PLASMA ETCHING OF SILICON NITRIDE WITH CF4/02

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ABSTRACT

Plasma etching of silicon nitride with CF4/02 was investigated to determine the effect of pressure, rf power and oxygen concentration on the etch rate, undercutting and selectivity. The experiments were carried out in a parallel plate reactor. The results showed the undercutting of silicon nitride to increase with increasing pressure. The etch rate of silicon nitride is higher than that of silicon dioxide. The selectivity of silicon nitride with respect to silicon dioxide is almost independent of the rf power and gas pressure.

1. INTRODUCTION

The selective plasma etching of silicon nitride with respect to silicon dioxide is an essential step in the fabrication of silicon VLSI circuits. It has been carried out in barrel reactors (1,2,3) and in parallel-plate reactors (4,5,6).

The present paper reports the results of plasma etching of silicon nitride with CF_4/O_2 in a parallel-plate reactor. Etch rate and undercutting of masked silicon nitride films and the selectivity of silicon nitride relative to silicon dioxide were investigated at different gas pressures, rf powers, and oxygen concentrations in the CF_4/O_2 plasma.

2. EXPERIMENTAL

The experiments were carried out in a conventional parallel-plate plasma etcher (7). Fig. 1 is a schematic representation of the radial-flow plasma etcher used. The wafers to be etched are placed on a grounded aluminum plate 61 cm in diameter. The water-cooled aluminum counterelectrode is powered by an rf generator (13.56 MHz) through an impedance matching network. The electrode spacing is 13 mm. The temperature of the grounded electrode is held constant at 30°C. The chamber is pumped by a rotary pump with a throttle valve. Pressure is measured with a capacitance manometer (MKS Baratron) and controlled via a throttle valve in the gas outlet. Flow rates are measured with thermal mass flowmeters and controlled by piezoelectric valves in the gas inlet. The rf power is automatically controlled. The reflected rf power is held at a minimum by way of an automatic impedance matching network.

The experiments were carried out over a pressure range of 25 Pa to 130 Pa using rf powers of 250 W to 1000 W. In all experiments the input flow rate of CF4/02 was 100 sccm. During a run, the rf power, flow rate, and gas pressure were held constant. Etch rates were calculated from the etch depth.

Silicon nitride of thickness 100 nm was deposited on 50 nm thermally grown silicon dioxide on a silicon wafer 76 mm in diameter by a low pressure CVD process. Shipley AZ 1450J photoresist was used for the etch mask.

The emission intensity of atomic fluorine in the ${\rm CF_4/0_2}$ plasma was measured at a wavelength of 703.7 nm in the same way as described by Harshbarger et.al. (4).

3. RESULTS AND DISCUSSION

It has be shown by many authors that the undercutting of plasma-etched films depends on the etching mechanisms (8,9). If the chemical reaction between the reactive species of the plasma and the surface to be etched is initiated by ion or electron bombardment, the etch profile of masked films will be anisotropic. If the chemical reaction occurs without particle bombardment, neutral species of the plasma will then be responsible for etching. The etch profile obtained will be isotropic and undercutting will occur.

Fig. 2 shows the normalized pattern undercut of plasmaetched masked silicon-nitride films as a function of gas pressure. The length of undercut is normalized by etch depth. At pressures above 60 Pa the edge profile is almost isotripic as a result of neutrals predominating as etchant. Undercutting decreases with the pressure. This effect is attributable to an increasing ion or electron-initiated chemical etch reaction.

Fig. 3 shows the etch rates of silicon nitride and silicon dioxide as a function of the oxygen concentration in the CF4/02 plasma. The etch rate of SiO2 is proportional to the density of the atomic fluorine concentration as measured from the emission intensity of fluorine at a wavelength of 703.7 nm (Fig.4). This result, also observed by Mogab, Adams, and Flamm (10), suggests atomic fluorine to be the predominant etchant for SiO2. The etch rate of Si3N4 is proportional to the fluorine cencentration up to about 20 % 02 in the CF4/02 plasma. In contrast to the fluorine concentration, the maximum etch rate of Si3N4 occurs at about 40 % 02. This indicates that, with an oxygen concentration of more than 20 %, reactive species in addition to atomic fluorine will be responsible for etching. With below 20 % 02 in the CF4/02 plasma the chemical etch reactions are assumed to be

$$4 F + Si02$$
 — $SiF4 + O2$ (1)
 $12 F + Si_3N_4$ — $3 SiF_4 + 2 N_2$ (2)

Fig. 5 shows the etch rates of Si3N4 and SiO2 as a function of rf power in a CF4/O2 plasma containing 5 % O2. Both etch rates increase with increasing rf power as a result of the increasing density of the reactive species.

The etch rate depends on the binding energy of the atoms in the material to be etched, and increases with decreasing binding energy (10). This energy is expressed by the free enthalpy of bonding ΔG_B . For SiO₂, Si₃N₄, and SiF₄ are ΔG_B (11):

Molecule	SiO ₂	Si3N4	SiF4
ΔG_{R} (kJ/mole)	-804.6	-647.3	-1510

For Si3N4 the binding energy is less than for Si02, which might be responsible for the higher etch rate of Si3N4 compared to Si02 (Fig.5). The free enthalpy of bonding for the etch reaction product SiF4 is higher than that for Si3N4 and Si02, indicating that the etch reactions (1) and (2) occur spontaneously without the need for the addition of energy.

In a CF4/02 plasma with 5 % 02 the selectivity of Si3N4 with respect to Si02 is independent of the rf power (Fig.6). From this result it can be expected that, within the observed range of rf power, only one type of reactive species, probably atomic fluorine, will be responsible for etching.

Fig. 7 shows the etch rates of Si3N4 and SiO2 as a function of gas pressure. Both etch rates increase with the gas pressure, probably due to the increasing density of reactive species in the plasma.

Fig. 8 shows the selectivity of SigN4 with respect to SiO2 as a function of pressure. Above a pressure of about 65 Pa the selectivity is constant, while below this level the selectivity decreases with pressure as a result of the increasing component of the ion- or electron-initiated chemical etch reactions (Fig. 2).

4. CONCLUSIONS

Plasma etching of Si3N4 with CF4/O2 in a parallel-plate reactor is governed by two mechanisms: etching by neutral reactive species and etching by ion- or electron-initiated chemical reaction at the surface to be etched. Etching with neutral species increase with increasing gas pressure. At pressures above 60 Pa and an 02 concentration up to 20 % in the CF4/02 plasma, the predominant etchant for Si3N4 and SiO2 is probably atomic fluorine. At higher oxygen concentrations, additional reactive species will influence the etching of SigN4. The etch rate of SigN4 is higher than that of SiO2, probably due to the lower binding energy of the Si-N bond as compared to the Si-O bond.

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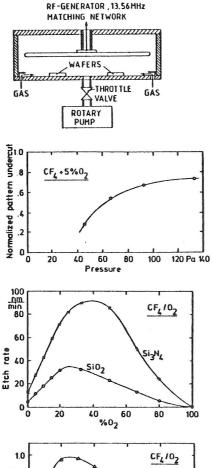
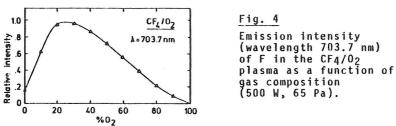


Fig. 1
Radial-flow plasma etcher (7).

Fig. 2
Normalized pattern
undercut of Si3N4 as
a function of gas
pressure
(CF4 + 5 % O2, 500 W).

Fig. 3
Etch rates of Si3N4 and Si02 as a function of gas composition CF4/02 (500 W, 65 Pa).



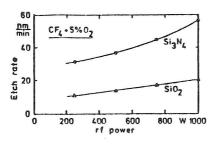


Fig. 5
Etch rates of SigN4 and SiO₂ as a function of the rf power (CF4 + 5 % O₂, 65 Pa).

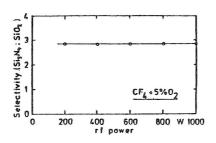


Fig. 6
Selectivity of Si₃N₄ to Si₀2 as a function of the rf power (CF₄ + 5 % 0₂, 65 Pa).

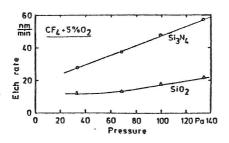


Fig. 7
Etch rates of Si3N4 and Si02 as a function of the gas pressure (CF4 + 5% 02, 500 W).

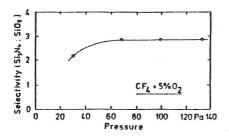


Fig. 8
Selectivity of Si3N4 to Si02 as a function of the gas pressure (CF4 + 5% 02, 500 W).