Electronic Materials Letters, Vol. 6, No. 3 (2010), pp. 107-112
DOI: 10.3365/eml.2010.09.107 Published 30 September 2010

Low Damage and Anisotropic Dry Etching of High-*k* Dielectric HfO_2 Films in Inductively Coupled Plasmas

Jong Cheon Park,[1] Sungu Hwang,[2] Jong-Man Kim,[1] Jin Kon Kim,[1] Jun Hyuk Seo,[3] Duck-Kyun Choi,[3] Hee Soo Lee,[4] and Hyun Cho[1,*]

[1]Department of Nanomechatronics Engineering, Pusan National University, Gyeongnam 627-706, Korea
[2]Department of Nanomedical Engineering, Pusan National University, Gyeongnam 627-706, Korea
[3]Department of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea
[4]School of Materials Science & Engineering, Pusan National University, Busan, 609-735, Korea

The etch characteristics of high-*k* dielectric HfO_2 films and the etch selectivity for HfO_2 over Si in fluorine- and chlorine-based inductively coupled plasmas have been studied. Fluorine-based ICP discharges produced practical and controllable etch rates and the etched HfO_2 surfaces sustained similar or better RMS roughness values than that of the unetched control sample under most of the conditions examined. Anisotropic pattern transfer with a vertical sidewall profile ($\theta = 97°$) was performed in CF_4/Ar ICP discharges and no significant change in the dielectric property of HfO_2 films was detected. $5Cl_2/10O_2$ ICP discharges produced high etch selectivities > 6.3 (max. ~7.6) for HfO_2 over Si.

Keywords: low damage, anisotropic dry etching, HfO_2 films, inductively coupled plasmas, surface morphology, etch selectivity

1. INTRODUCTION

As dimensions of structures continue to be reduced in complementary metal-oxide-semiconductor (CMOS) devices, gate width is expected to be scaled down to less than 50 nm, and gate oxide thickness is also projected to be reduced down to 2 nm. The technological challenge has continued for the growing of ultrathin, high quality SiO_2 or SiON films that can sustain the gate capacitance without increasing the gate leakage current. However, SiO_2 and SiON gate dielectrics cannot meet the requirements of low standby power CMOS devices due to their high gate current leakage characteristics for thicknesses below 20 Å. Therefore, the ultimate solution would rely on high dielectric constant (*k*) materials. High-*k* (> 20) dielectric materials can potentially extend scaling to an equivalent oxide thickness in the sub-10 Å regime.[1-5] In addition to high-*k* values, the choices of gate dielectrics for advanced CMOS devices are determined by a set of criteria such as the thermodynamic stability at the dielectric-Si interface, ability to achieve low interface state defect densities, diffusion resistance to dopants and impurities, and availability of conformal deposition over morphological features.

Many metal oxides and metal silicates with high dielectric constants ($8 < k < 80$) including Al_2O_3,[6] Ta_2O_5,[7,8] TiO_2,[9,10] $ZrSiO_4$,[11] $Zr_{1-x}Al_xO_y$,[5,12] $ZrSi_xO_y$[13] have been proposed as gate dielectric materials for advanced CMOS devices; HfO_2 is one of the most promising candidates due to its modest dielectric constant ($k \approx 25$) and thermal stability at the interface with Si.[14,15] In order to integrate HfO_2 gate dielectric with conventional CMOS fabrication processes, a precise and controllable dry etching is essential to reduce the contact resistance and ensure reliable device performance. Dry etching of HfO_2 dielectric layer using high density plasma techniques[16,17] is required to satisfy the requirements of smooth surface morphology, residue-free state, anisotropy, and selectivity to Si. Norasetthekul *et al*. reported Cl_2-, SF_6- and CH_4-based inductively coupled plasma (ICP) etching of HfO_2 films; they achieved a maximum etch selectivity of ~ 5 for HfO_2 over Si in the Cl_2/Ar discharges.[18] Sha *et al*. presented an electron cyclotron resonance (ECR) plasma etching of HfO_2 in halogen chemistries with a marginal selectivity of ~1.6 for HfO_2 over Si at high microwave conditions.[19] Using Cl_2/HBr/O_2-based ICP chemistries, Maeda *et al*. obtained a maximum etch selectivity of ~2 for HfO_2 over SiO_2 under the condition in which an etch rate of ~20 Å/min for HfO_2 was produced.[20] Nakamura *et al.* also reported the ECR plasma etching of HfO_2 and a maximum etch selectivity of >10 for HfO_2 over Si and SiO_2 with an etch rate of ~50 Å/min for HfO_2.[21] Despite the results of these previous works, it is still required to establish the etch process win-

*Corresponding author: hyuncho@pusan.ac.kr

dow in which high etch selectivity for HfO_2 over Si with practical and controllable etch rates can be achieved. Moreover, no attention has been paid to low damage etching of HfO_2 film, which prevents the degradation in dielectric property, which prevention is critical in the fabrication of novel floating gate MOSFET devices. In this paper, we report on low damage, anisotropic ICP etching of HfO_2 films with high etch selectivity to Si, and practical and controllable etch rates. The effect of plasma composition, ion flux and ion energy on the material etch rate, surface morphology and etch selectivity for HfO_2 over Si were examined.

2. EXPERIMENTAL PROCEDURE

HfO_2 films were deposited by atomic layer deposition (ALD) onto 4" Si substrates; typical film thicknesses were ~500 Å. HfO_2 films were patterned with either AZ 4330 photoresist or ~1000 Å thick nickel layer. High density plasma etching was performed in a planar inductively coupled plasma source operating at 13.56 MHz and power up to 1000 W; the samples were thermally bonded to an Si carrier wafer that was mechanically clamped to an He backside-cooled, rf-powered (13.56 MHz, up to 450 W) chuck. Fluorine- (CF_4 and SF_6) and chlorine- (BCl_3 and Cl_2) based inductively coupled plasmas were employed to etch HfO_2 films. Ar or O_2 gas was used as an additive gas and process pressure was varied from 2-20 mTorr, with a gas load of 15 standard cubic centimeters per minute (sccm). The etch rates were measured by stylus profilometry after removal of the mask materials. The surface morphology was characterized by tapping mode atomic force microscopy (AFM) and the anisotropy of etched features was examined by field-emission scanning electron microscopy (FE-SEM). The effect of plasma etching on the dielectric property was examined by comparison of the C-V characteristics of the etched HfO_2 films with those of the unetched control sample.

3. RESULTS AND DISCUSSION

Figure 1 shows the influence of plasma composition on the HfO_2 etch rate in inductively coupled plasma CF_4/Ar and SF_6/Ar discharges at 500 W source power, 200 W rf chuck power and 2 mTorr pressure. In the CF_4/Ar plasma chemistry, the HfO_2 etch rate initially increases as CF_4 is added and reaches ~760 Å/min; rate then decreases beyond 67% CF_4 content. The decrease in the HfO_2 etch rate at a high CF_4 percentage is attributed to the build-up of a fluorinated selvedge layer that is not efficiently removed by the lower ion energy and ion density under Ar-deficient conditions. By contrast, the HfO_2 etch rate increases continuously as the volume ratio of SF_6 in the gas load increases; this indicates the presence of the chemical component of the etching. Under these conditions the neutral-to-ion ratio in the plasma is maintained

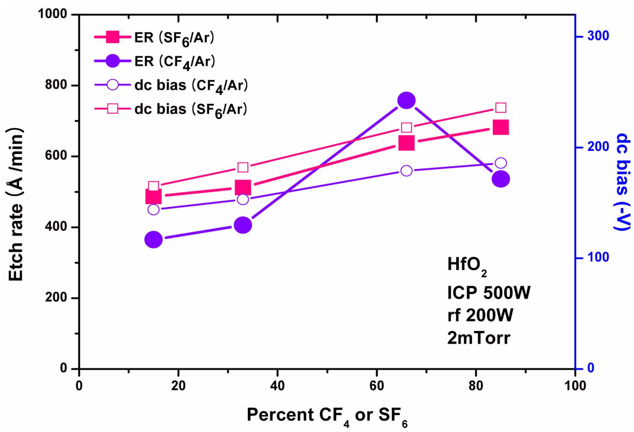

Fig. 1. HfO_2 etch rates as a function of plasma composition in CF_4/Ar and SF_6/Ar ICP discharges (500 W source power, 200 W rf chuck power, 2 mTorr).

within the range of optimal values that provide sufficient fluorine surface coverage and reaction, and subsequent etch product desorption.

The effect of rf chuck power on the HfO_2 etch rate in 300 W ICP source power, 2 mTorr $10CF_4$/5Ar and $10SF_6$/5Ar plasmas is shown in Fig. 2. For SF_6/Ar discharges, the HfO_2 etch rate shows a strong dependence on the rf chuck power, indicating the presence of the physical component of the etching. The HfO_2 etch rate monotonically increases as the rf chuck power increases due to the enhanced ion-assisted desorption of the hafnium fluoride etch products. A maximum etch rate of ~820 Å/min was obtained at a low ICP source power (300 W) and a relatively high rf chuck power (300 W) condition for SF_6/Ar ICP discharges. For CF_4/Ar discharges, the increase in rf chuck power does not produce a noticeable increase in the HfO_2 etch rate above 150 W. At rf chuck power conditions higher than 150 W in the CF_4/Ar, the density of the reactive chlorine involved in the reaction with the

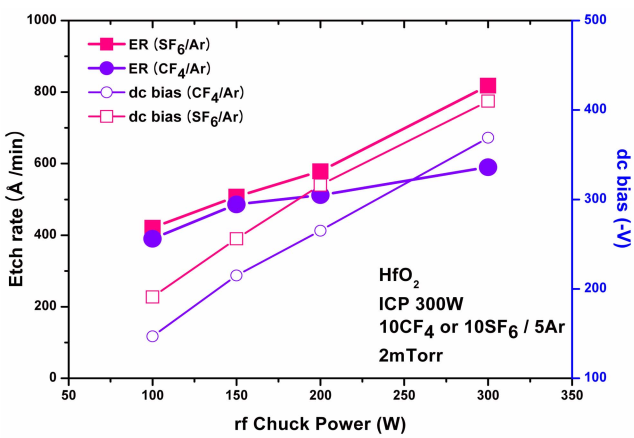

Fig. 2. HfO_2 etch rates as a function of rf chuck power in $10CF_4$/5Ar and $10SF_6$/5Ar ICP discharges (300 W source power, 2 mTorr).

surface atoms seem to be limited to some extent by the ion-enhanced desorption of the reactive fluorine species from the surface.

Figure 3 presents the AFM scan images of the HfO_2 surfaces etched in $10CF_4/5Ar$ ICP discharges; Fig. 4 shows the normalized roughness values acquired from the HfO_2 surfaces etched in the fluorine-based ICP discharges as a function of ICP source power (top) and rf chuck power (bottom) at fixed plasma composition and pressure. In each case, the etch depth was maintained at ~250 Å and the as-deposited root-mean-square (RMS) roughness was ~1.75 nm. A very smooth surface morphology was obtained at a relatively high rf chuck power (300 W) condition in the $10SF_6/5Ar$ discharges; this situation was most likely due to the activated ion-enhanced removal of metal fluoride etch products or sharp features from the surface. The etched surfaces of HfO_2 show similar or better RMS roughness values than that of the unetched control sample under most of the conditions examined. These data show that there is a wide process window for maintaining high quality surfaces with CF_4/Ar and SF_6/Ar ICP discharges.

Figure 5 shows SEM micrographs of features etched into HfO_2 films using $10CF_4/5Ar$ ICP discharges with a 300 W source power, 200 W rf chuck power, and 2 mTorr pressure. Note that the Ni mask layer is still in place. The etched surface shows a smooth morphology, as shown in Fig. 4; an anisotropic pattern transfer with a vertical sidewall profile (θ = 97°) was performed in CF_4/Ar ICP discharges.

In some microelectronic device fabrication processes, e.g. magnetic tunnel junction devices (MJTs) and variable capacitors in MEMS devices, the etched high-*k* dielectric layer is required to sustain the same dielectric property as the unetched surface. In order to examine the effect of plasma etching on the dielectric property of HfO_2 films, HfO_2 films of 2×2 cm^2 were etched in $10CF_4/5Ar$ ICP discharges (300 W source power, 2 mTorr) with different rf power conditions, and the C-V characteristics of the etched HfO_2 films was compared with the unetched control sample. The thicknesses of the etched HfO_2 films were maintained constant at ~300 Å to compensate for the thickness effect. The C-V curves of as-deposited and etched HfO_2 films measured in the range of -4 V to 4 V (1 MHz frequency) are shown in Fig. 6. The etched HfO_2 films present capacitance values similar to those of the as-deposited sample with a deviation of $\leq \pm 10\%$, but this is tolerable when we take into account the typical error in etch depth uniformity (±5-10% in our case). Also, no noticeable change in the flat-band voltage due to the variation in the positive fixed charge was monitored for the etched HfO_2 films, indicating detectable ion damage was not introduced with plasma etching.

Figure 7 shows the HfO_2 and Si etch rates (top) and etch selectivity for HfO_2 over Si (bottom) as a function of source power in Cl_2/O_2 ICP discharges at a fixed plasma composition, rf chuck power (200 W) and pressure (2 mTorr). HfO_2

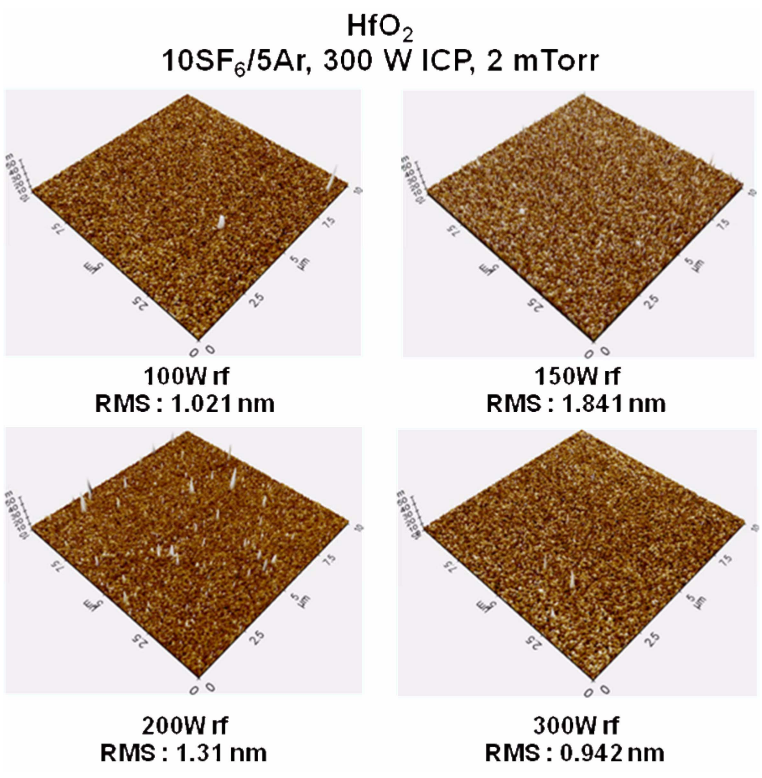

Fig. 3. AFM scan images of HfO_2 films etched in $10SF_6/5Ar$ ICP discharges (300 W source power, 2 mTorr).

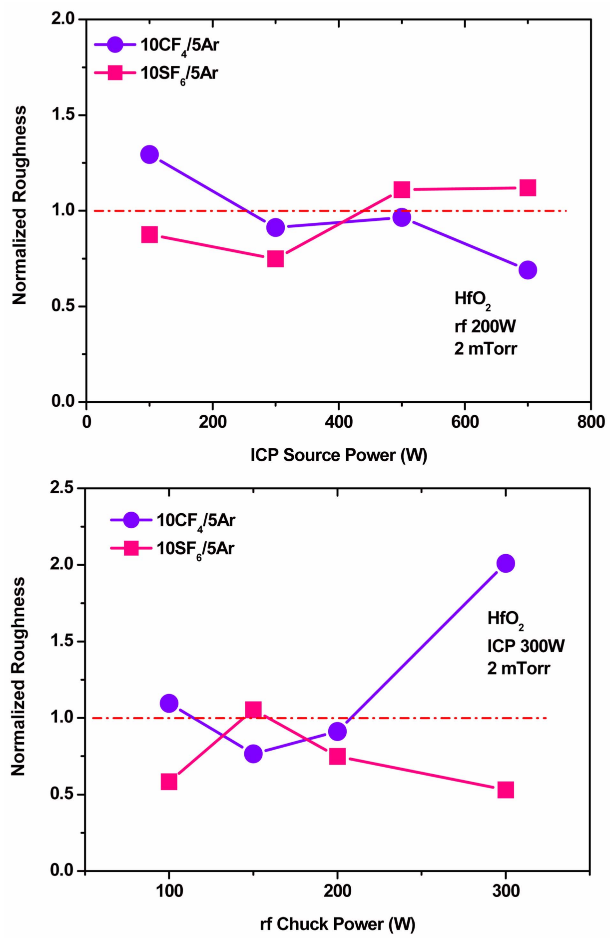

Fig. 4. Dependence of HfO_2 normalized etched surface roughness on source power (top) and rf chuck power (bottom) in $10CF_4/5Ar$ and $10SF_6/5Ar$ ICP discharges (2 mTorr).

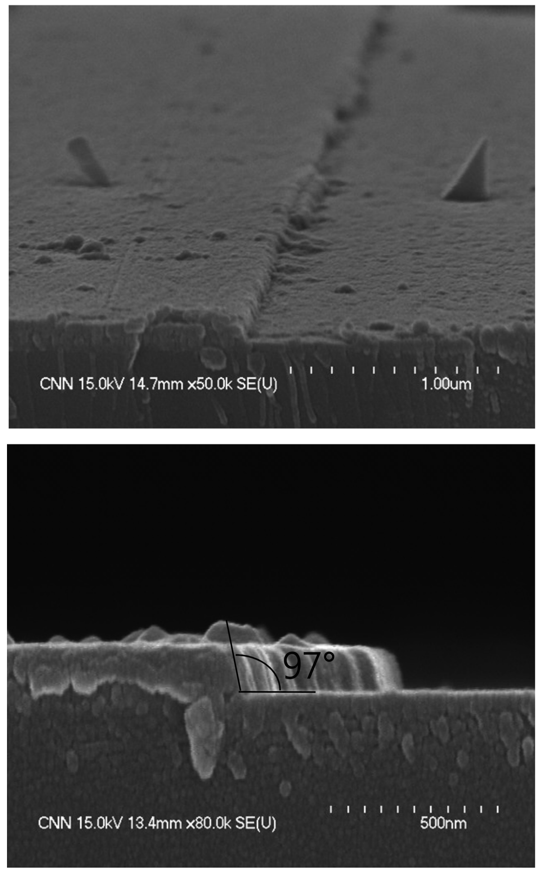

Fig. 5. SEM micrographs of features etched into HfO_2 using $10CF_4$/5Ar ICP discharges (300 W source power, 200 W rf chuck power, 2 mTorr).

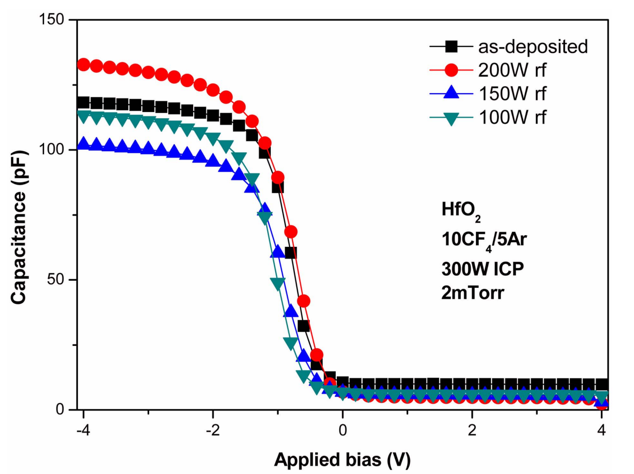

Fig. 6. C-V characteristics of HfO_2 films etched with different rf chuck power conditions in $10CF_4/5Ar$ ICP discharges (300 W source power, 2 mTorr).

etch rate increases as source power increases and reaches ~150 Å/min; it then slightly decreases beyond 500 W, indicating that the etch reaction is limited by the ion-assisted removal of hafnium chloride etch products from the surface. On the contrary, very low etch rates were obtained for Si and it was found that increasing source power does not produce a significant enhancement in Si etch rate, which leads to high etch selectivities (> 6.3) for HfO_2 over Si. The behavior of Si etch rate is assumed to have a close relation with Si-O bond formation on the surface under these conditions. Under the oxygen-rich plasma composition in Cl_2/O_2 ICP discharges, volatile $SiCl_x$ etch products are expected to be formed by the surface reaction between the reactive chlorine neutrals and Si, but some of the reactive oxygen neutrals in the plasma may react with the surface atoms of Si. Since the Si-O bond is much stronger than the Si-Cl bond (comparing the bond strength: Si-O bond: 799.6 kJ/mol; Si-Cl: 406.6 kJ/mol), it is energetically more favorable for Si to bond to O than to bond to Cl.[22,23] Once non-volatile SiO_x reaction products are partially formed on the Si surface, the formation of volatile $SiCl_x$ etch products could be disturbed or the etching could be retarded by the removal of non-volatile SiO_x products from the surface. A maximum etch selectivity of ~7.6 for HfO_2 over Si was obtained in $5Cl_2/10O_2$ ICP discharges at a

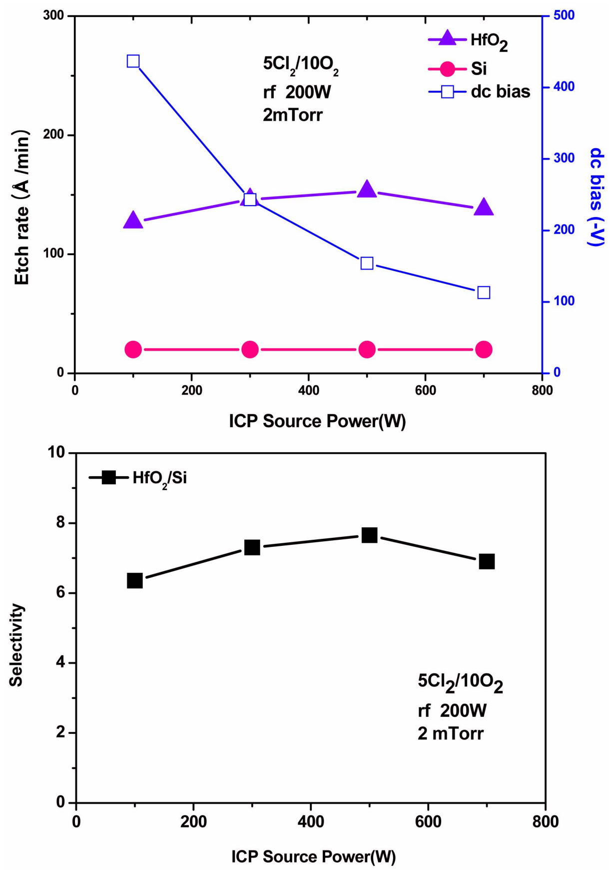

Fig. 7. HfO_2 and Si etch rates (top), and etch selectivity for HfO_2 over Si as a function of source power in $5Cl_2/10O_2$ ICP discharges (200 W rf chuck power, 2 mTorr).

700 W source power, 200 W rf chuck power, and 2 mTorr pressure.

Summary and Conclusions

In the plasma etching of high-*k* dielectric HfO_2 films for advanced microelectronic device applications, it is necessary to satisfy the requirements of smooth surface morphology, residue-free state, anisotropy, and selectivity to Si. The ALD-deposited HfO_2 films were etched in chlorine- and fluorine-based inductively coupled plasmas, and the effect of the process parameters on the etch rate, surface morphology and etch selectivity for HfO_2 over Si was examined. Practical and controllable etch rates were obtained for both chemistries and a maximum etch rate of ~820 Å/min was obtained at a low ICP source power (300 W) and a relatively high rf chuck power (300 W) condition for SF_6/Ar ICP discharges. HfO_2 surfaces etched in fluorine-based ICP discharges show RMS roughness values similar to or better than that of the unetched control sample under most of the conditions examined. The etched HfO_2 films present capacitance values similar to those of the as-deposited sample; no noticeable change in the flat-band voltage was monitored, indicating that detectable ion damage was not introduced with plasma etching. High etch selectivities > 6.3 (max. ~7.6) for HfO_2 over Si were obtained in $5Cl_2/10O_2$ ICP discharges.

ACKNOWLEDGMENTS

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (MEST) (D00486).

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