the scaling of equivalent oxide thickness (EOT) is a great challenge in the complementary metal oxide semiconductor (CMOS) technology. For a small EOT, the use of high-k gate dielectrics which have high dielectric constant than that of SiO_2 has been required such as HfO_2 or HfSiON [1, 2]. Furthermore, a low leakage current should be realized with a small EOT to obtain a good performance in metal-insulator-semiconductor field-effect

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transistors (MISFETs). Despite of the high dielectric constant, however, the formation of an interface layer (IL) with low dielectric constant between the high-k dielectric and silicon causes the increase of EOT. To realize 0.5 nm EOT or below, the IL formation should be suppressed. Therefore, the direct contact of high-k dielectric is required on Si substrate [3]. The direct contact high-k/Si interface has one monolayer of Si dioxide, and this structure contributes to obtaining a small EOT. On the other hand, most of the high-k dielectrics contain oxygen, which leads to the IL formation. Nitride dielectrics are the candidate materials as a gate dielectric instead of oxide dielectrics to suppress IL formation. However, the most of the nitride dielectrics reported so far, such as SiN or AlN, show low relative dielectric constants below 10 [4, 5]. For SiN gate dielectrics, numerous attempts have been reported, however, nitride/Si interface properties as well as high densities of bulk traps still are the issue to introduce in scaled CMOS [6]. To overcome this problem, X. Wang et al. reported that a modest anneal treatment in a steam furnace yields remarkable improvement of transconductance as well as its current drivability for devices containing nitrided while preserving their excellent reliability. They investigated the effect of anneal either in forming gas (FG, $N_2/5\%H_2$) or water vapor at 400°C for 30 min. The water vapor anneal treatment has been demonstrated to improve the properties and reliability of nitride/Si interface, while it does not have any noticeable effect on thermal oxide [7, 8]. In addition, the nitrogen-rich hafnium-nitride (HfN) has high dielectric constant such as 30 compared with other nitride dielectrics [9]. Generally, the stoichiometric hafnium mononitride is a metal. On the other hand, the nitrogen-rich HfN is reported to be a transparent insulator [10]. Kim et al. reported the atomic layer deposition of ultrathin insulating nitride layer such as Hf_3N_4 on p-Ge(100) substrate as an IL and it showed good electrical property [11].

In this paper, we investigated nitrogen-rich HfN insulator on p-Si(100) substrate to prevent to form an IL by electron-cyclotron-resonance (ECR) plasma sputtering method (MES-AFTY AFTEX-3400UD-12). ECR sputtering is a minimal-damage process and is expected to form ultra-thin films with an excellent quality [12]. The deposition of nitrogen-rich HfN does not require high-temperature process that can be detrimental to the device performance. We investigated the effect of FG anneal (FGA) on the electrical and chemical characteristics of nitrogen-rich HfN insulator directly formed on silicon.

2 Experimental procedure

P-Si(100) substrate was cleaned by sulfuric-peroxide mixture (SPM) and dilute-hydrofluoric (DHF). Then, 4 nm-thick nitrogen-rich HfN film was deposited by ECR plasma sputtering with a hafnium target at sputtering gas pressure of 0.19 Pa (Ar/N_2: 20/8 sccm) at room temperature. The back pressure of the chamber was 1×10^{-4} Pa. The resistivity of HfN thin films is changed by the N_2 flow ratio [13]. Therefore, we chose the N_2 ratio over

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28% to obtain amorphous thin film with dielectric property. Before the deposition, the Ar pre-sputtering for Hf-target surface cleaning was carried out for 10 min. The post deposition anneal (PDA) was carried out at 400°C for 30 min in FG (N_2/4.9%H_2) and nitrogen ambient utilizing rapid thermal anneal (RTA) system (ULVAC MILA-5000). The flow rate of gases was approximately 1 SLM. Finally, Al electrodes were deposited by evaporation. The fabricated Al/HfN/p-Si(100) MIS diodes were characterized by capacitance-voltage (C-V), current-voltage (J-V), and x-ray photoelectron spectroscopy (XPS) measurements. The EOTs were evaluated using exponential potential based quantum mechanical extraction (EPOQUE) method [14]. The Terman method was performed to evaluate the density of interface states (D_{it}) [15].

3 Results and discussion

In order to evaluate the nitrogen concentration of nitrogen-rich HfN, we first deposited 30 nm-thick HfN film with 400°C FGA for 30 min, and then the XPS depth profile measurements were performed. Figure 1 (a) shows the depth profile of atomic concentrations for Hf, Si, N, and O in the film. Since the number of photoelectron of an element is dependent upon the atomic concentration of that element in the sample, XPS is used to not only identify the elements but also quantify the chemical composition. The surface of film was oxidized in air and less than 5% oxygen occupied in the film. Near the interface between the HfN and p-Si(100), the concentration of oxygen was found to be increased. In the HfN film, the atomic concentration ratio

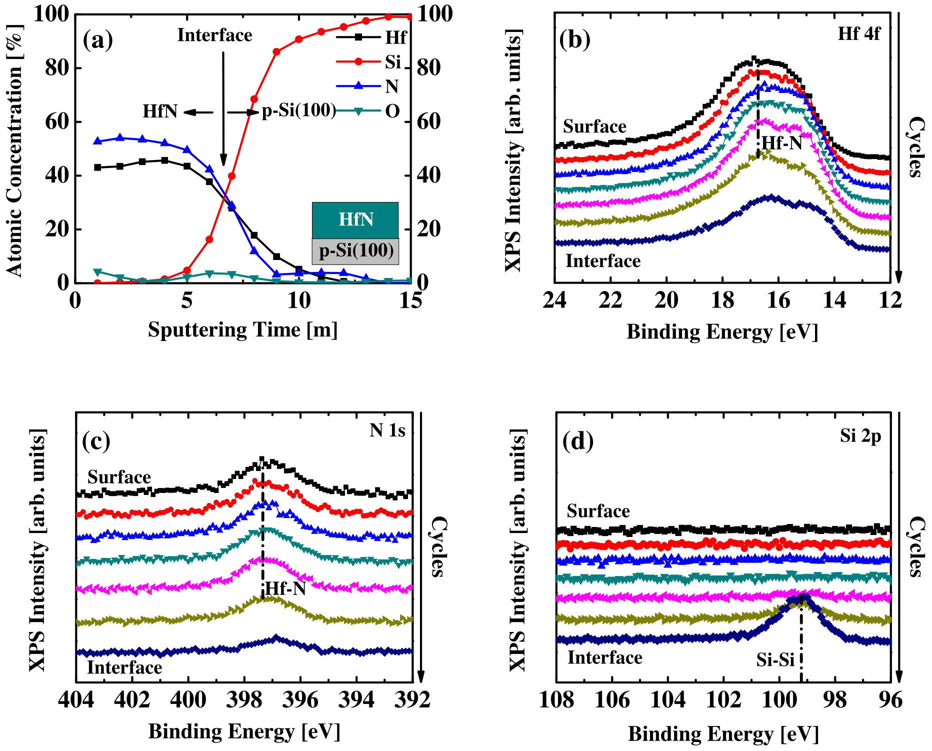

Fig. 1. (a) Depth profile of atomic concentrations for Hf, Si, N, and O in the deposited film, (b) Hf 4f, (c) N 1s, and (d) Si 2p XPS spectra.

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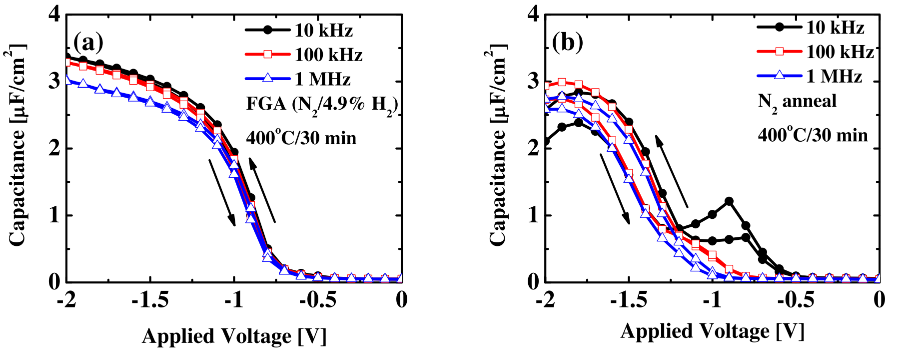

Fig. 2. C-V characteristics of Al/HfN/p-Si(100) for (a) FGA and (b) N_2 anneal.

of hafnium and nitrogen was confirmed as 1:1.2 by the XPS depth profile. Figures 1 (b) and 1 (c) show the XPS spectra of Hf 4f and N 1s obtained from the Ar^+ etching cycles in the film for the sample formed with FGA, respectively. As shown in Fig. 1 (b), the spectrum of Hf 4f shows a doublet shape due to spin-orbital splitting into the Hf $4f_{5/2}$ and Hf $4f_{7/2}$. The binding energy of Hf $4f_{7/2}$ centered at 15.1 eV was determined to correspond to the Hf-N bond in the nitrogen-rich HfN film, which was consistent with the reported values by Fix et al. for the nitrogen-rich HfN film [10]. The binding energy of 397.4 eV was attributed to the Hf-N bond in the nitrogen-rich HfN film as shown in Fig. 1 (c). Moreover, the XPS spectrum of Si 2p shows only Si-Si bonding at the interface in Fig. 1 (d). It means that there is no IL such as SiN or SiON. We confirmed that the deposited film became an insulator without IL.

Next, we fabricated Al/HfN/p-Si(100) MIS diodes to evaluate the electrical characteristics of HfN thin films. Figures 2 (a) and 2 (b) show C-V characteristics for the fabricated samples after PDA in FG and N_2 ambient, respectively. In case of N_2 anneal, the capacitance was much smaller than that of the FGA sample. Furthermore, the frequency dispersion and hysteresis were observed in the C-V curves. On the contrary, the small frequency dispersion and negligible hysteresis were obtained for the FGA sample. When depositing the nitrogen-rich HfN on Si, we used the sputtering system. It means that the sputtering damage should be considered during the deposition of the film. F. H. P. M. Habraken and P. Balk et al. reported that the active hydrogen diffuses through pores and reaches the Si-SiN interface and reacts as Si-H to form a silane bond [16, 17]. B. Swaroop further suggested that the effect of hydrogen was observed for the SiN-Si interface annealed in atomic hydrogen, which reduced the D_{it} [18]. Because the nitrogen-hydrogen gas mixture was used for anneal, the formation of Si-N-H bonding (or hydrogen passivation) would reduce the chance to generate interface states, which led to improve the electrical characteristics [19]. In case of the nitrogen-rich HfN/p-Si(100) gate stack, the same mechanism was considered. During the anneal process, hydrogen leads to form a bonding configuration such as Si-H. This bonding attributes to decrease the D_{it} in the HfN film. From the effect

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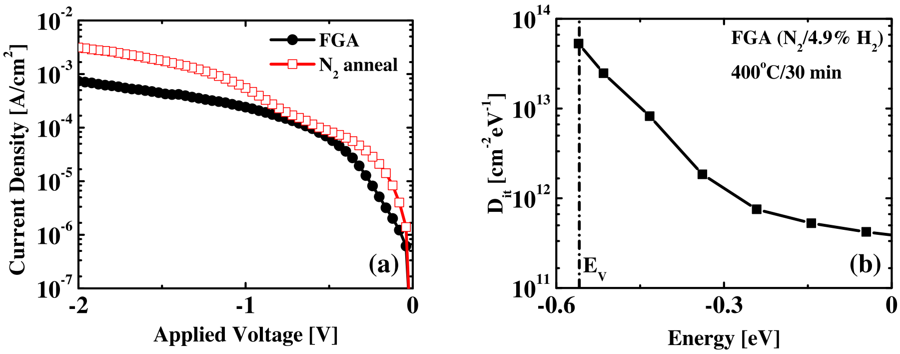

Fig. 3. (a) J-V and (b) D_{it} for the Al/HfN/p-Si(100) diodes.

of FGA, it is sure that the electrical property of HfN film was improved due to hydrogen effect compared to N_2 anneal as mentioned above.

Figure 3 (a) shows J-V characteristic of the fabricated MIS diodes after FGA and N_2 anneal. The leakage current of 3.7×10^{-3} A/cm^2 (@ V_{FB} -1 V) in case of N_2 anneal decreased to 6.2×10^{-4} A/cm^2 in case of FGA. D_{it} for the fabricated MIS diode after FGA was also evaluated by Terman method as shown in Fig. 3 (b). For 400°C FGA, the D_{it} was an order of magnitude lower than that of N_2 annealed sample. Therefore, it was suggested that the FGA causes diffusion of hydrogen at the interface of nitrogen-rich HfN film and p-Si(100), and then the electrical properties were improved by hydrogen anneal effect.

4 Conclusion

In conclusion, we investigated nitrogen-rich HfN insulator on p-Si(100) substrate to prevent to form an IL by ECR plasma sputtering method. It was found that FGA improved the electrical properties of Al/HfN/p-Si(100) gate stack. The EOT of 0.64 nm with low leakage current of 6.2×10^{-4} A/cm^2 (@ V_{FB} -1 V) was obtained.

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