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Improvement on Electrical Characteristics of HfO_2 MIS Capacitor with Dual Plasma Treatment

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There have been some researches described that nitridation processes could improve thermal stability and dielectric constant of Hf-based dielectrics. The improvement of electrical characteristics of HfO_2 thin films with plasma nitridation has been examined. Moreover, CF_4 plasma treatment on HfO_2 thin films in order to suppress leakage current and passivate defect were also proposed. In this study, we proposed to combine two kinds of plasma treatment, CF_4 pre-treatment and nitrogen post-treatment, in order to have further improvement on electrical characteristics. The capacitance-voltage (C-V) characteristics, current-voltage (J-V) characteristics, and hysteresis of the samples were preformed to estimate the improvement effect. According to this study, dual plasma treatment would be an effective technology to improve the electrical characteristic and the hysteresis of pure HfO_2 thin films.

Introduction

In order to replace conventional SiO_2 as a gate dielectric thin film, high-κ materials have been investigated, such as HfO_2, ZrO_2, TiO_2, La_2O_3, Ta_2O_5, Al_2O_3, and $SrTiO_3$ (1-3). Among all these high-κ materials, HfO_2 is a promising gate dielectric layer because it has high dielectric constant (κ ~ 25), relatively large band gap (Eg ~ 5.7 eV), large conduction band offset with Si (~1.5 eV), and stable contact with Si (4). However, the formation of an interfacial layer (IL) at HfO_2/Si interface during the growth of dielectric thin film and post processing appears to be a critical issue due to gate dielectric scaling. Because of low dielectric constant of IL, IL limits the reduction of the effective oxide thickness (EOT) (5, 6). Wang et al noted that the applied electric field would be largely distributed at low-κ layer in high-κ/low-κ stack layer; as a result, the first breakdown happened in the low-κ layer (7).

Recently, several studies have been reported that nitrogen incorporated into dielectric layer can improve the dielectric performance (8, 9). Incorporating nitrogen into dielectric layer is widely used to increase dielectric constant, reduce EOT, and suppress leakage current about 3-4 orders of magnitude (10, 11). Oxygen vacancy related states in HfO_2 band gap can be eliminated by nitrogen atoms (12). In addition, fluorine incorporation also has some improvement on electrical characteristics (13, 14). Fluorine incorporated into dielectric layer could improve IL quality because of stronger bonding energy of Si-F bonds (5.73 eV) compared to Si-H bonds (3.18eV) (15). Furthermore, IL at HfO_2/Si interface could be suppressed by CF_4 pre-treatment (16).

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In this study, we proposed to combine two kinds of plasma treatment (CF_4 pre-treatment and nitrogen post-treatment) in order to have further improvement on electrical characteristics of HfO_2 MIS capacitor. First of all, single nitrogen post-treatment and single CF_4 pre-treatment are examined respectively. Second, samples treated by dual plasma treatment are examined in order to determine the best condition. The capacitance-voltage (C-V) characteristics, the current-voltage (J-V) characteristics, and the hysteresis of the samples were performed to estimate the improvement.

Experimental

In this research, Al/Ti/HfO_2/Si stack structures were fabricated. HfO_2 thin film was deposited by MOCVD system and post deposition annealing (PDA) was set at 600 ^oC for 30 sec by RTA system. Ti films and Al films were deposited by e-beam evaporation system. Thereafter, top electrodes were defined by lithography process and the area is 5000 μm^2.

There are three different kinds of experiment of plasma treatment in this study. First, for single nitrogen post-treatment, samples were nitrided in nitrogen plasma (N_2 or NH_3) by PECVD system after HfO_2 deposition and PDA. After plasma nitridation, post nitridation annealing (PNA) was performed to eliminate plasma damage, which was set at 600 ^oC for 30 sec. Second, for single CF_4 pre-treatment, Si substrate was treated in CF_4 plasma by PECVD system before HfO_2 deposition. Third, for dual plasma treatment, CF_4 pre-treatment and nitrogen post-treatment were combined in Al/Ti/HfO_2/Si capacitors. The capacitance-voltage (C-V) and current-voltage (I-V) characteristics of MIS capacitors were measured by C-V measurement (HP 4284) and semiconductor parameter analyzer (HP 4156C), respectively.

Results and Discussion

Single Plasma Treatment

Figure 1 shows the C-V and I-V characteristics of the HfO_2 thin films with N_2 post-treatment for different process durations. The sample treated in N_2 plasma for 120 sec perform the maximum capacitance density among these samples. The leakage current density is suppressed for the sample treated in N_2 plasma for 120 sec. The capacitance is degraded and the leakage current is increased while the samples treated longer than 120 sec, owing to plasma damage. It can be observed that the sample treated in N_2 plasma for 120 sec with RF power 50W performs the best performance. Similarly, the sample treated in NH_3 plasma with RF power 40W for 120 sec displays the best C-V and I-V characteristics than other samples, as shown in Figure 2. These two conditions will be chosen for dual plasma treatment.

Figure 3 depicts the C-V and I-V characteristics of the HfO_2 thin films with CF_4 pre-treatment for different process durations. The sample treated in CF_4 plasma for 10 sec with RF power 20W shows higher capacitance density and smaller leakage current than other samples. The factor of improvement might be the fluorine incorporation at the HfO_2/Si interface, which could suppress the formation of IL (16) and improve the quality of interface (14).

In order to combine two kinds of plasma, the samples treated in CF_4 plasma (denoted as CF_4 pre-treatment) for different durations and N_2 or NH_3 plasma (denoted as nitrogen post-treatment) for 120 sec is examined.

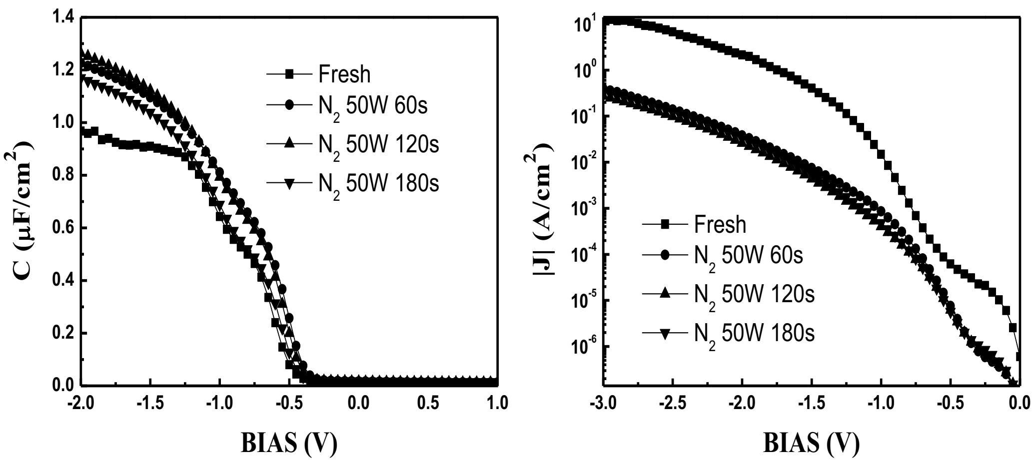

Figure 1. The C-V and I-V characteristics of the HfO_2 thin films with N_2 post-treatment for different process durations.

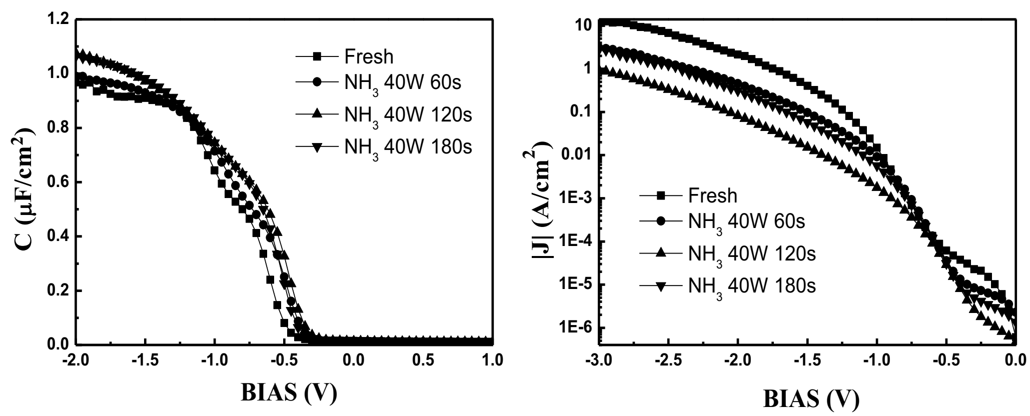

Figure 2. The C-V and I-V characteristics of the HfO_2 thin films with NH_3 post-treatment for different process durations.

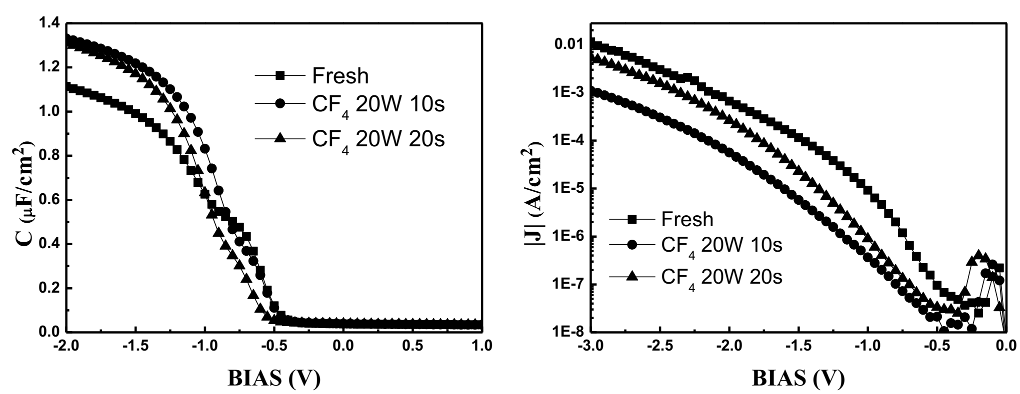

Figure 3. The C-V and I-V characteristics of the HfO_2 thin films with CF_4 pre-treatment for different process durations.

Dual Plasma Treatment

Figure 4 shows the C-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and N_2 plasma for 120 sec. The capacitance density was enhanced by nitridation process because nitrogen incorporated into dielectric layer could enhance the ionic polarization, resulted in the increase of dielectric constant (11). However, the capacitance density and interface characteristic could be further improved by the combination of CF_4 pre-treatment for 10 sec (RF power = 20 W) and N_2 post-treatment for 120 sec (RF power = 50 W). The hump in the depletion region is severe for the fresh sample. Although the sample treated by N_2 plasma shows relatively smaller hump than the fresh sample, the sample treated by dual plasma (CF_4 plasma for 10 sec and N_2 plasma for 120 sec) exhibit nearly no hump (as shown in the inset of Figure 4) due to the improvement of interface states. The capacitance and hump characteristics became worst while CF_4 pre-treatment time is longer than 10 sec due to plasma damage at the HfO_2/Si interface.

Figure 5 displays the J-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and N_2 plasma for 120 sec. The inset of Figure 5 is the leakage current density of the fresh sample. The leakage current is greatly suppressed about 4 orders of magnitude for the sample with dual plasma treatment (CF_4 pre-treatment for 10 sec and N_2 post-treatment for 120 sec), owing to defect passivation by nitrogen atom and fluorine atom (12, 13). The passivated defect states within HfO_2 band gap lead to the absence of electron leakage path. On the other hand, the gate leakage increased while fluorine pre-treatment time is longer than 10 sec, owing to plasma damage at the HfO_2/Si interface.

In Figure 6 and Figure 7, the C-V and J-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and NH_3 plasma for 120 sec are shown. By similar analysis as earlier, it could be observed that the best condition of dual plasma treatment is CF_4 pre-treatment for 10 sec (RF power 20 W) and NH_3 post-treatment for 120 sec (RF power 40 W).

Figure 8 demonstrates the hysteresis characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and N_2 plasma for 120 sec. Hysteresis measurement was measured from accumulation to inversion (-2 V to 1 V) and backward form inversion to accumulation (1V to -2 V) by sweeping the voltage. Because positive and negative carrier might be trapped at the inner interface during voltage sweeping (14), the hysteresis phenomenon could be observed for all the samples. Although single N_2 plasma treatment could improve the hysteresis characteristic, the hysteresis characteristic could be further improved by dual plasma treatment (CF_4 pre-treatment for 10 sec and N_2 post-treatment for 120 sec). The C-V curve shift of the sample treated by the combination of CF_4 pre-treatment for 10 sec and N_2 post-treatment for 120 sec is about 14 mV, which is smaller than the fresh sample (27 mV) and the sample with N_2 plasma treatment (17 mV). Moreover, the fresh sample shows a hump in the depletion region of the C-V characteristics, due to higher D_{it} at the interface (17). After dual plasma treatment (CF_4 pre-treatment for 10 sec and N_2 post-treatment for 120 sec), the hump could be effectively eliminated. It can be speculated that interface quality could be enhanced by dual plasma treatment. On the other hand, the hump and hysteresis became worst while CF_4 pre-treatment time is longer than 10 sec due to plasma damage at the HfO_2/Si interface. Similarly, the sample treated by the combination of CF_4 pre-treatment for 10 sec and NH_3 post-treatment for 120 sec shows the best hysteresis and interface characteristics than other samples, as shown in Figure 9.

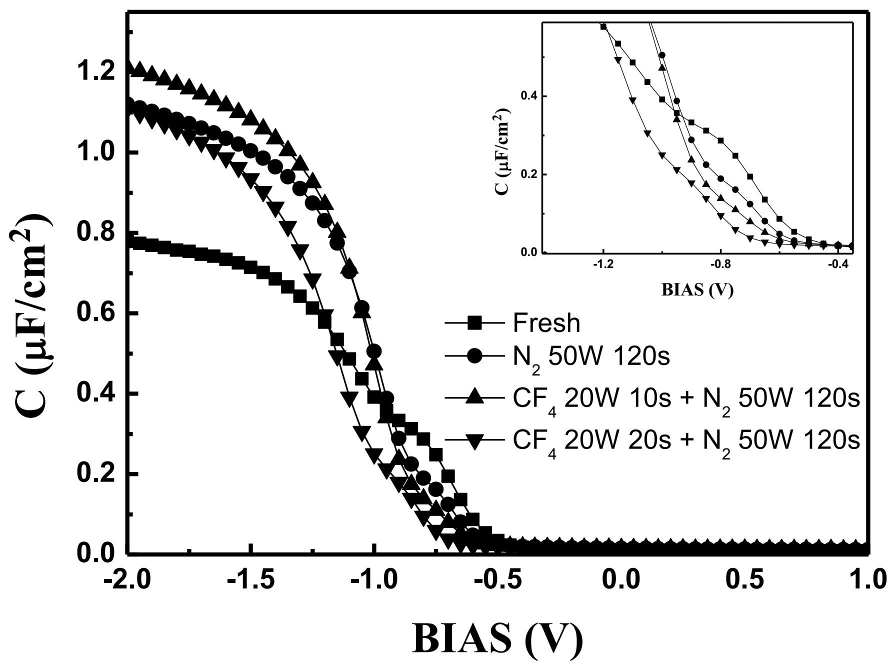

Figure 4. The C-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and N_2 plasma for 120 sec.

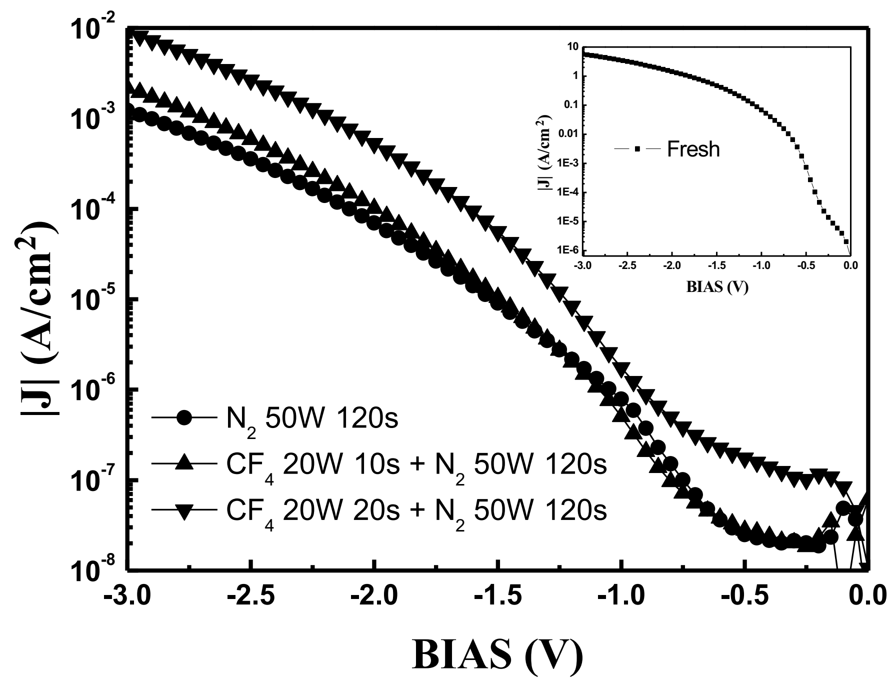

Figure 5. The J-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and N_2 plasma for 120 sec.

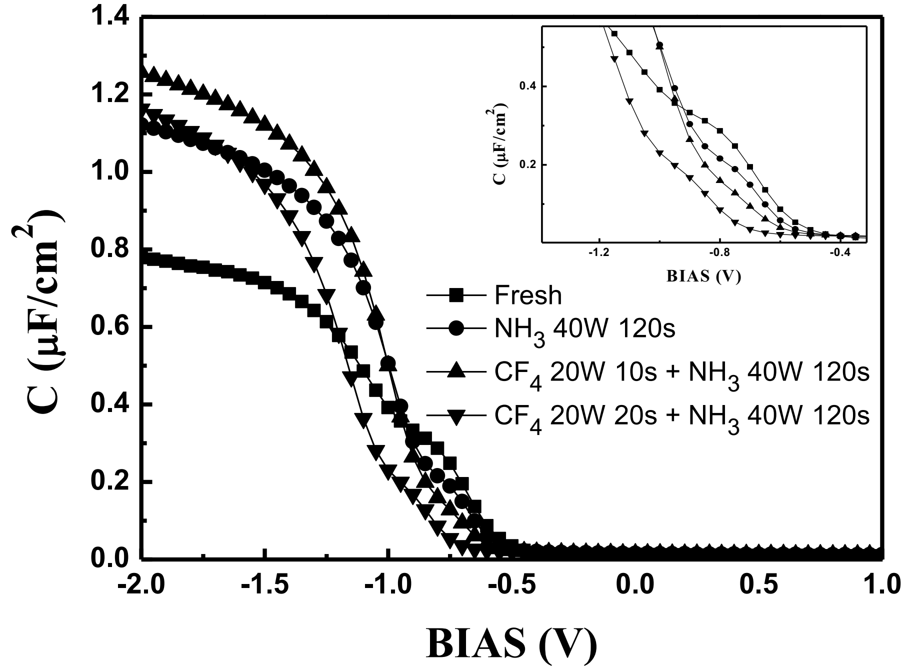

Figure 6. The C-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and NH_3 plasma for 120 sec

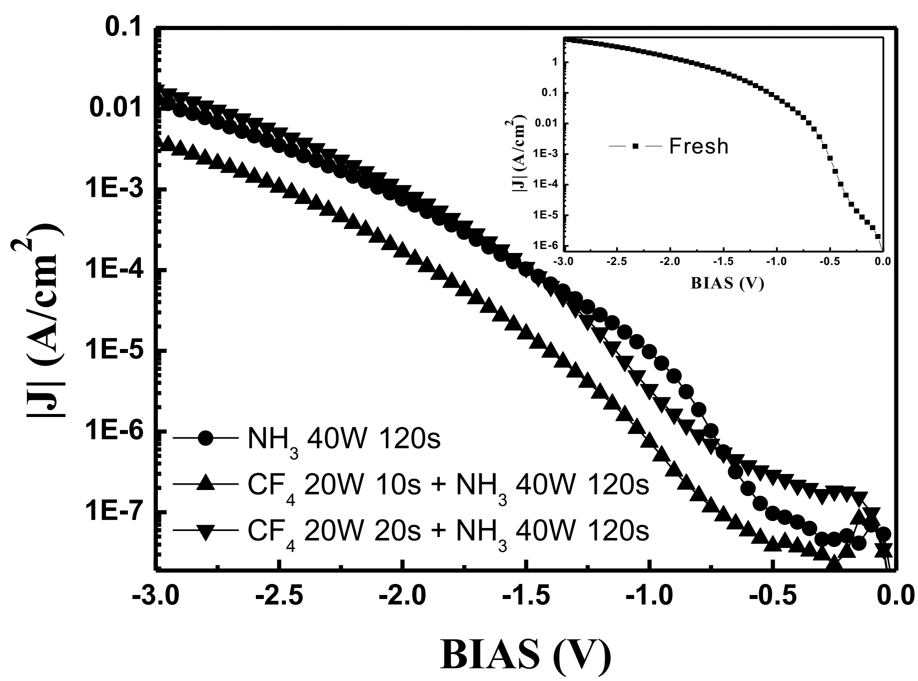

Figure 7. The J-V characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and NH_3 plasma for 120 sec

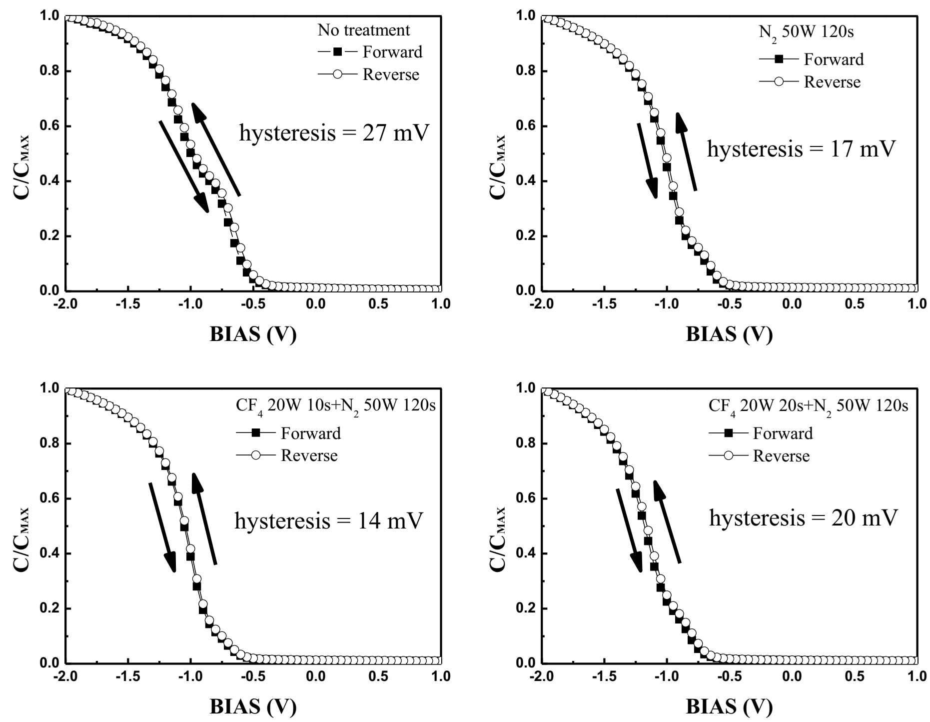

Figure 8. The hysteresis characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and N_2 plasma for 120 sec.

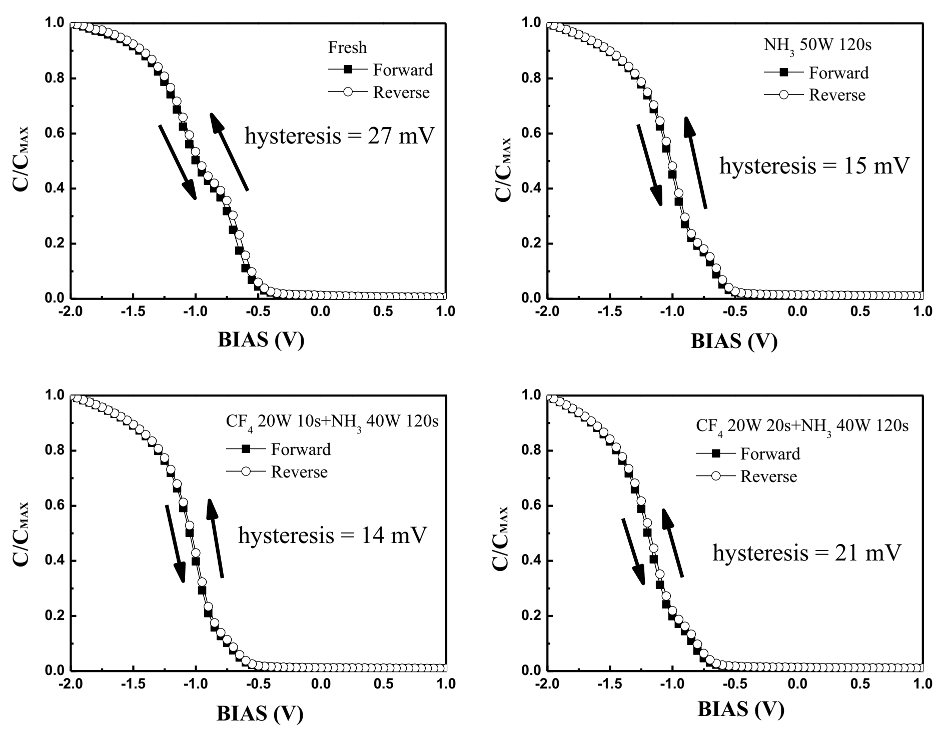

Figure 9. The hysteresis characteristics of the HfO_2 thin films treated in CF_4 plasma for different process durations and NH_3 plasma for 120 sec.

Conclusion

We have demonstrated the electrical characteristics of HfO_2 gate dielectrics treated by N_2 post-treatment, CF_4 pre-treatment, and dual plasma treatment (CF_4 pre-treatment and N_2 post-treatment). HfO_2 gate dielectric properties including capacitance density, gate leakage current density, and hysteresis could be improved by dual plasma treatment. The best condition of dual plasma treatment is as follows: CF_4 pre-treatment for 10 sec and N_2 (NH_3) post-treatment for 120 sec. In summary, the dual plasma treatment could be better than single plasma treatment and achieve the best performance of HfO_2 thin films

Acknowledgments

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