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Dry etching of polysilicon with high selectivity using a chlorine-based plasma in an ECR reactor

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Abstract

Halogen-bearing gases have proved to be useful plasma discharge etchants for the fabrication of sub-micron poly-Si gate structures. In this paper, investigations of chlorine-based plasmas generated by an electron cyclotron resonance (ECR) reactor for poly-Si etching is studied. The influences of added oxygen, microwave power and RF power on etching characteristics are discussed. In addition, the etching mechanisms of the underlying oxide are developed. Finally, the $Cl_2/HBr/O_2$ mixed system is examined. The combined plasma exhibits the features of high selectivity, high anisotropy and high etching rate.

Keywords: Chlorine-based plasmas; Electron cyclotron resonance; Polysilicon etching

1. Introduction

As device geometries shrink to the sub-micron level and topographies get more complex, process conditions are becoming increasingly critical. To improve the device performance and yield, the requirements for poly-Si etching include high etching rate, high selectivity, vertical profile and low etch-induced damage. In conventional reactive ion etching (RIE), high RF power is used to achieve high plasma density and high ion energy. Therefore, a high etching rate and vertical profile are obtained. However, the high-energy ions cause problems such as low selectivity to the mask material and to the underlying oxide as well as induce damaged lattices in the oxide during overetching time. In this work, the chlorine-based plasmas generated by electron cyclotron resonance (ECR) were used for poly-Si etching. The ECR source offers a number of processing advantages at the sub-micron level. It produces a high plasma density that results in a high etching rate and separates control of the plasma density and the energy of the ions that can sustain high selectivity and low etch-induced damage simultaneously. In addition, by controlling the RF bias of the wafer, excellent etching behavior can be achieved.

In this paper, chlorine-containing (e.g., Cl_2, Cl_2/O_2 and $Cl_2/HBr/O_2$) gaseous systems have been developed. The etching behavior of poly-Si, oxide and photoresist are investigated and the etching mechanism of oxide is established. The influences of three etching parameters, the feed oxygen concentration, the microwave power and RF power, on the etching features are also discussed. Finally, the $Cl_2/HBr/O_2$ mixed system was studied. Experimental results confirm that this combined plasma is one approach for satisfying the requirements of high etching rate and high selectivity as well as precise pattern width control for ULSI circuit delineation.

2. Experimental

The ECR reactor used in this study was an ANELVA ECR-6001 system, as shown in Fig. 1. The microwave power (2.45 GHz) is delivered through a wave guide structure with one moving short-circuit for impedance matching. The magnetic field of 875 G, necessary to reach electron cyclotron resonance, is pro-

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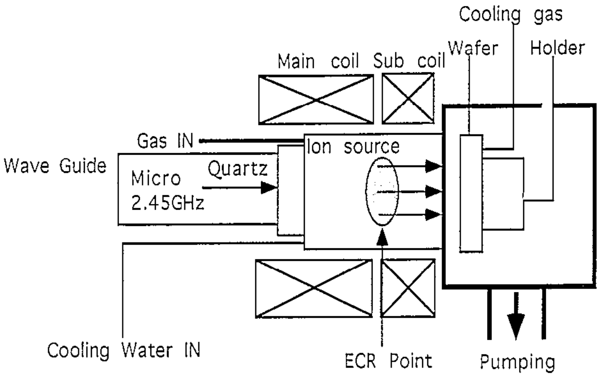


Fig. 1. A schematic diagram of the experimental apparatus.

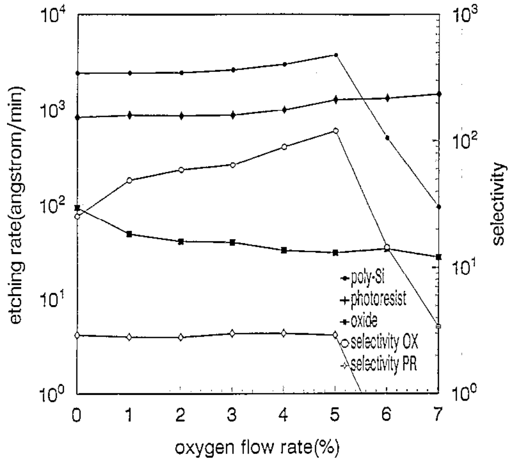


Fig. 2. The etching characteristics of Cl_2 plasma with various added oxygen flow rates. The total flow rate is 100 sccm, pressure = 3 mtorr, microwave = 250 W and RF power = 35 W.

duced by the main coil. The sub coil is used to control the uniformity of plasma fluxes arriving on the wafer surface, and cooling is performed by N_2 gas with a 10 sccm flow rate to maintain the wafer temperature during etching. The RF power is 400 kHz for wafer biasing. The undoped poly-Si is formed in a tubular furnace by low pressure chemical vapor deposition (LPCVD) under the following conditions: temperature 625 °C, pressure 560 mtorr, feed gases SiH_4/H_2, deposition time 100 min (6500 Å), and substrate material 6 in. poly-Si(100) wafer with a 1000 Å gate oxide. The oxide samples were prepared by wet oxidation at 980 °C. The photoresist samples were bare silicon coated with FH-6400L.

Prior to the main etching step, the native oxide residues on the poly-Si had to be removed to facilitate an accurate etching process. Hence, a preliminary etching step was required. The currents applied to main and sub coils were 21 and 11 A. The microwave power was 250 W, the chamber pressure was 3 mtorr and the RF power was 70 W (i.e., it caused 210 V of $V_{d.c.}$). The etchants were Cl_2/O_2 gaseous mixture with 95/5 sccm and the time was 7 s. Thus, an oxide-free surface was obtained. For analysis, Nanospec/AFT, scanning electron microscopy (SEM) and secondary ion mass spectrometry (SIMS) were employed as tools to examine the etching rates of poly-Si, oxide and photoresist, the etching profiles and the composition of the post-etched surface, respectively. In addition, an FTIR microscope was used to scrutinize the plasma-induced polymers that were deposited on the surface.

3. Results and discussion

Fig. 2 shows the etching characteristics of Cl_2 etchant with various added oxygen concentrations; the poly-Si etching occurs in pure chlorine plasma (i.e., added oxygen = 0%) because the strength of the Si–Si bonds (54 kcal mol^{-1}) is weaker than that of the Si–Cl bonds (109 kcal mol^{-1}). It is noted that when low level oxygen (< 5% of total flow rate) is added, the etching rate of poly-Si increases with increasing O_2 concentration. This is because of the deposition of a silicon oxychloride film on the reactor. This film is formed by the reaction between etching products ($SiCl_x$) and added oxygen that eliminates the Cl radical loss through surface recombination [1–4]. Therefore, it promotes the concentration of Cl radicals and leads to an improved poly-Si etching rate. The etching rate and selectivity reach a maximum when the feed O_2 is at about 5% of the total flow rate. Nevertheless, an excess of oxygen will oxidize the poly-Si surface and thus suppress poly-Si etching. In addition, the photoresist etching rate rises with increasing O_2 flow rate. This is caused by the higher oxygen concentration eroding the photoresist faster.

When the devices are scaled down for ULSI applications, the gate oxide thickness is typically less than 150 Å. The selectivity to underlying oxide during overetching time plays a very important role in the electrical properties of the devices. Equally, the oxide etching mechanism determines selectivity and gives predictions on the performance of devices. As a result, in this study, detailed discussions of the oxide etching mechanism are emphasized. Previous studies [5,6] state that the oxide etching rate is related to the amount of silicon chlorides produced during etching of poly-Si and to the electrically polarized level of these products when they are deposited on the oxide surface. As shown in Fig. 3, the lower-order silicon chlorides such as SiCl and $SiCl_2$ connect with O atoms in solid SiO_2 by Coulomb force, since both silicon chlorides and SiO_2 are electrically polarized. The Si–O bond strength in solid SiO_2 (108 kcal mol^{-1}) is weaker than that in a diatomic molecule (188 kcal mol^{-1}) composed of a silicon atom from the silicon chloride and an O atom from SiO_2. Consequently, the O atom in SiO_2 is removed by the silicon chlorides and the silicon oxychloride is formed. Hence

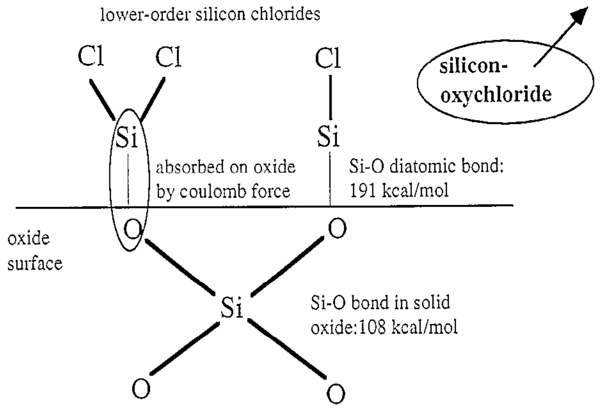


Fig. 3. A schematic diagram of the oxide etching mechanism.

oxide etching occurs. Moreover, the feed oxygen can diminish the probability of low-order silicon chlorides (reactive etching species) reacting with the O atom in solid SiO_2. Therefore, the oxide etching rate decreases with increasing amount of added oxygen, as shown in Fig. 2. In addition, based on previous descriptions, the influences of the carbon-containing species on oxide etching behavior are also studied. We infer that the low-order silicon chlorides are not the only etching species that cause oxide etching. A large amount of carbon-containing species (e.g., CO, COCl, C_xCl_y, etc.) come from the reaction between the photoresist and the diversified radicals in the plasmas by the etching process. These species are also electrically polarized and can be adsorbed on the oxide surface by Coulomb force. The bond strength of a diatomic molecule C–O (256.7 kcal mol^{-1}) is much larger than that of a Si–O bond in solid SiO_2 (108 kcal mol^{-1}). Accordingly, we think that the existence of carbon during the overetching period plays a more important part than those low-order silicon chlorides in the oxide etching mechanism. Experimental proof is indicated in Table 1. The oxide samples with 90% coverage of photoresist give a higher etching rate than those with 50% coverage of photoresist. Also, the blanket oxides (i.e., carbon elimination) have the lowest etching rate, which leads to the highest selectivity.

Fig. 4 reveals the effect of the microwave power on etching characteristics. The etching rates of poly-Si, oxide and photoresist first increase with increasing microwave power, because the concentrations of Cl radicals and ions are proportional to the input power. However, excessive power induces a drastic decrease in etching. It is estimated that the high microwave power enhances the impact dissociation rate ($e^- + O_2 \rightarrow O + O + e^-$) of added oxygen in the plasma. The amounts of silicon oxychloride increase rapidly, because the excess O atoms react with the reactive etching species and are deposited on the etched materials. Thus the etching process is decompressed. It is clear that the etching rates decrease even down to negative values at 500 W of microwave power, because the deposition rate of the silicon oxychloride is faster than that of the etching step. To verify our speculation, we examined the difference of SIMS signals between the clear oxide and the post-etched oxide with 500 W of microwave power, as shown in Fig. 5. It shows that the obvious signals of Cl and O exist in the oxide treated with 500 W of microwave power (i.e., sample b) which comes from the deposited silicon oxychloride film. Another analysis, done by FTIR microscope, is shown in Fig. 6 ((a) is clean oxide and (b) is the oxide exposed under 500 W of microwave power). There is an expanded stretch toward larger wavenumbers from the main peak (1090 cm^{-1}) in sample (b). It is due to the existence of electrically negative back bonds (Cl–O–Si) in the Si–O–Si structures. In addition, Fig. 7 shows the effect of RF power on the etching features. The etching rates of poly-Si and photoresist rise with rising RF power. Nevertheless, the oxide shows a clear jump when RF reaches 50 W. It is surmised that this is caused by the following mechanism: At lower RF power (< 50 W), the energies of energetic ions accelerated by RF biasing are not high enough to break the Si–O bonds (109 kcal mol^{-1}) in the SiO_2. Hence, the ion bombardment plays an insignificant role in oxide etching, and the etching rate is about four times smaller than that at the high

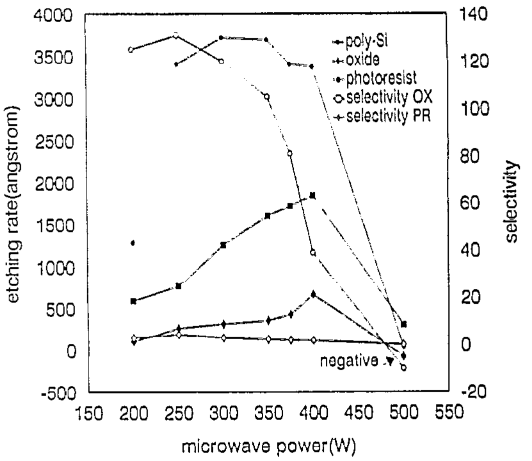
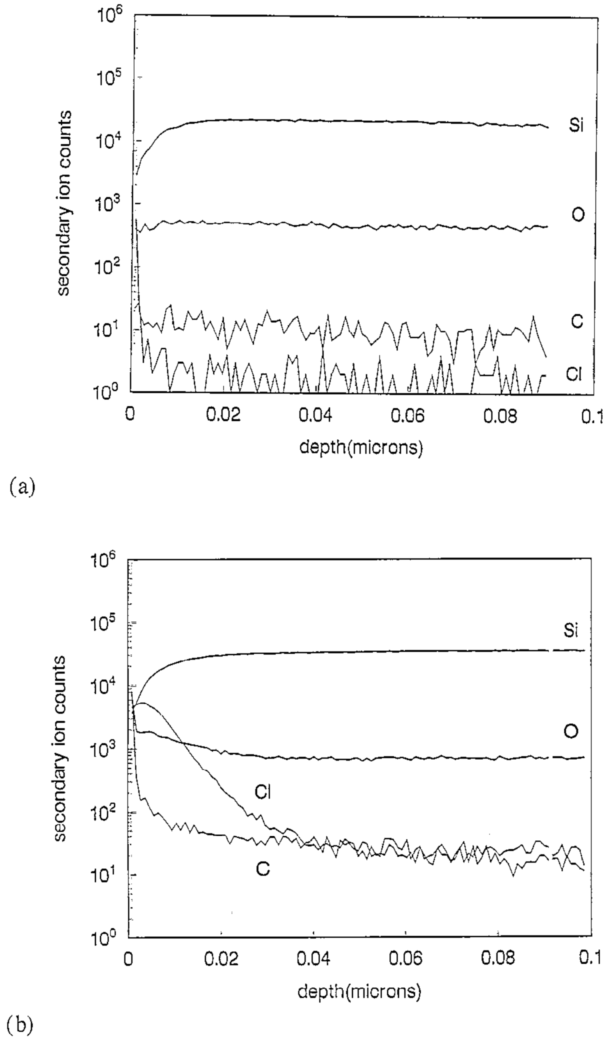


Fig. 4. The etching characteristics of Cl_2/O_2 plasma with various microwave powers. Flow rate of Cl_2/O_2 is 95/5 sccm, pressure = 3 mtorr, RF power = 35 W.

Table 1
The influence of carbon-containing species on the oxide etching mechanism

	Blanket oxide	Photoresist coverage oxide	
		50%	90%
Etching rate (Å min^{-1})	35	41	49



(a)

(b)

Fig. 5. The SIMS signal of two different samples: (a) the clean oxide; (b) the oxide etched under the following conditions: flow rate of Cl_2/O_2 is 95/5 sccm, pressure = 3 mtorr, RF power = 35 W, microwave = 500 W, etching time = 9 min. It causes a 200 Å thick layer deposit on the oxide surface.

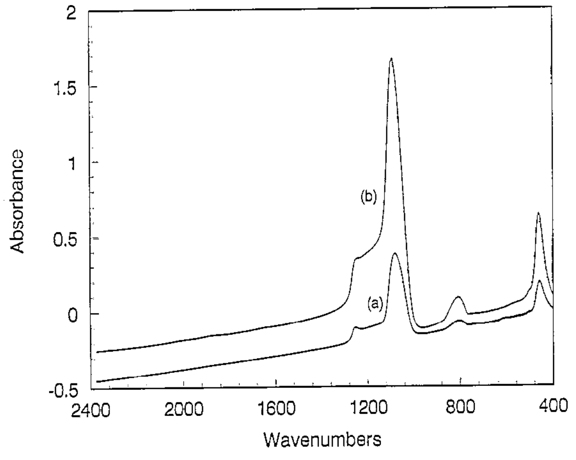


Fig. 6. The FTIR signals of two different samples: (a) the clean oxide; (b) the oxide etched under the following conditions: flow rate of Cl_2/O_2 is 95/5 sccm, pressure = 3 mtorr, RF power = 35 W, microwave = 500 W, etching time = 9 min. It causes a 200 Å thick layer deposit on the oxide surface.

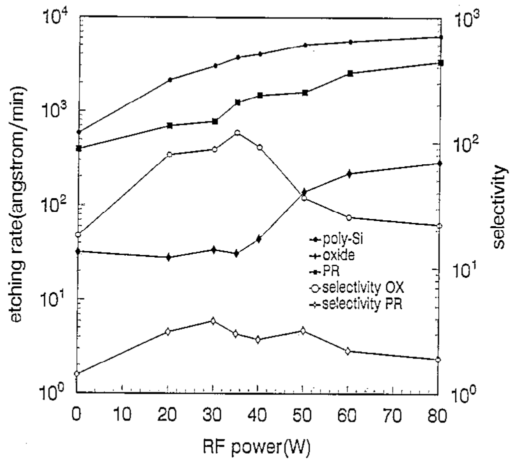


Fig. 7. The etching characteristics of Cl_2/O_2 plasma with various RF powers. Flow rate of Cl_2/O_2 is 95/5 sccm, pressure = 3 mtorr, microwave power = 250 W.

RF power. When a larger RF power is applied, the ion bombardment dominates the etching mechanism and the etching rate is commensurate with the RF power. Equally, the weaker Si–Si bond (54 kcal mol^{-1}) in ploy-Si can be broken at lower ion energy. Therefore, by choosing a proper RF biasing (about 35 W), the highest selectivity can be obtained, as indicated in Fig. 7. Finally, the mixture of $Cl_2/HBr/O_2$ gases at the plasma source is studied. By combining the specialties of the Cl_2 system (high poly-Si etching rate) with the advantages of the HBr plasma (high selectivity and high anisotropy), excellent etching characteristics are achieved. Fig. 8 displays the etching properties of this mixed system. It is found that larger selectivity is obtained as the flow rate of $Cl_2/HBr/O_2$ reaches 144/50/6 sccm. In addition, the anisotropy examined by SEM is near unity. The experimental results prove that this mixed $Cl_2/HBr/O_2$ gas has the potential for satisfying

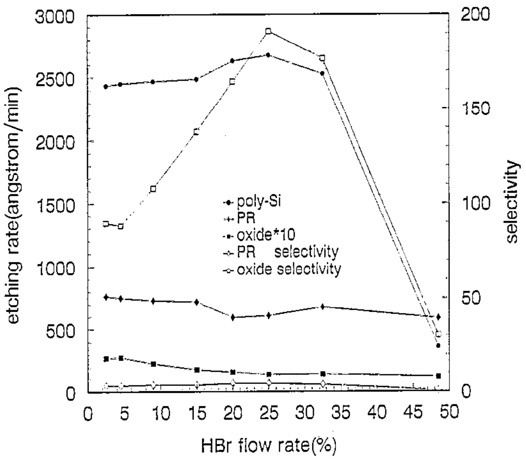


Fig. 8. The etching characteristics of $Cl_2/HBr/O_2$ mixed system. The total flow rate is 200 sccm, added oxygen is 6 sccm, pressure = 3 mtorr, microwave = 250 W, RF power = 35 W.

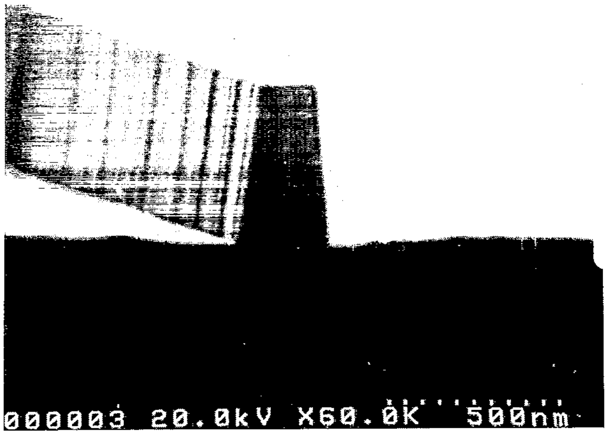


Fig. 9. The SEM picture of etching profile (linewidth = 0.35 μm) under the following conditions: $Cl_2/O_2 = 95/5$ sccm, pressure = 3 mtorr, microwave = 250 W, RF power = 35 W.

the requirements such as high etching rate, large selectivity and high anisotropy for ULSI applications

4. Conclusions

In this paper, the use of the chlorine-based plasmas generated by an ECR reactor as the etchants for poly-Si etching is developed. The etching characteristics such as etching rate, selectivity and anisotropy and the influences of the diverse etching parameters (i.e., microwave power, RF power and added oxygen concentration) are also discussed. It is found that the best values of added oxygen, microwave power and RF power are 5% of the total flow rate, 250 and 35 W, respectively. An SEM picture of the etching profile (linewidth = 0.35 μm) is shown in Fig. 9. Finally, the mixtures of $Cl_2/HBr/O_2$ gases as the plasma sources are investigated. Experiments show that the mixed system $Cl_2/HBr/O_2$ gives the best etching characteristics at the flow rate of 144/50/6 sccm.

Acknowledgements

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References

[1] G.C.H. Zau and H.H. Sawin, *J. Electrochem. Soc.*, *139* (1992) 250.

[2] M. Nakamura, K. Iizuka and H. Yano, *Jpn. J. Appl. Phys.*, *128* (1989) 2142.

[3] T.D. Bestwick and G.S. Oehrlein, *J. Vac. Sci. Technol. A*, *8* (1990) 1696.

[4] R. d'Agostino and D.L. Flamm, *J. Appl. Phys.*, *52* (1981) 162.

[5] M. Nakamura, K. Koshino and J. Matsuo, *Jpn. J. Appl. Phys.*, *31* (1992) 1917.

[6] K. Tokashiki et al., *Jpn. J. Appl. Phys.*, *30* (1991) 3174.