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n^+-Polysilicon Etching with Both High Anisotropy and High Selectivity by Nitrogen Chemisorption in Chlorine and Nitrogen Mixed ECR Plasma

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n^+-polysilicon etching with both, high anisotropy and high selectivity, for ULSI fabrication has been realized by irradiating the chlorine and nitrogen mixed plasma under a low ion energy condition using an ultraclean ECR etcher. From XPS analysis, it is found that the high anisotropy is caused by the formation of Si-N bonds by N radicals on the shallow surface of n^+-polysilicon. Based on the evaluation of the enthalpy change for reactions together with the added N_2 dependence of the etch rate, it has been proposed that etching in the N_2 added Cl_2 plasma can be analyzed as competitive reactions with an equation similar to Langumuir's adsorption isotherm.

1. INTRODUCTION

n^+-polysilicon etching with both, high anisotropy and high selectivity, is extremely important for ULSI fabrication. For the purpose, time modulation etching at temperatures as low as -110 - -130^{0}C has been reported.[1)] The problem of this method consists in controlling the wafer temperature. A gas chopping method with N_2 and SF_6 has also been reported.[2)] However, the reported selectivity of Si to SiO_2 in such a system is only about 10. In our previous work,[3,4)] an induction period for SiO_2 etching has been found and perfect selective Si to SiO_2 etching has been achieved with high anisotropy for undoped polysilicon patterns, using an ultraclean Cl_2 ECR plasma under a damage suppressed condition.

In the present work, n^+-polysilicon etching has been investigated in pure Cl_2 and N_2 added plasmas using an ultraclean ECR etcher. In a pure Cl_2 plasma, n^+-polysilicon etching is highly selective but not anisotropic. By adding N_2 to the Cl_2 plasma, high anisotropy and high selectivity in etching of n^+-polysilicon are achieved. Moreover, based on the results of XPS analysis, sidewall protection of n^+-polysilicon against Cl radical attack by N chemisorption is suggested. Evaluating the enthalpy change for the reactions and using an equation similar to Langumuir's adsorption isotherm, the reaction mechanisms are discussed.

2. EXPERIMENTAL

An ultraclean ECR plasma apparatus[3,4)] was used to obtain high selectivity. Precise amounts of high purity Cl_2 and N_2 were premixed before introducing them into the plasma chamber. The reactor pressure was measured with an MKS Baratron gauge.

The samples etched were 450 nm thick P doped n^+-polysilicon of about 20 Ω/□ and undoped polysilicon formed on thermally oxidized Si wafers. Thermally grown SiO_2 was used as a mask, since C contamination from organic resist will degrade selectivity to

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the underlying SiO_2. The vertical etch rate of polysilicon was determined by film thickness combined with etching end point measurements,[3] and the horizontal one from cross sectional SEM measurements. The etched thickness of the thermally grown SiO_2 on Si wafers was determined separately by ellipsometric measurements before and after etching. The etched surface of n^+-polysilicon was analyzed by XPS. Plasma emission near the wafer was measured with Photal IMUC-7000 spectrometer.

3. RESULTS AND DISCUSSION

The horizontal etch rate of undoped polysilicon was low enough to give an anisotropic etch profile over the whole measured pressure range(Fig.1). For n^+-polysilicon, the horizontal etch rate was very high and the anisotropy is very low even at low pressures, where selectivity is low (Fig.1). From these results, it is clear that Cl radical attack on sidewalls is dominant in n^+-polysilicon etching at high pressures.

Figure 2 shows the effects of N_2 addition on the n^+-polysilicon etching characteristics at 4 mTorr. Anisotropy is highly improved by the addition, although the vertical etch rate is decreasing. The selectivity was as high as 160 at 10% N_2 concentration, although the etched thickness of SiO_2 slightly increased and the induction period shortened with the N_2 addition. Typical etched n^+-polysilicon patterns are shown in Fig. 3. It is seen that by the N_2 adding method, anisotropic etching of 0.3 μm n^+-polysilicon patterns is achieved under the condition with a selectivity to SiO_2 as high as 160. This performance has not been obtained by the conventional side wall protection technique using C and/or S atoms in compound gas molecules.

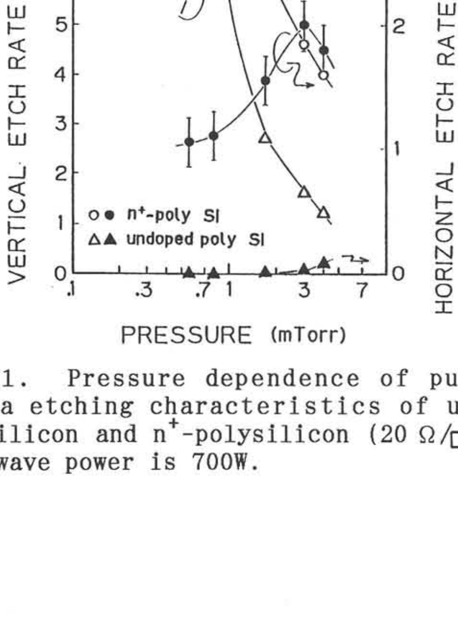


Fig. 1. Pressure dependence of pure Cl_2 plasma etching characteristics of undoped polysilicon and n^+-polysilicon (20 Ω/□). The microwave power is 700W.

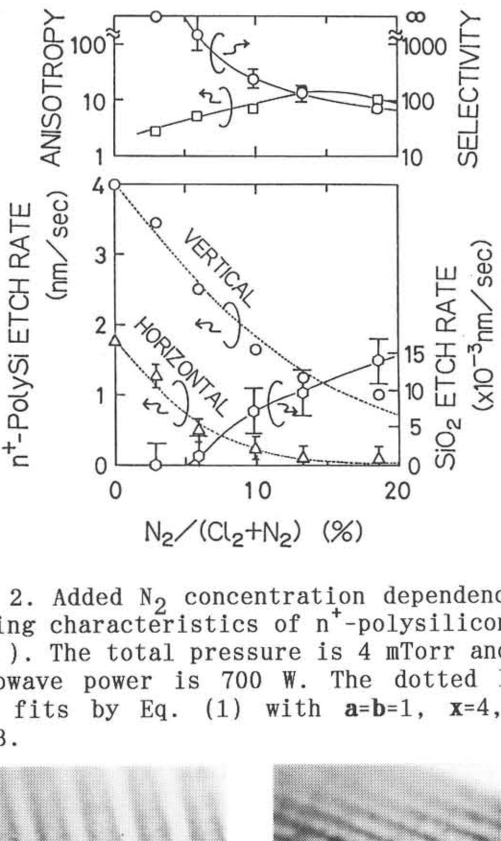


Fig. 2. Added N_2 concentration dependence of etching characteristics of n^+-polysilicon (20 Ω/□). The total pressure is 4 mTorr and the microwave power is 700 W. The dotted lines show fits by Eq. (1) with **a**=**b**=1, **x**=4, and **y**=4/3.

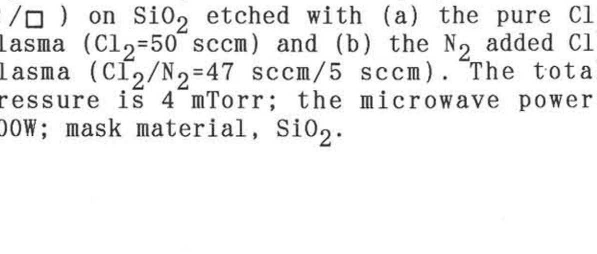


Fig. 3. Etch profiles of n^+-polysilicon (20 Ω/□) on SiO_2 etched with (a) the pure Cl_2 plasma (Cl_2=50 sccm) and (b) the N_2 added Cl_2 plasma (Cl_2/N_2=47 sccm/5 sccm). The total pressure is 4 mTorr; the microwave power, 700W; mask material, SiO_2.

From XPS analysis of the plasma-irradiated n^+-polysilicon surface, the following results were obtained (Fig.4): ① On the n^+-polysilicon surface exposed to the (Cl_2 + N_2) plasma, N atoms are adsorbed even when the shutter is closed which interrupts the direct incidence of ions(Fig.4a). These adsorbed N atoms were removed by stopping the N_2 addition even with closed shutter. ② The Si^{4+} peak appears at an energetically equivalent point to the peak of Si in an Si_3N_4 film formed by LPCVD(Fig.4b). It is considered that the Si-N bonds similar to those in Si_3N_4 are formed on the n^+-polysilicon surface by N radicals. This is believed to be the reason for suppression of Cl radical etching at the side wall. ③ Exposure to air of the n^+-polysilicon surface after the plasma irradiation causes desorption of N atoms (Fig.4c) and oxidation of the surface (Fig.4d). Therefore, it is considered that the Si-N bonds are so weak or exist only at a very thin surface layer that they can be removed by the exposure to Cl radical or air.

The enthalpy change (ΔH_f) for a variety of supposed surface reactions was evaluated using the bond strengths.[5] Some typical values are listed in Table I. The Si-N bond forming reaction(a) and the chlorine etching reaction(b) have comparable ΔH_f values. Moreover, the reactions in which N and Cl chemisorbed on the n^+-polysilicon surface are substituted by Cl and N radicals, have negative ΔH_f values ((c) and (d), respectively). Therefore, etching and nitridation are considered to occur competitively.

If Cl and N are adsorbed competitively on the Si surface under a quasi-equilibrium condition, the competitive adsorption and reaction can be described by an equation similar to Langumuir's adsorption isotherm

$$\mathbf{R = A \cdot P_{Cl2}{}^{a \cdot x} / (1 + B \cdot P_{N2}{}^{b \cdot y})^{x}} \ , \ (1)$$

where **R** is the etch rate, **A** and **B** fitting parameters, $\mathbf{P_{Cl2}}$ and $\mathbf{P_{N2}}$ the partial pressure of Cl_2 and N_2, respectively, **a** and **b** constants depending on the radical generation, and **x** and **y** constants depending on the surface reaction. Here, the following assump-

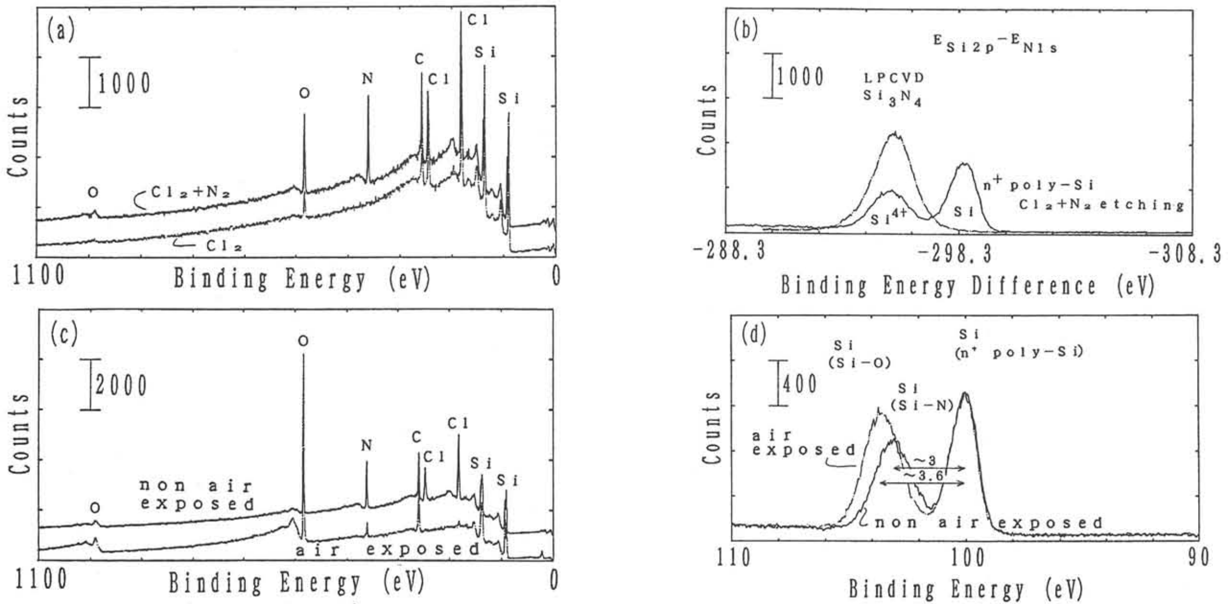
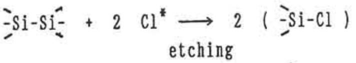
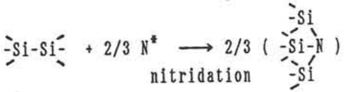
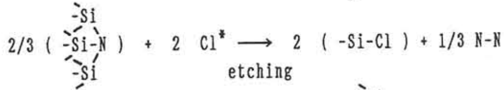
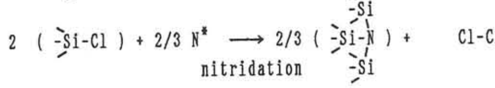


Fig. 4. XPS spectra for n^+-polysilicon surfaces irradiated with ECR plasma at 4 mTorr. (a): Survey spectra for Cl_2/N_2 = 47 sccm/5 sccm and 50 sccm/ 0 sccm. (b): Si 2p spectra of the n^+-polysilicon surface during N_2 added etching and of an LPCVD Si_3N_4 film. The binding energy is measured from the N 1s peak energy in order to cancel out the charging effects of insulating samples. (c,d): Change of survey spectra(c) and Si 2p spectra(d) by exposure to air of the n^+-polysilicon surface after the N_2 added plasma irradiation.

Table I. The enthalpy changes ΔH_f for some supposed surface reactions of Si in a N_2 added Cl_2 plasma. The surface bond strengths of Si-N and Si-Cl are assumed to be equal to those in Si_3N_4 solid and in $SiCl_4$ gas, respectively.

	Reaction	ΔH_f(eV)
(a)	 $\text{-Si-Si-} + 2\ \text{Cl}^* \xrightarrow[\text{etching}]{} 2\ (\text{-Si-Cl})$	−5.8
(b)	 $\text{-Si-Si-} + 2/3\ \text{N}^* \xrightarrow[\text{nitridation}]{} 2/3\ (\text{-Si-N})$	−4.6
(c)	 $2/3\ (\text{-Si-N}) + 2\ \text{Cl}^* \xrightarrow[\text{etching}]{} 2\ (\text{-Si-Cl}) + 1/3\ \text{N-N}$	−4.5
(d)	 $2\ (\text{-Si-Cl}) + 2/3\ \text{N}^* \xrightarrow[\text{nitridation}]{} 2/3\ (\text{-Si-N}) + \text{Cl-Cl}$	−1.3

tions have been made: ① Concentrations of Cl and N radicals in a gas phase are proportional to $\mathbf{P_{Cl2}}$ and $\mathbf{P_{N2}}$, powered by **a** and **b**(1/2 for the thermal equilibrium and 1 for the rate limited condition), respectively. ② Si is etched as $SiCl_{\mathbf{x}}$(**x**=1, 2, 3, and 4) and N is bonded on the surface as $SiN_{\mathbf{y}}$(**y**=4/3, 4/2, and 4/1). ③ As an approximation, the adsorbed surface concentration of N is assumed to be large and that of Cl small, i.e. the adsorbed Cl atoms rapidly etch Si while the N atoms rest on the surface. It was examined whether Eq.(1) could fit the dependence on the added N_2 shown in Fig. 2 for **a**=1/2, 1, **b**=1/2, 1, **x**=1, 2, 3, 4, and **y**=4/3, 4/2, 4/1, with a parameter **A** obtained from the pure Cl etch rate and a fitting parameter **B** to be varied. Figure 2 shows the comparison of the results obtained by Eq.(1) (dotted lines) with the experimental data. The agreement is very good for the horizontal etch rate with **b·y**=4/3 and 2, and for the vertical etch rate with **b·y**=1 and 4/3, while the fit was very insensitive to the choice of **a** and **x** in the present $\mathbf{P_{N2}}$ region. The emission intensity from N radicals in the plasma increased almost linearly with the added N_2 concentration, which suggests a value of **b**=1. Therefore, for the vertical etching **y** is most probably 4/3. This is consistent with the XPS result that the Si-N bonds formed on the surface are similar to those in Si_3N_4. For horizontal etching the value of **y** is also expected to be 4/3 rather than 1, since the adsorption at the sidewall is expected to be more tight than at the bottom surface, where ion incident etching proceeds.

4. CONCLUSIONS

Etching of n^+-polysilicon with high anisotropy and high selectivity has been realized by using an ultraclean low ion energy plasma, consisting of simple-substance Cl_2 and N_2 gas mixture. From XPS analysis, it was found that high anisotropy is caused by the formation of Si-N bonds similar to those in Si_3N_4 by N radicals on the shallow surface of n^+-polysilicon. It is believed from the evaluation of the enthalpy change that Cl etching and nitridation occur competitively on the n^+-polysilicon surface. It has been proposed that etching in the N_2 added Cl_2 plasma can be analyzed as competitive reactions with an equation similar to Langumuir's adsorption isotherm, since the analysis also suggests that the surface Si-N bonds are similar to those in Si_3N_4.

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