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CHARACTERISITCS OF CHLORINE IND DUCTIVELY COUPLED PLASMAS AND THEIR SILICON ETCH PROPERTIES

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ABSTRACT

Chlorine containing high density plasmas are widely used to etch various materials in the microelectronic device fabrication. In this study, the characteristics of inductively coupled Cl_2 (O_2/N_2) plasmas and their effects on the formation of silicon etching have been investigated using a Langmuir probe, quadrupole mass spectrometry(QMS), X-ray photoelectron spectroscopy(XPS), and Scanning Electron Microscopy(SEM). The addition of oxygen for chlorine plasmas reduced ion current densities and chlorine radical densities compared to the nitrogen addition by the recombination of oxygen with chlorine.

Also, when silicon is etched in Cl_2/O_2 plasmas, etch products recombined with oxygen such as $SiCl_xO_y$ emerged. However, when nitrogen is added to chlorine, etch products recombined with nitrogen or Si-N bondings on the etched silicon surface were not found. All the silicon etch characteristics were dependent on the plasma conditions such as ion density, radical density, etc. As a result submicron vertical silicon trench etch profiles could be effectively formed using optimized etch conditions for Cl_2/O_2 and Cl_2/N_2 gas combinations.

INTRODUCTION

Chlorine containing plasmas are widely used to etch various materials such as silicon, metal, silicides, Ⅲ-V compounds, etc.(1-3) Pure chlorine plasmas, however, have some problems in silicon trench etching. Etched trench profiles often deviate from ideal sidewall profiles and the selectivity of silicon with respect to mask layer or photoresist is not often as high as desired. As plasma sources suitable to this diverse applications, high density plasma sources for dry etching are considered to meet the manufacturing challenges posed by advanced devices. High density plasma sources such as electron cyclotron resonance(ECR) plasma,(4.5) helicon wave plasma,6) inductively coupled plasma (ICP),7.8) and helical resonator9) were studied by many researchers and they have higher density plasmas at low pressure, higher ionization ratios, and more controllable ion energies. Currently, various high density plasma sources are actively studied for semiconductor processing. Silicon etching processes including polysilicon etching and single crystal-line silicon etching have been applied to semiconductor integrated circuit processing for many years. Most of the studies of silicon etching using high density plasmas are concentrated on the polysilicon etching of gate structures in semiconductor integrated circuits. Only a few publications using Cl_2 based high density plasmas by ECR[4,5] or HR[9] can be found for silicon trench etching that can be applied to the device isolation, trench capacitors, or micro-electromechanical systems (MEMS).[10,11] Although chlorine high density plasmas are widely utilized in the diverse range of semiconductor processing, their effects on the etch properties applied to silicon trenches are not well understood.

On the other hands, characteristics of the plasmas measured by plasma diagnostic tools such as a mass spectrometer, an optical emission spectroscope, a Langmuir probe, etc. can be used to understand the etch rates and selectivities and can be also helpful for the understanding of the change of etch profile of silicon trenches.

The purpose of this work was to study the characteristics of inductively coupled chlorine based plasmas for trench etching of single crystal silicon. As additive gases to chlorine plasmas, oxygen and nitrogen was used to reduce the sidewall etching of silicon trenches, and the effects of the additive gas on the characteristics of plasmas, sidewall residue formation, and submicron trench profile were investigated.

EXPERIMENTAL PROCEDURE

Etching was performed in a planar inductively coupled plasma etcher shown in Figure 1 using a chlorine-based gas mixed with oxygen or nitrogen of 0-20% at 5mTorr. High density discharges are generated with 13.56 MHz rf power by inductive coupling of a plasma source coil to the gas in the process chamber. The coupling occurs through a 1cm-thick quartz window which forms the top of the process chamber.

A small dc bias voltage is generated at the wafer surface by a second 13.56 MHz rf power source which drives the lower electrode. Inductive power was varied from 200 to 800 Watts, and dc self-bias voltage from 0 to 80 volts. The dc-self bias voltage was measured using a high voltage probe (Tektronix P6015A).

A quadrupole mass spectrometry(QMS; Balzers QMG/E 125) located at the sidewall of the process chamber was used to monitor the species such as dissociated radicals and etch products in the plasmas. A single Langmuir probe was also inserted at the center of the chamber to estimate ion densities

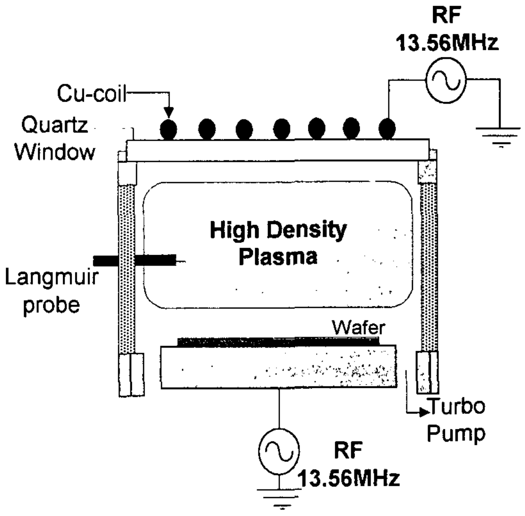


Fig. 1. Schematic diagram of the planar inductively coupled plasma(ICP) reactor used in this experiment.

of the plasmas. X-ray photoelectron spectroscopy(XPS; Fison Surface Systems ESCALAB 220i) has been used to estimate the residues remained on silicon trenches after the etching for different gas combinations and bias voltage conditions. To investigate the effects on silicon etch rates and selectivities over SiO_2 mask layer of the various process parameters such as inductive power, bias voltage, gas combination, etc., 1 μm-thick undoped polysilicon and 0.3μm-thick oxide grown on silicon wafers were etched respectively in the same etch conditions. Etch rates and selectivities were estimated using a Nanospec by measuring the thickness of the films before and after the etching. From this basic etch results, some process conditions for silicon trench etching were selected. To etch silicon trenches, a 0.3μm-thick thermal oxide grown on silicon wafers were patterned with a photomask and etched to make layers after removing the photoresist. After silicon trench etching, scanning electron microscopy (SEM) was used to observe the silicon trench profiles.

RESULTS AND DISCUSSION

In our study, a single Langmuir probe and a quadrupole mass spectrometer have been used to characterize chlorine based inductively coupled plasmas. The Langmuir probe was biased at-40 volts to collect ion currents and ion current densities used as a measure of ion densities.[8] Figure 2 shows the measured ion current densities as a function of inductive power for 10% additive gas combinations. As the inductive power increased, the ion current density increased almost linearly, however, the addition of oxygen or nitrogen to chlorine reduced the ion current densities. Also, the addition of nitrogen showed the higher ion current densities compared to that of oxygen for the same percentage of the additives. Even though ionization energy for nitrogen is the highest among oxygen(13.6eV), nitrogen (14.5eV), and chlorine(12.9eV), lowest ion current densities for the Cl_2/O_2 plasmas appear to be related to higher electronegativity compared to nitrogen

Figure 3 shows the effects of inductive power on the chlorine radical densities measured by QMS for the same conditions as Figure 2. Increase of inductive power increased radical densities, however, oxygen added chlorine plasmas also showed the lowest chlorine radical densities. The chlorine radical density was reduced not only by the reduction of chlorine gas density at the same pressure by the addition of oxygen but also by

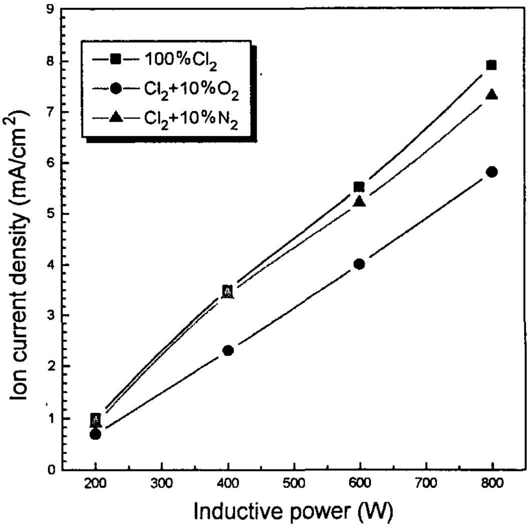


Fig. 2. Ion current densities measured by a Langmuir probe as functions of inductive power for 100% Cl_2, Cl_2+10% O_2, and Cl_2+10%N_2 plasmas at 5 mTorr.

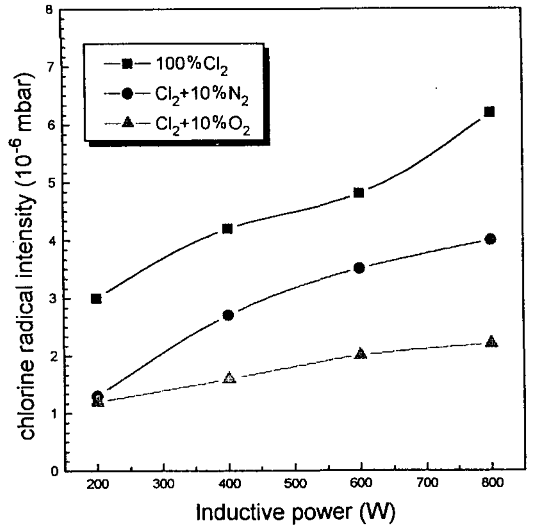


Fig. 3. Cholorine radical species measured by QMS as a function of inductive power for the same conditions of Fig. 2

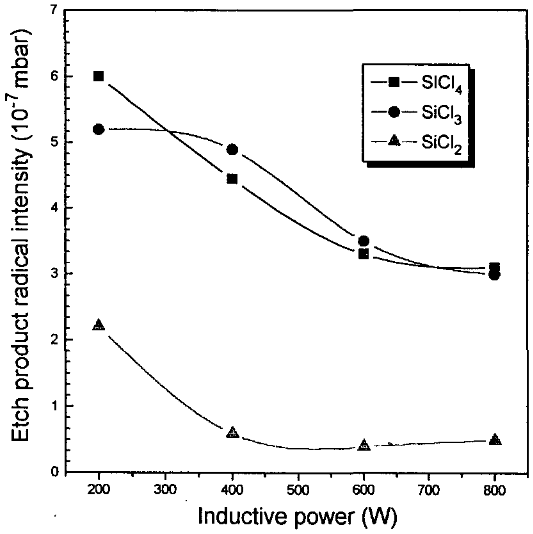


Fig. 4. Etch product radical species as a function of inductive power for 100% Cl_2 planmas.

the re-combination of chlorine radicals with oxygen atoms in the plasma. From the QMS analysis for the inductive power over 600W, the mass peak corresponding to Cl_2O was observed even though it is not the same species such as ClO_X- reported by other researchers while operating oxygen contained chlorine plasmas. In case of Cl_2/N_2 plasmas,[12] no such recombined species were found and only feed gases and their radicals were observed.

When the plasmas were observed using QMS during etching silicon, other species related to silicon etch byproducts were also observed and is shown in Figure 4 for 100% chlorine plasmas as a function of inductive power. Main etch products were SiClx (x=2, 3,4) and the most abundant species was $SiCl_3$ or $SiCl_4$ depending on process conditions. As the inductive power increased, the SiClx etch products decreased, and it is probably due to the increased redissociation of the etch products at higher inductive power conditions.[5, 9]

As oxygen is added to chlorine plasmas, new etch products such as $SiCl_xO_y$ are observed in accordance with other researcher's results[11-13] and, at the same time, the total amounts of $SiCl_xO_y$ such as $SiCl_2O$, $SiClO_3$, and $SiClO_2$ within the mass range limit (200amu) increased with the increase of added oxygen percentage.[14,15] Also, $SiCl_2$ became the most abundant etch product while other main radicals such as Cl, $SiCl_3$, and $SiCl_4$ are reduced. When silicon is etched in nitrogen added chlorine plasmas, nitrogen radical itself was observed and no other etch products recombined with nitrogen radical were observed, and the plasmas were similar to the 100% chlorine plasmas.

Figure 5 shows Si 2p narrow scan XPS data for silicon surfaces etched in Cl_2(a), $Cl_2/15\%O_2$(b), or $Cl_2/15\%N_2$(c) plasmas with- and without -40volts of applied dc self bias voltage. Differences of the residue composition with and without bias voltages(or ion

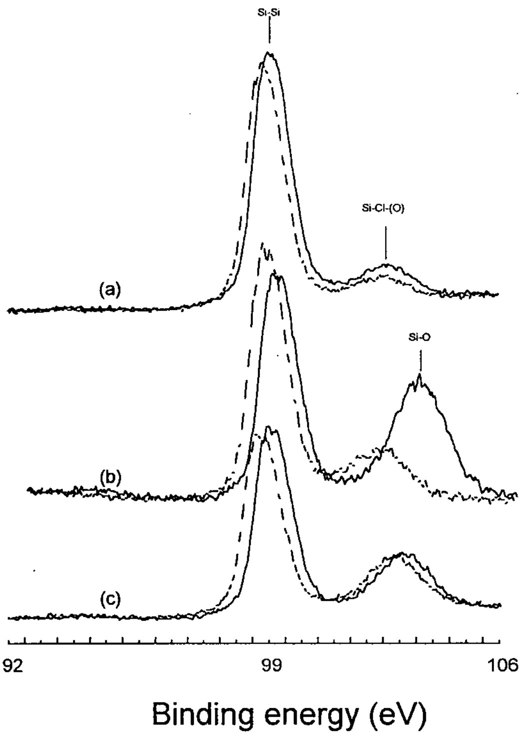


Fig. 5. Silicon 2p narrow scan data measured by XPS on the silicon surfaces etched by (a) Cl_2+15%N_2, and (c) Cl_2+15%N_2 discharges with(solid line) and without(dotted line)-40 volts of applied dc selfbias voltage and at 600Watts of inductive ppwer.

bombardment energy) can be related to the chemical states of the silicon surfaces at the bottom and the sidewall of the silicon trenches, respectively. Si-Si(99.5eV) and Si-Cl-O (102.5eV) bond peaks measured for silicon etched with -40volts of dc bias voltage are similar to those for silicon without dc bias voltage for the pure Cl_2 case. In case of silicon etched in Cl_2/O_2 plasmas without applied dc bias voltages show another peak at 103.5eV corresponding to Si-O bondings. However, silicon etched with -40volts of dc bias voltage in the Cl_2^+ 10%O_2 plasma did not show the peak corresponding to Si-O bondings and the silicon 2p peak shape was similar to that of 100% chlorine. This result is considered to be from the reduction of the residue layer by enhanced ion bombardment. In case of silicon etched in Cl_2/N_2 plasmas, no peaks were found corresponding to Si-N, and peak shapes were similar to those of 100% chlorine plasmas and there were no significant differences in peak areas found between with and without applied bias voltages.

From the separate work condcted in our experiments,[14] it is considered that oxygen found on the silicon etched in 100% Cl_2 plasmas or Cl_2/N_2 plasmas is possibly not only from the exposure to air before the XPS analysis but also from the quartz window erosion during the silicon etching with a planar ICP as reported by other researchers for HR for silicon etching[16] or for ICP during oxide etching.[17] Therefore, the presence of oxygen on the etched silicon wafers is inevitable even though no oxygen was added to the feed gas combinations, but the degree of erosion has decreased with the increase of bias voltage.

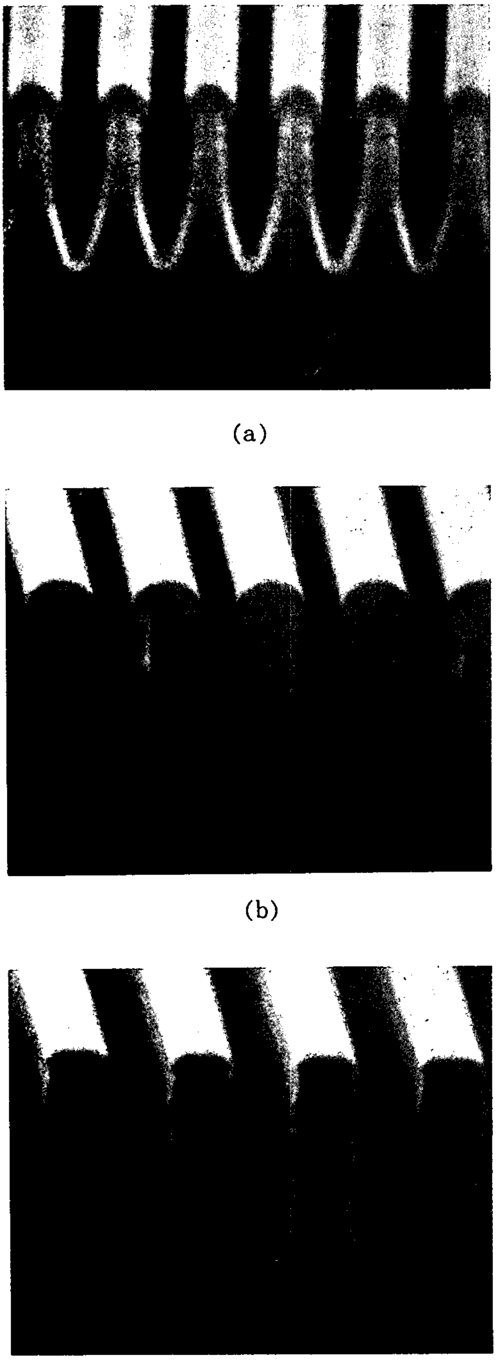
Polysilicon etch rates increased with the increase of inductive power, however, the etch selectivity over oxide mask layer decreased. For example, polysilicon etch rates increased from 800Å/min to 1700Å/min as the inductive power increased from 200 to 600 Watts in the 100% Cl_2 plasmas. The maximum etch selectivity could be obtained by lowering bias voltages but the decrease of the bias voltage reduced the anisotropy of the etch profile.[15] As oxygen or nitrogen is added to chlorine, the silicon etch rates decreased due to the reduction of chlorine ions and radicals available for silicon etching as shown in Figure 2 and 3, however, decreased at much faster rates for Cl_2/O_2 plasmas compared to the Cl_2/N_2 plasmas, which is possibly due to less chlorine ions and radicals for oxygen added plasmas as shown in Figure 2 and 3, and also possibly due to the recombination of oxygen with silicon as shown in XPS data of Figure 5. The etch rates of the thermal oxide were also decreased with the addition of oxygen or nitrogen, and the etch rates for the oxygen added plasmas were much smaller than those for Cl_2/N_2 plasmas. Therefore, silicon etch selectivities over thermal oxide were higher for Cl_2/O_2 plasmas. When nitrogen was added, the etch selectivity decreased linearly with the increase of nitrogen addition, however, when the oxygen was added, the etch selectivity showed a maximum in the range of oxygen percentage of 10-15% and it is probably related to the formation of Si-O bonding on the silicon surface at a certain oxygen percentage under a fixed bias voltage as described above.

The addition of O_2 and/or N_2 to Cl_2 plasmas reduces the sidewall etching of silicon trenches by the sidewall passivation or by the lack of the chlorine radicals on the sidewall. Etched silicon trenches were observed using SEM and the effects of additive gases on silicon submicron trench profiles are shown in Figure 6 for 600 Watts of inductive power and -40 volts of dc self bias with 100%Cl_2 (a), Cl_2/5%O_2(b), or Cl_2/N_2(c). When silicon trenches were etched, the characteristics of Cl_2/N_2 and Cl_2/O_2 plasmas changed the thickness of sidewall residue and trench profiles. Thick sidewall residue were formed for Cl_2/O_2 plasmas at the higher oxygen percentage, while no sidewall residues were found for Cl_2/N_2 plasmas. Vertical submicron (0.3~0.4㎛) trench profiles could be obtained by controlling the residue thickness formed on the trench sidewall using Cl_2/N_2 or Cl_2/O_2 plasmas.

CONCLUSIONS

Characteristics of inductively coupled chlorine-based plasmas (Cl_2, Cl_2/N_2, and Cl_2/O_2) and their effects on the silicon etching processes were investigated. Ion current density measured by a Langmuir probe and Cl radical density observed by QMS decreased with the addition of nitrogen or oxygen, however, the addition of oxygen to chlorine reduced the ion current density and the Cl radical density more significantly compared to the nitrogen addition by the recombination of oxygen with chlorine. When silicon is etched, oxygen in chlorine plasmas also changed main etch products to $SiCl_2$ from $SiCl_3$ or $SiCl_4$ and other etch products recombined with oxygen such as SiClxOy emerged. However, nitrogen in chlorine plasmas did not recombine with chlorine nor recombine with etch products. XPS analysis of the silicon surfaces etched with or without bias voltages in Cl_2/N_2 or Cl_2/O_2 plasmas showed that silicon surfaces etched with or without bias voltage in Cl_2/N_2 plasma are similar each other, while the silicon surfaces etched in Cl_2/O_2 plasmas are not. A peak related Si-O bindings corresponding to a passivation layer was found without bias voltages for Cl_2/O_2 plasmas.

All the silicon etch characteristics were dependent on the plasma conditions. In addition, for Cl_2/O_2 plasmas, the interaction between oxygen in the plasmas and silicon surface,



(a)

(b)

(c)

Fig. 6. SEM micrographs of the submicron silicon trenches etched by (a) Cl_2, (b) Cl_2 +5% O_2, and (c) Cl_2+10% N_2 plamas at 600Watts of inductive power and -40 volts of applied dc self bias voltage.

during the etching has profound effects on the etch characteristics. The addition of O_2 and/or N_2 to Cl_2 plasma reduces the sidewall etching of silicon trenches by the sidewall passivation or the lack of the chlorine radicals on the sidewall. When silicon trenches were etched, the characteristics of Cl_2/N_2 and Cl_2/O_2 plasmas changed the thickness of sidewall residue and trench profiles. Thick sidewall residue were formed for Cl_2/O_2 plasmas at the higher oxygen percentage, while no sidewall residues were found for Cl_2/N_2 plasmas. Vertical submicron trench profiles could be obtained by controlling the residue thickness formed on the trench sidewall using Cl_2/N_2 or Cl_2/O_2 plasmas.

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