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Selective Etching of HfO_2 by Using Inductively-Coupled Ar/C_4F_8 Plasmas and the Removal of Etch Residue on Si by Using an O_2 Plasma Treatment

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HfO_2 thin films were etched using an Ar/C_4F_8 inductively-coupled plasma (ICP) for high etch selectivity of HfO_2/Si and the fluorocarbon remaining on the silicon surface after the HfO_2 etching was removed by using an oxygen ICP and its effect was investigated. The etching of HfO_2 using Ar/C_4F_8 magnetically-enhanced ICP (MEICP) improved the etch selectivity of HfO_2/Si by more than three times, possibly due to the differences in the thicknesses of the fluorocarbon polymer layers formed on the surfaces of HfO_2 and Si. In addition, the oxygen ICP treatment after the HfO_2 thin film etching by using Ar/C_4F_8 ICP removed the polymer layer on the silicon surface effectively, so for the HfO_2-nMOSFET (n-type metal-oxied-semiconductor-field-effect-transistors) devices, an improvement in drain current of more than 60 % could be observed after the O_2 ICP treatment.

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I. INTRODUCTION

Hafnium oxide (HfO_2) is a material having a high dielectric constant (25 ∼ 30), a wide band gap, a low-leakage current and superior thermal stability [1–4]. Therefore, HfO_2 has been investigated as a gate dielectric material in metal-oxide-semiconductor field effect transistors (MOSFETs).

If HfO_2 is to be used in MOSFETs, the HfO_2 should be patterned by dry etching because with wet etching, it is difficult to completely remove compounds such as hafnium silicate ($HfSi_xO_y$) formed at the interface between HfO_2 and silicon during the deposition of HfO_2 on silicon. In addition, wet etching is incapable of etching high-resolution features [5, 6]. For the dry etching of HfO_2 as a gate material, not only is a precise etch rate required due to the low thickness of the material instead of high etch rate but also an extremely high etch selectivity over the underlayer material is required.

In general, for the dry etching of oxide materials, gas combinations having fluorocarbon gases such as CF_4, CHF_3 and C_4F_8 have been widely used to improve the etch selectivity of oxide materials including silicon dioxide to silicon due to the formation of a passivation layer on the silicon during the etch process, resulting in a low etch rate or an etch stop of silicon. Especially, higher C/F ratios for fluorocarbon gases lead to increased selectivity to silicon [7]. However, the use of fluorocarbon gas having high C/F ratios causes contamination of the silicon surface by a polymer layer and a degradation of the devices formed after the etching.

Therefore, in this study, to obtain higher HfO_2/Si etch selectivities, we carried out HfO_2 film etching using Ar/C_4F_8 inductively coupled plasmas (ICPs) and we investigated the effect of oxygen ICP on the properties of the silicon surface. Also, the electrical characteristics of

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HfO_2-nMOSFETs after the oxygen ICP treatment were investigated.

II. EXPERIMENT

The HfO_2 etch behavior was characterized with a homemade magnetically-enhanced inductively-coupled plasma (MEICP) system. The tool consisted of a five-turn Au-coated copper coil located on the top of the process chamber, separated from the plasma environment by a 1-cm-thick quartz window. A 13.56-MHz r.f. power supply was connected to the coil to generate the inductively coupled plasmas. A separate 13.56-MHz r.f. power supply was attached to the 6-inch-diameter substrate electrode to provide a d.c. bias voltage to the sample. The distance between the quartz window and the substrate electrode was 7.5 cm. The substrate was cooled by chilled water, keeping the substrate temperature at near room temperature. Four sets of permanent magnets, each producing a field of 2000 G, were installed around the chamber wall to increase the plasma's density and uniformity by confining the plasma. The details of this MEICP system are described elsewhere [8].

As the samples, HfO_2 films (35 Å) were deposited on Si wafers by using atomic layer deposition (ALD) and were patterned by using a photoresist to estimate the etch rate. Ar/C_4F_8 gas mixtures were used to etch the HfO_2 thin films. Other etch parameters, such as the inductive power, the dc-bias voltage, the operating pressure and the substrate temperature, were kept at 250 W, −100 V, 10 mTorr and room temperature, respectively. After the HfO_2 etching, the silicon surface was treated by using a MEICP in 10-mTorr O_2 at an inductive power 500 W without biasing for 1 min.

The HfO_2 etch rate was determined using stylus profilometry (Tencor Instrument, Alpha Step 500) of the feature depth after stripping the photoresist. X-ray photoelectron spectroscopy (XPS, Thermo VG, MultiLab 2000, Al kα source) was also used to analyze the etch products remaining on the etched Si surface before and after the O_2 plasma treatment. An atomic force microscope (AFM, Termomicroscope, CP Research) was used to measure the surface roughness. A parameter analyzer (HP, 4155B) was utilized to analyze the current-voltage (I-V) characteristics of the HfO_2-nMOSFET.

III. RESULTS AND DISCUSSION

Figure 1 shows the etch rates of silicon and HfO_2 and the etch selectivity of HfO_2/Si measured as functions of the C_4F_8 percentage added to pure Ar. As references, the etch rates of the photoresist (PR) and the SiO_2 and the etch selectivities of PR/Si and SiO_2/Si are also shown. The operating conditions were a 250-W inductive power, a −100-V d.c. bias voltage and a 10-mTorr

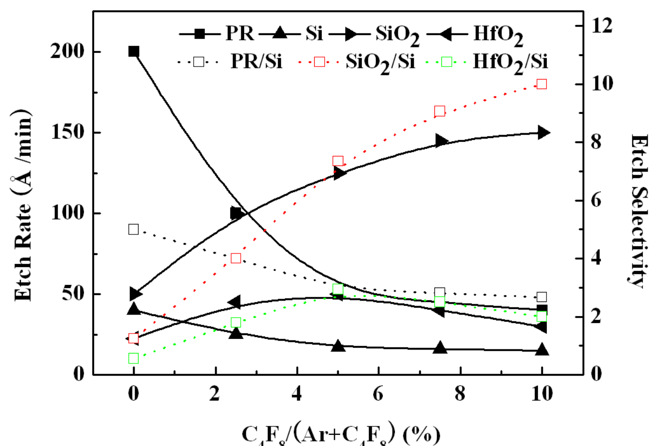

Fig. 1. Etch rates of HfO_2 and Si and etch selectivities of HfO_2/Si as functions of the Ar/C_4F_8 gas mixture. As references, the etch rates of the photoresist (PR) and SiO_2 and the etch selectivities of PR/Si and SiO_2/Si are also shown [process condition: inductive power (250 W), dc bias voltage (−100 V) and operating pressure (10 mTorr)].

operating pressure. As shown in the figure, for the pure Ar plasma, the etch rates of HfO_2 and Si were 23 Å/min and 40 Å/min, respectively and the etch selectivity of HfO_2/Si was as low as 0.56. However, with increasing C_4F_8 percentage in the gas mixture of Ar/C_4F_8, the Si etch rate decreased consistently while the HfO_2 etch rate show a maximum of about 50 Å/min at about 5 % of C_4F_8. In the case of the etch selectivity of HfO_2/Si, similar to the etch rate of HfO_2, it initially increased with increasing C_4F_8 percentage and showed a maximum of about 3 at 5 % of C_4F_8 ; further increases of C_4F_8 in the gas mixture decreased the etch selectivity. In the case of the PR etch rate, the etch rate decreased consistently from about 200 to less than 50 Å/min with increasing C_4F_8 percentage from 0 to 10 % in the gas mixture similarly to the etch rate of Si with increasing C_4F_8 percentage. The SiO_2 etch rate increased constantly from 50 to about 180 Å/min with increasing C_4F_8 percentage. Therefore, the etch selectivity of PR/Si decreased from 5 to 2.9 while the etch selectivity of SiO_2/Si increased from 1.2 to 10 with increasing C_4F_8 percentage from 0 to 10 %.

The low etch selectivity of HfO_2/Si for pure Ar is believed to be related to the bond strength of the materials, which affects the sputter yield by Ar^+ ion-bombardment. The bond strengths of Si-Si and Hf-O are 3.39 and 8.32 eV, respectively ; therefore, the bond strength of Si-Si is lower than that of Hf-O and a lower etch rate of Si compared to that of HfO_2 is expected for pure Ar^+ ion sputtering [9]. The decrease in the Si etch rate with increasing C_4F_8 addition to Ar is related to the formation of a fluorocarbon polymer layer formed on the Si surface. With increasing C_4F_8, due to the difficulty of vaporizing carbon on the silicon surface due to the high C/F ratio, a thick fluorocarbon polymer layer is formed on the sil-

icon surface and its thickness increases with increasing C_4F_8 percentage in the gas mixture. The fluorocarbon layer formed on the silicon surface blocks the diffusion of fluorine atoms to the silicon surface and prevents the formation of volatile compounds, such as SiF_x, in addition to decreasing the physical etching of silicon by the ion bombardment. As a result, the fluorocarbon polymer layer formed on the silicon surface acts as a protecting layer that prevents chemical and physical etching of silicon. Therefore, with increasing C_4F_8 percentage in the gas mixture, the etch rate of silicon decreases. However, in the case of HfO_2 etching with increasing C_4F_8 percentage in Ar/C_4F_8, carbon can be removed by a reaction with the oxygen in the HfO_2 through the formation of volatile products, such as carbon monooxide (CO) and carbon dioxide (CO_2). In fact, due to the removal of oxygen from HfO_2 by the carbon in C_4F_8 for easier formation of volatile HfF_x compounds, the etch rate of HfO_2 is initially increased when the C_4F_8 was added up to 5 %. However, due to the low vapor pressure of HfF_x, the excessive carbon remains on the HfO_2 surface when the C_4F_8 percentage is increased to higher than 5 % and a fluorocarbon polymer layer is formed on the HfO_2 surface even though the thickness is much thinner than that formed on the silicon surface due to the continuous removal of carbon by the oxygen in the HfO_2 [10]. In the case of SiO_2, due to the higher vapor pressure of SiF_x compounds compared to HfF_x compounds, the etch rate was not saturated up to 10 % C_4F_8 addition to Ar, so, the etch rate of SiO_2 increased continuously with increasing C_4F_8 percentage up to 10 % while the etch rate of HfO_2 showed a maximum at 5 % of C_4F_8.

Figure 2(a) shows the XPS narrow scan data of the C 1s peak observed on the silicon surface after the complete etching of HfO_2 (35 Å) on the silicon substrate by using an Ar/C_4F_8 (5 %) plasma. The other etch parameters are the same as those in Figure 1. As shown in the figure, after the removal of HfO_2, a thick fluorocarbon layer was formed on the exposed silicon surface and the binding states of the carbon were composed of C-C (285 eV), C-CF_x (287.1 eV), C-CF (289 eV), C-F_2 (291.1 eV) and C-CF_3 (293.2 eV) bonds, which are related to a thick fluorocarbon polymer layer. Figure 2(b) shows the roughness of the silicon surface observed by using an AFM after the etching the HfO_2 under the same etch conditions as those for Figure 2(a). As shown in the figure, the etch roughness was as high as about 3.71 Å, which is believed to originate from the fluorocarbon polymer layer formed during the etching by the high-C/F-ratio gas composition. Even though the formation of a thick fluorocarbon polymer layer on the silicon surface can improve the etch selectivity of HfO_2/Si during the etching of HfO_2, the remaining fluorocarbon layer on the silicon surface will increase the contact resistance between the metal and the silicon after the source/drain metallization processing, which is followed by the HfO_2 etch process. Therefore, an oxygen plasma treatment process was carried out after the HfO_2 etching to remove the fluorocarbon polymer layer formed on the silicon surface.

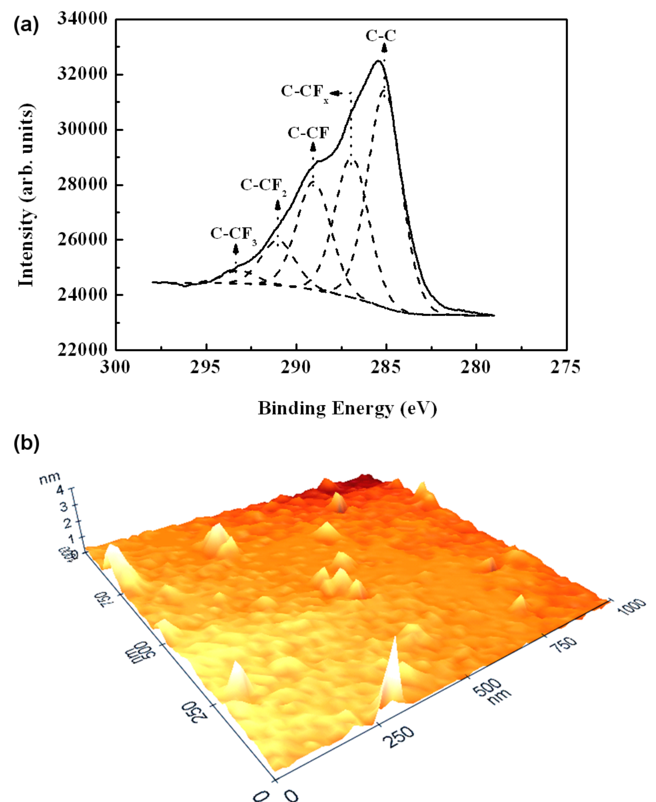

Fig. 2. (a) XPS C1s narrow scan spectra and (b) AFM image of the Si surface exposed to an Ar/C_4F_8 (5 %) plasma. [process condition: inductive power (250 W), dc bias voltage (−100 V) and operating pressure (10 mTorr)].

Figures 3(a) and (b) show the XPS narrow scan data of the C 1s peak and the AFM surface roughness measured on the silicon surface, respectively, after an oxygen plasma treatment of the silicon surface shown in Figure 2. The oxygen plasma treatment was carried out using the same MEICP chamber at a 500-W inductive power at 10-mTorr oxygen for 1 minute without biasing the substrate. As shown in Figure 3(a), after the oxygen plasma treatment, the XPS C 1s peak remaining on the silicon surface showed small peaks due to C-CF_x, C-CF and C-C (285 eV) bonds, so, most of the fluorocarbon polymer layer appeared to be removed after the oxygen plasma treatment. In addition, as shown in Figure 3(b), the RMS surface roughness was decreased to 1.1 Å, similar to the roughness of the original silicon surface. Therefore, we believe that, through the oxygen plasma treatment, the fluorocarbon polymer layer formed during the etching by Ar/C_4F_8 was almost completely removed by the formation of CO and CO_2 due to oxygen.

To investigate the effect of the oxygen plasma treatment on the properties of the device after the etching of the HfO_2 gate dielectric by the Ar/C_4F_8(5 %) plasma in Figure 2, unfabricated HfO_2-nMOSFET devices having Ta metal gates and we investigated their electrical prop-

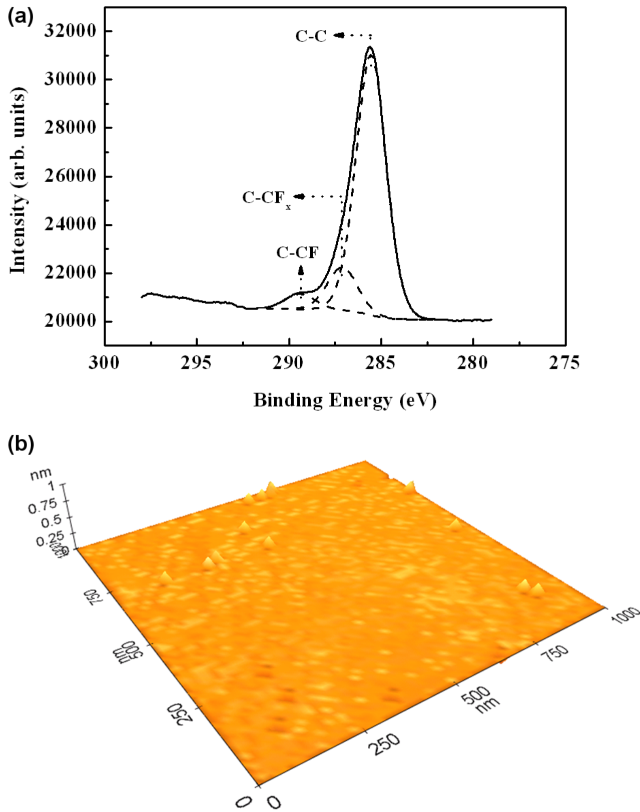

Fig. 3. (a) XPS C1s narrow scan spectra and (b) AFM image of the Si surface after O_2 plasma treatment. [process condition: inductive power (500 W) and operating pressure (10 mTorr)].

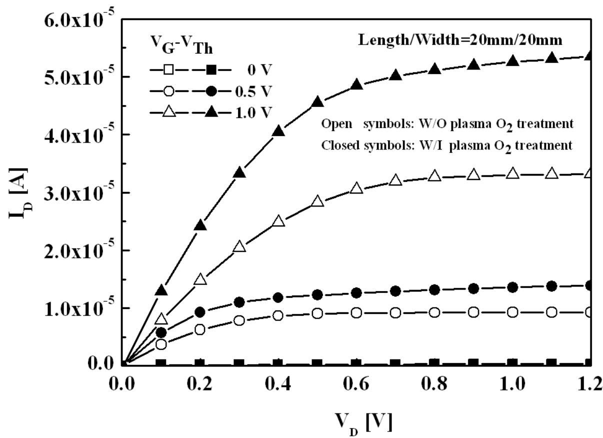

Fig. 4. V_D-I_D characteristics of HfO_2-nMOSFETs fabricated before and after O_2 plasma treatment. (Process condition: Etching - inductive power (250 W), dc bias voltage (−100 V) and operating pressure (10 mTorr), O_2 plasma treatment - inductive power (500 W) and operating pressure (10 mTorr)).

erties. Figure 4 shows the V_D-I_D characteristics of HfO_2-nMOSFETs fabricated with/without the oxygen plasma treatment after the etching of HfO_2. The source/drain metallization was formed on the silicon surface by sputter deposition of Ti (300 Å)/Al (2000 Å), followed by conventional FGA (forming gas annealing) at 400 °C for 30 min. As shown in the figure, after the oxygen plasma treatment, the device showed about a 60 % improvement in the drain current (at $V_G - V_{Th} = 1$ V) compared to the device fabricated without the oxygen plasma treatment. The improved drain current was related to a decrease in the contact resistance caused by effectively removing the fluorocarbon polymer layer formed on the silicon surface of the source/drain by the oxygen plasma.

IV. CONCLUSIONS

In this study, the etch rates of HfO_2 and Si and the etch selectivity of HfO_2/Si were investigated by adding of C_4F_8 to Ar in a MEICP system to obtain a high etch selectivity of HfO_2/Si for gate-dielectric applications in next-generation MOSFET devices and the effect of oxygen plasma treatment on the properties of the MOSFET devices was investigated. The addition of C_4F_8 to Ar increased the etch selectivity of HfO_2/Si until 5 % of C_4F_8 had been added to Ar. This was due to the differences in the thickness of the fluorocarbon polymer layer formed on the silicon surface and the HfO_2 surface during the etching. A thick fluorocarbon polymer layer was formed on the silicon surface due to the carbon remaining on the silicon surface when a high-C/F-ratio gas was used, that decreased the silicon etch rate with increasing C_4F_8 percentage in Ar/C_4F_8. In the case of HfO_2, due to the removal of carbon by the oxygen in HfO_2, the HfO_2 etch rate was increased until 5 % C_4F_8 had been added to Ar. However, further increases in the C_4F_8 percentage in Ar decreased the HfO_2 etch rate and the HfO_2/Si etch selectivity due to excessive carbon on the HfO_2 surface, which forms a fluorocarbon polymer layer on the HfO_2 surface even though its thickness is thinner than that formed on the silicon surface. The fluorocarbon layer formed on the silicon surface for the high HfO_2/Si etch selectivity condition decreased the performance of the MOSFET device by increasing the contact resistance after the metallization of source/drain. The fluorocarbon layer formed on the silicon surface after the HfO_2 etching could be successfully removed by using an oxygen plasma by showing 60 % improvement of drain current of a MOSFET device after the plasma treatment.

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