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High-performance and Damage-free Plasma Etching Processes for Future ULSI Patterning

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Novel etching techniques, such as the use of pulse-time-modulated plasma and a selective radical generation method, have been developed. The pulse-time-modulated plasma makes possible highly selective, high-rate, and charge-up-damage-free etching. And the new radical injection method using nonperfluorocarbon gases (CF_3I and C_2F_4) in high-density plasma enables polymerization and etching rate to be controlled independently through the selective generation of CF_2 and CF_3 radicals in the plasma.
Key words: Plasma, Etching, Damage, Microloading

1.Introduction

High-density plasmas, such as electron cyclotron resonance (ECR) plasma, helicon wave plasma, inductive coupled plasma, and surface wave plasma have many advantages. For example, a higher-density plasma can be generated at a lower pressure, ionization ratios are higher, and ion energies are more controllable. Even with high-density plasmas, however, there is a tradeoff between anisotropy and selectivity and between high etching rates and charge-free etching. This is especially true in the etching of submicron patterns. It is very difficult, in the conventional plasma etching, to obtain an optimally collimated ion flux and the lower ion energy needed to prevent charging damage. Additionally, it is very difficult to simply scale-up the chamber for conventional plasma sources when we want to process substrates more than 12-inches in diameter because these sources have complex components such as a magnetic coil, a waveguide, and loop antenna. The use of perfluorocompounds for the etching of silicon dioxide and silicon nitride is also considered problematic from an environmental standpoint. Most perfluorocomponuds are extremely long-lived species and can trap heat more efficiently than any other molecules in the atmosphere. That is, they can act as greenhouse gases and contribute to the warming of the earth surface (global warning).

We have therefore proposed three novel etching techniques, such as (1) pulse-time-modulated plasma,[1-3] (2) ultra-high-frequency plasma source with a spokewise antenna,[4,5] and (3) a new radical-injection-method with non-perfluorocompound gas chemistries.[6-8] The pulse-time-modulated plasma makes possible highly selective, high-rate, and charge-build-up-damage-free etching of gate electrodes and Al electrodes. These superior etching characteristics are results of being able to produce, within a few tens of microseconds, a large quantity of negative ions at a low electron temperature during the pulsed plasma after-glow. The ultrahigh frequency (UHF) plasma source with the spokewise antenna can produce uniform (within ± 5%), plasma with a density of more than 10^{11} cm^{-3} and low temperature of 1.5-2.0eV in a large-scale plasma source more than 30 cm in diameter. No magnetic field is needed to maintain the high-density plasma. Consequently, the plasma source is fairly simple and lightweight. A new radical injection method for high-performance SiO_2 patterning using non-perfluorocarbon gases (CF_3I and C_2F_4) in high-density plasma have been proposed recently. This method enables polymerization and etching to be controlled independently through the selective generation of CF_2 and CF_3 radicals. As a result, it can provide both a high etching rate and a high etching selectivity during the formation of high aspect contact-hole (more than 10). The gas chemistries can also suppress charging damage during SiO_2 etching by maintaining a low-electron-temperature in the plasma.

This paper reviews the role of pulse-time-modulated plasma in reducing topography-dependent charging in Al etching processes and reviews the new radical injection method for high-performance SiO_2 etching.

2.Pulse-Time-Modulated Plasma Etching[1-3]

The Electron Cyclotron Resonance (ECR) plasma system used in the work reviewed here is schematically shown in Fig. 1. A large-diameter ECR plasma was produced by a flat-disk-type compact plasma source (Nichimen Co., 300DECR) with a cylindrical permanent-magnet array 300 mm in diameter and 80 mm high. Microwaves at 2.45 GHz were fed through the flat waveguide to a disk-type slot antenna in front of the magnet array. The source power was set at 1 kW. In the pulse-time-modulated (TM) plasma, the pulse duration was 50 μ sec, and the pulse interval was changed from 30 to 100 μ sec. A radiofrequency (rf) bias of 600 kHz was supplied to the substrate. The substrate temperature was 0°C. To investigate the charge-up damage occurring in the Al-etching process, we used a NMOSFET that had an edge-intensive metal antenna with several aspect ratios (Fig. 2). The gate length was 0.34 μm and the gate width was 2.5–10 μm. The gate oxide thickness was 4.5 nm. The metal (TiN/AlSi/TiN), having a thickness of 0.6 μm, was etched using a resist mask. The discharge gas was Cl_2, with a flow rate of 50 sccm and a pressure of 3 mTorr. The initial and the final thickness of the resist were 1.6 μm and 0.6 μm, respectively. The antenna space ranged from 0.4 μm to 3.0 μm. The antenna ratio was defined as the ratio of the metal edge length to the gate oxide area. After the metal etching, the oxide degradation was evaluated without annealing the sample. The charge-to-breakdown (Qbd) was measured at $J=1(A/cm^2)$ at 25°C or 100°C, and the threshold voltage (Vth) was defined at a drain current of 20 (nA/μm).

Charge-to-Breakdown

We first evaluated the oxide degradation by monitoring the Qbd value. In the continuous wave (CW) plasma (Fig. 3 (a)), a clear degradation of Qbd was observed when the antenna space was narrow (0.4 μm) and the antenna ratio was large (188 K). The Qbd at 50% (median) degraded to about 1/3 of that of the MOSFET without an antenna. With the pulse-time-modulated (TM) plasma, the Qbd of the antenna MOSFET improved with an increase in the pulse interval (Fig. 3 (b) and (c)), and at the pulse interval of 100 μsec, the Qbd distribution became almost identical to that of the MOSFET without an antenna. When the antenna space was larger, the Qbd degradation became smaller. This indicates that the charging is topography dependent, and this dependence is known to result from the electron shading effect.

The Qbd, however, is not effective for assessing the charging damage because Qbd values scatter. As shown in Fig. 3, the Qbd distribution ranges over about one order of magnitude. Therefore, when using Qbd to compare charging damage, we needed to analyze a lot of data statistically. To assess the charging more easily and accurately, we used the threshold voltage.

Threshold Voltage

The shift in the threshold voltage (Vth) of a device with an antenna from that of a device without an antenna indicates the amount of charging-induced oxide trapped charge. In CW plasma (Fig. 4(a)), the Vth showed a positive monotonic increase with increasing antenna ratio. This suggests that the number of electrons trapped in the oxide increased with an increase in the antenna ratio and a decrease in the antenna space. This result also clearly indicates that the charging responsible for this Vth shift results from the topography-dependent charging. We also studied an ICP etcher with CW plasma and found that the degree of topography-dependent charging produced was similar to that produced by the CW plasma source used in the work reviewed here (Fig. 4(a)).

When the TM plasma was used, the Vth shift became smaller when the pulse interval was increased from 30 μsec to 100 μsec (Fig.4(a) and (b)). At the pulse interval of 100 μsec, the differences between the MOSFETs with various antenna spaces became very small, indicating that the topography-dependent charging was significantly suppressed.

Estimation of Injected Current and Charge

The Vth shift was then correlated to the amount of the current and the charge that is injected from the plasma to the gate oxide through the metal antenna. This was done by comparing the etching-induced Vth shift (in Fig. 4) with the Vth shift of an electrically stressed MOSFET without antenna. The electrical stress was applied at 100°C, which was assumed to be the wafer temperature during etching.

The injected current at the antenna edge length of 80 mm is shown in Fig. 5 as a function of the pulse interval. Figure 5 shows how much the charging current was reduced in the TM plasma. For example, when the pulse interval was 100 μsec, the current was decreased to about 1/4 or 1/5 of that in the CW plasma. Also note that the injected current decreased with an increase in the antenna space.

The injected current can be converted to the injected charge by multiplying the current by the stress time. The stress time was assumed to be 10 sec, considering that the charging current is injected near the etching endpoint when the latent antenna is present. The obtained charge injected is plotted in Fig. 6. The antenna space was fixed at 0.4 μm. The Qbd value of the MOSFET without an antenna, which is about 20 C/cm^2, is also shown in Fig. 6. Since Qbd value scatters, its median value (at 50%) is used.

The relationship between the injected charge of the antenna MOSFET and its Qbd is understood as follows: The injected charge in CW plasma at an antenna ratio of 188 K is about 13 C/cm^2. This means that the estimated Qbd of this device is 7 C/cm^2, which is about 1/3 of the value without charging. This agrees with the data in Fig. 3(a), in which Qbd (at 50%) degraded to about 1/3 from 55 to 18 C/cm^2. And for TM plasma with the pulse interval of 50 μsec, Qbd degraded to 3/4 of the value without charging.

Mechanism of Charging Suppression in TM Plasma

A mechanism proposed to account for the suppression of charging in TM plasma can be briefly explained as follows. During the power-off period in TM plasma, the electron temperature decreases and negative ions are generated (Fig. 7). The negative ions are injected toward the substrate by the low-frequency RF bias and help to reduce the positive charges that accumulated during the power-on period (Fig. 7).

The amount of charge reduction in TM plasma can be estimated from Fig. 6. The charge accumulation in TM plasma was reduced to about 1/2 that in CW plasma when the pulse interval was 30 μsec, and it was reduced about 1/5 the charge accumulation in CW plasma when the pulse interval was 100 μsec.

We have shown that topography-dependent charging damage during metal etching can be significantly reduced by using pulse-time-modulated plasma. At a pulse interval of 100 μsec, the amount of charging in the MOS device is reduced to nearly 1/5 of what it is when in continuous-wave plasma is used. Thus, the use of pulse-time-modulated plasma is an effective and promising technique for suppressing the topography-dependent charging.

3.New Radical Injection Method for High-performance SiO_2 Etching[6-8]

SiO_2 etching is done with fluorocarbon gas plasmas in order to provide high etching selectivity for SiO_2 in preference to the underlying-silicon or silicon nitride. In this plasma, the precise control of both CF_2 radicals and CF_3 radicals is important because the CF_2 radicals determine the etching selectivity through their role in polymerization, and the CF_3 radicals determine the rate of SiO_2 etching because they are the main source of etchant ions CF_3^+ (CF_3+e→CF_3^+). When using a conventional perfluorocarbon gas (usually C_4F_8), however, it is difficult to control the balance between the radical flux (CF_2 radicals) and the ion flux (CF_3^+ ions) because the gas dissociation processes are complex. Thus the polymerization and the SiO_2 etching cannot be independently controlled. There are serious limitations related to a low etching rate, microloading, and interruption of the etching ("etch stop"). Although Ar dilution (over 80%) of C_4F_8 is widely used to better control the polymerization in contact holes, this decreases the etching rate and the etching selectivity, and it increases the charge-up damage that occurs during SiO_2 etching. We have therefore developed a new radical injection method based on selectively generating CF_2 and CF_3 radicals from CF_3I and C_2F_4 in low-electron-temperature ultrahigh-frequency (UHF) plasma.

A new non-perfluorocarbon gas chemistry has been developed for generating selected radicals in UHF plasma. We found that CF_3I and C_2F_4 plasmas were good sources of CF_3 (CF_3^+) and CF_2 radicals in the UHF plasma (Fig.8), probably because of the weak C-I and C=C bonds in these molecules. By applying ultrahigh frequency (UHF: 500 MHz) power to a high-density fluorocarbon plasma,[1] non-Maxwellian electron-energy distribution functions (EEDFs) can be produced (Fig.9). Since the peak electron energy is about 2.5 eV (electron temperature T_e: 2.5 eV) in the UHF fluorocarbon gas plasma, the C-I bond of about 2.4 eV and the C=C bond of 2.8 eV are selectively dissociated from CF_3I and C_2F_4, whereas the C-C bond of 4.3 eV and C-F bond of 5.6 eV remains unbroken because of their much higher bond energies.

In the experiment reviewed here, the gas flow rate was 100 sccm, the pressure was 5 mTorr and the UHF power was 1 kW. The ability of the new gas chemistries to suppress charging damage was evaluated by observing the charge-up damage that occurred during the contact-hole etching for an NMOSFET with a poly-Si antenna (Fig.10). The gate oxide thickness was 4.5 nm. The antenna ratio was defined as the ratio of total contact area to the gate oxide area and was changed from 5.36 to 997. The gate oxide leakage current and the charge-to-breakdown (Q_{bd}) were measured.

The measured radical densities in the CF_3I and C_2F_4 plasmas show that they are more efficient sources of CF_3 (CF_3^+) and CF_2 radicals than are the conventional C_4F_8 (C-C bond) and C_2F_6 (C-C bond) plasmas (Fig.11a). The C-I and C=C bonds respectively dissociates 6 times and 3.6 times more easily than do C-C bonds. We also found that the density ratios of CF_2 and CF_3 (CF_3^+) could be independently controlled by changing the gas-flow ratio of the CF_3I and C_2F_4 mixture (Fig.11b). Additionally, the CF_3I (more than 20%) /C_2F_4 mixture plasma had a high plasma density of over 1×10^{11} cm^{-3}, whereas conventional C_4F_8 plasma density saturated at 5×10^{10} cm^{-3}. This suggests that the addition of CF_3I contributed in increasing the ion density because the ionization thresholds of I^+ (9 eV) and CF_3^+ (10 eV) ions from CF_3I are lower than the ionization thresholds of CF_2^+ ions (16.4 eV) from C_4F_8. These results suggest that a high-density of CF_3^+ ions (more than $10^{11}cm^{-3}$) and CF_2 radicals were generated in the gas mixture containing CF_3I and C_2F_4. Increasing the C_2F_4 gas flow rate greatly improved the etching selectivity for SiO_2. A selectivity greater than 20 was obtained when the gas mixture contained 80% C_2F_4 (Fig.12). Under this condition, the rate of thermal SiO_2 etching was 4000-5000 A/min, about twice than that obtained with a conventional Ar (80%)/C_4F_8 gas. We think the high etching rate and the high selectivity are due to the balance between the SiO_2 etchant CF_3^+ and the CF_2 that play a important role in polymerization. A highly anisotropic 0.05 μ m contact-hole etching profile of more than 88 degrees was achieved while maintaining a high etching rate (BPSG: 7000 A/min) and high SiO_2 etching selectivity of more than 50 to the underlying-Si without any pattern size dependence in the C_2F_4/CF_3I plasma (Fig.13).

The new gas chemistries also suppressed the charge-up damage during the over-etching of the contact holes because of the lower electron temperature and larger amount of negative ions (I^-). In the conventional C_4F_8/Ar (80%) gas plasma, however, gate oxide degradation (in gate leakage current and Q_{bd}) was observed for higher antenna ratios (Fig.14). The Ar dilution increases T_e (3-4 eV) and eliminates negative ions because of the higher ionization threshold of Ar (16eV) even in the UHF plasma. That is, the number of higher-energy electrons is increased by Ar dilution.

The new radical injection method reviewed here provides both a high etching rate and high selectivity during the formation of contact-holes because CF_2 and CF_3 radicals are efficiently generated from the CF_3I and C_2F_4 gas mixture. This gas mixture also reduces charge-up damage during the over-etching of high-aspect contact holes. Additionally, these gases are alternatives to perfluorocarbon gases (C_4F_8 etc.) from an environmental viewpoint, because they have very short lifetimes in the atmosphere.

4.Conclusion

The pulse-time-modulated plasma described here makes possible charge-up-damage-free etching for Al electrode patterning because a large quantity of negative ions with a low-electron temperature are produced during the afterglow in the pulsed plasma. And the new radical injection method also described here make possible high-performance SiO_2 patterning using gas mixture of C_2F_4 and CF_3I by controlling polymerization and etching independently through the selective generation of CF_2 and CF_3 radicals in the UHF plasma. These etching technologies are very promising candidates for future ULSI patterning.

5.References

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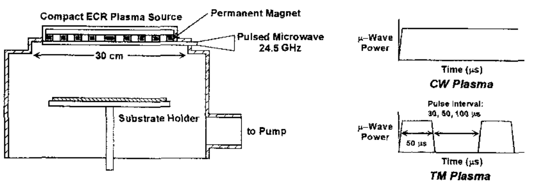

Fig. 1. Schematic of ECR plasma source. In the pulse-time modulated (TM) plasma, the pulse interval of the μ -wave power is varied from 30 μ sec to 100 μ sec, and the pulse width is set at 50 μ sec

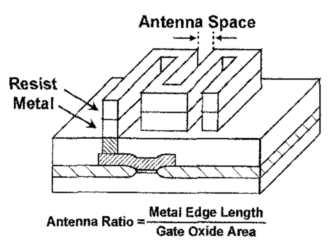

Fig. 2. Antenna MOSFET with edge intensive metal antenna. Antenna space ranges from 0.4 m μ to 3.0 μ m.

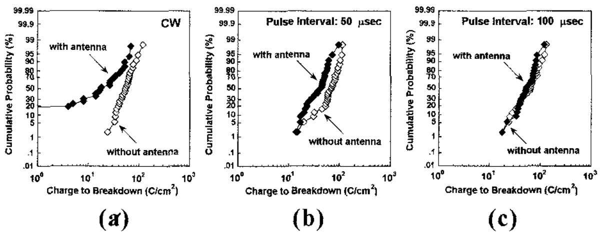

Fig. 3. Cumulative probability of the charge-to-breakdown of MOSFETs with and without antenna (space=0.4 μ m, antenna ratio=188 K, gate oxide area=0.34 μ m^2) for (a) CW plasma, (b) TM plasma with pulse interval of 50 μ sec, and (c) TM plasma with pulse interval of 100 μ sec. The measurement was performed at 25°C.

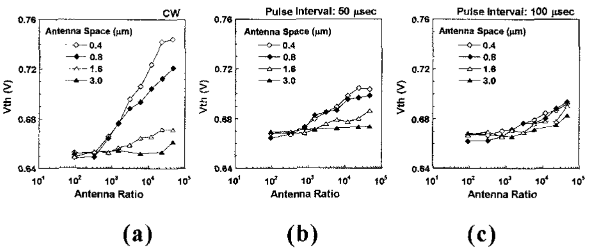

Fig. 4. Threshold voltage of antenna MOSFETs as a function of the antenna ratio for (a) CW plasma, (b) TM plasma with a pulse interval of 50 μ sec, and (c) TM plasma with pulse interval of 100 μ sec. The antenna space was varied from 0.4 to 3.0 μ m.

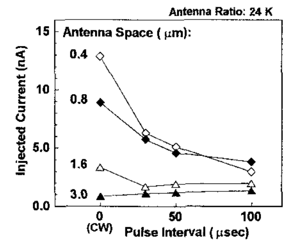

Fig. 5. The amount of current injected from the plasma to the metal antenna. The antenna edge length is 80 mm, which corresponds to the antenna ratio of 24 K. The gate oxide area is 3.4 μ m^2.

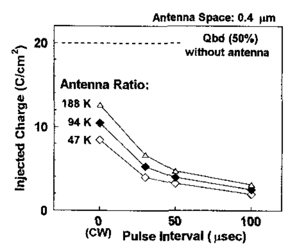

Fig. 6. The amount of injected charge per unit area of the gate oxide. The gate oxide area is 0.85 μ m^2. The median value of Qbd without antenna (at 100°C) is indicated in a broken line.

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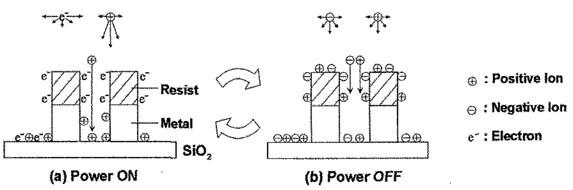

Fig.7. Suppression mechanism of topography-dependent charging during power and off periods in pulse-time-modulated plasma

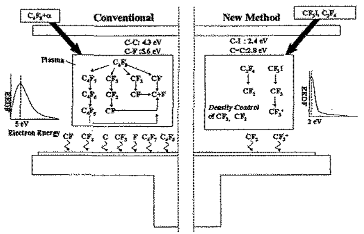

Fig. 8. The concept of new radical injection method. The CF_2 and CF_3 radical are selective generated from CF_3I and C_2F_4 gases in the plasma.

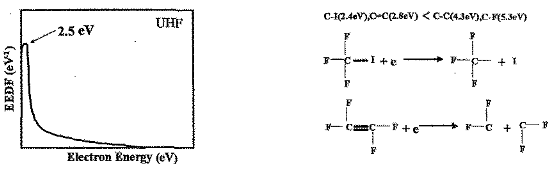

Fig. 9. Electron energy distribution function (EEDF) in UHF plasma. The C-I bond of CF_3I and the C=C bond of C_2F_4 are selectively dissociated in the UHF plasma.

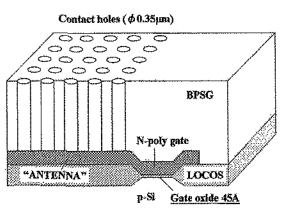

Fig.10. NMOSFET with a contact-hole antenna for measurements of charging damages during oxide etching (antenna ratio: 5.36 to 997).

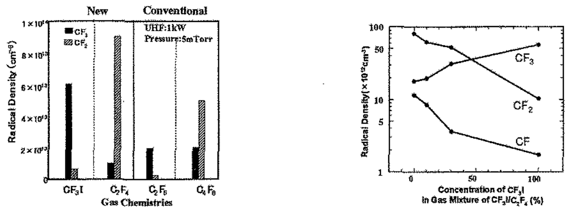

Fig. 11. (a) CF_3 and CF_2 radical density in CF_3I, C_2F_4, C_2F_6 and C_4F_8 UHF plasmas at the same discharge condition. CF_3I and C_2F_4 were good sources of CF_3 and CF_2 radicals, respectively. (b) The density ratios of CF_2 and CF_3 could be independently controlled by changing the gas-flow ratio of the CF_3I and C_2F_4 mixture in the UHF plasma.

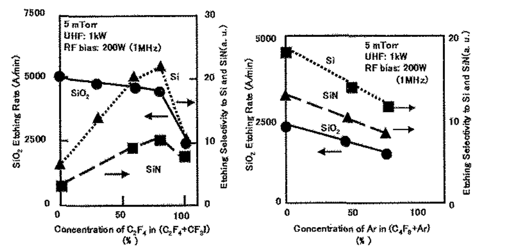

Fig. 12. SiO_2 etching rate and etching selectivity to Si (poly-Si) and SiN in the CF_3I /C_2F_4 gas mixture and C_4F_8/Ar gas mixture when RF bias of 200 W was supplied on the substrate. The sample was bare wafer.

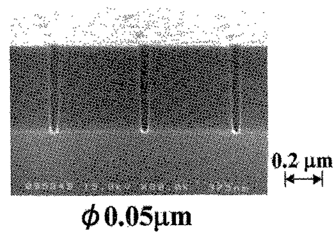

Fig. 13. A highly anisotropic 0.05 μ m contact-hole etching profile (Aspect ratio:10) in $C_2F_4/CF_3I(20\%)$ plasma.

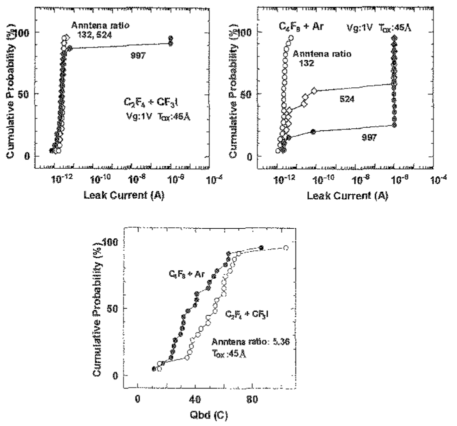

Fig.14. Leakage current and charge-to-breakdown of gate oxide in NMOSFET when the contact hole etching was carried out with CF_3I/C_2F_4 (80%) and C_4F_8/Ar (80%) gas.

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