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Reaction Mechanisms with Synchrotron Radiation-Stimulated Etching of Si and SiO_2

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Si and SiO_2 etching in SF_6 gas are carried out using synchrotron radiation (SR) as a light source. The etching rate depends on material properties and their effective activation energies are negative. Dependence of the etching rate on SF_6 pressure is evidence that a Langmuir type adsorption process contributes to the etching reaction. Based on these characteristics a surface reaction model containing SR-stimulated reactions between adsorbed F atoms and substrate Si atoms can be constructed.

I. Introduction

Synchrotron radiation (SR) is a potentially novel and powerful light source for semiconductor processes in which photochemical reactions of surface and/or gas phases are used. SR has advantages in these purposes, such as high photon energy and excellent directivity. In particular, interaction of high energy photons with gases, solids and adsorbates plays an important role in SR excited processes. Systematic investigation into the mechanism of SR excited reaction, therefore, opens up the possibility for new semiconductor processes in which SR instruments are utilized as fabrication equipment.

In recent years, several unique characteristics have appeared in both SR excited film deposition[1,2] and etching[2,3] processes. The Si and SiO_2 etching, unique etching selectivity quite different from that in the plasma etching case, was found. Furthermore, anisotropic etching with extremely high resolution was successfully demonstrated in SiO_2.[2] However, detailed investigations of Si and SiO_2 etching were not carried out in these prior papers.

This paper will discuss in detail reaction mechanisms with SR-stimulated etching of Si and SiO_2. Of primary interest are the differences in etching characteristics due to material properties, such as their crystallinity, and also due to basic etching conditions. Based on chemical kinetic analysis according to experimental results, a photo-stimulated surface reaction model for the present SR excited etching has been proposed.

II. Experiment

The etching apparatus was set in the beam line (BL-1C) at the Photon Factory of National Laboratories of High Energy Physics (KEK). A spectrum calculation of the incident beam indicates that the spectrum ranged from about 20Å to more than 1000Å in wavelength. The incident beam was introduced perpendicular to the sample surface. The beam spot size was about $3 \times 4 mm^2$. Reaction gas, 100% SF_6, was provided into the re-

action chamber and then evacuated by a differential vacuum pumping system. A quadrupole mass spectrometer (QMS) was placed in the etching chamber to analyze residual gas molecules and SR ionized ions.

Si samples were P-doped CVD films and single crystalline wafers, and SiO_2 samples were thermal oxide Si wafers and vitreous and crystalline quartz plates.

III. Results and discussion

First, etched profiles of Si and SiO_2 were compared with photo-intensity distribution. The etching reaction was observed only in the SR irradiated area, indicating that a surface excitation mechanism is dominant.

The etching rates of each sample per SR dose (storage ring current x etching time) under constant conditions (total pressure 0.13Torr, substrate temperature 300K) are listed in Table 1. Because the P-doped CVD Si, as deposited, is amorphous and the annealed one is polycrystalline, the Si etching rate depends on the crystallinity. On the contrary, the SiO_2 etching rate data indicate less dependence on the crystallinity. The Si etching rate under a constant SR dose was slightly dependent on storage ring current, that is, photon flux density.

Dependence of the SiO_2 (thermal oxide) etching rate on the total SF_6 pressure is shown in Fig.1. The etching rate increased

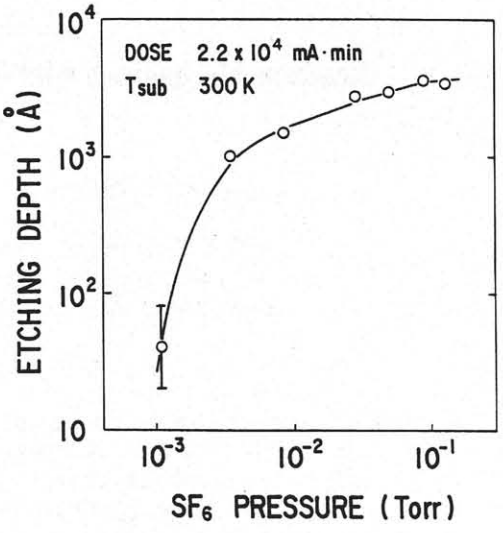

Fig.1 Dependence of the etching rate on SF_6 pressure.

with increasing SF_6 pressure. The rate is approximately proportional to the 4th power of the pressure at a low SF_6 region and gradually saturates at higher pressures, suggesting that the Langmuir-type adsorption process plays an important role in the etching reaction. Referring to the commonly known fact that SiF_4 is a stable etching product in plasma etching, the dominant reaction mechanism seen in this case can be explained as follows. The etching proceeds through the SiF_4 desorption induced by the reaction between substrate Si atoms and adsorbed F atoms which are produced by SF_6 photolysis. It was found from the mass spectrum analysis that the F^+ generation is the most efficient process in SR ionization

	Material	Etching Rate (10^{14}molecules/Amin)
Si	P-doped CVD Si (as deposited)	16.9
	(650°C annealed)	3.8
	Single crystal	no reaction
SiO_2	Thermal oxide	12.0
	Vitreous quartz	10.3
	Crystalline quartz	8.3

Table 1 SR-stimulated etching rates of Si and SiO_2.

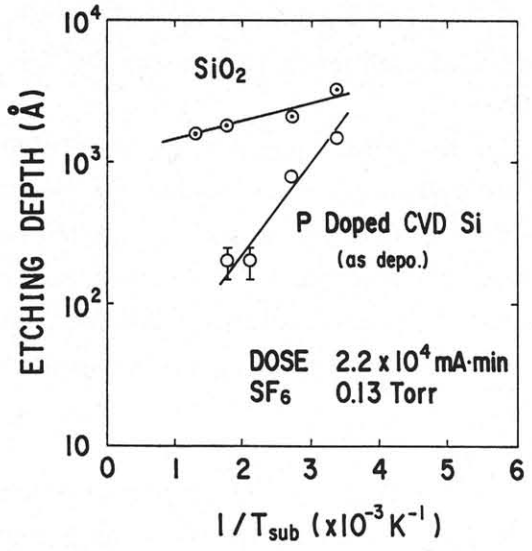

Fig.2 Dependence of the etching rate on substrate temperature.

of SF_6.

The dependence of P-doped CVD Si (as deposited) and SiO_2 (thermal oxide) etching rates on the substrate temperature is shown in Fig.2. This dependence indicates that the effective activation energy of the reaction is negative, as opposed to plasma etching cases, suggesting that the etching reaction is induced by photoexcitations, and not by thermal effects.

Based on these results, the reaction mechanism for the present etching is described as follows:

$$SF_6 + h\nu \rightarrow SF_5 + F(\text{radical or ion}) \quad [1]$$
$$F(g) \rightarrow F(a) \quad [2]$$
$$Si(s) + 4F(a) + h\nu \rightarrow SiF_4(g) \quad [3]$$

where (g), (a) and (s) indicate the gas phase, adsorbed layer and substrate, respectively. Furthermore, it is more reasonable to consider that the reaction [3] is induced by the electronic excitation of the substrate Si atoms, which are surrounded by adsorbed F atoms.

Several surface reaction processes are conceptually explained in Fig.3. Here, the potential energy curves, A and B, correspond to surface diffusion and thermal desorption of the adsorbed species, respectively. Conventional thermal etching reactions between adsorbed F atoms and substrate surface atoms are explained by the potential energy curve C. The excitation energy required for the etching is supplied by photoexcitations as shown in Fig.2. The present etching process is thus explained by the potential energy curve D or D' in Fig.3. We call this process photostimulated reactive desorption.

Considering the above experimental results, a reaction model for SR-stimulated etching (reaction eq.[3]) is proposed as follows:

1) Reactive excited sites (N_s^*:surface density, τ_s:lifetime) are generated on the substrate surface by SR irradiation.

2) Substrate surface is etched by the reaction between excited sites and surface adsorbed species (N_a:surface density, $_a$:ad-

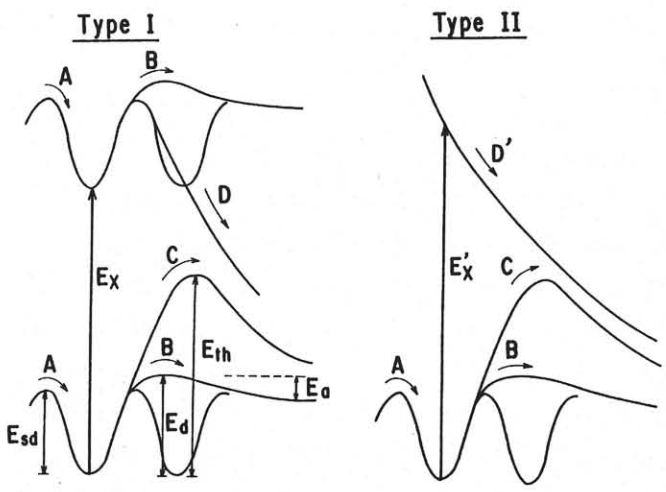

Fig.3 Conceptual potential energy curves explaining several surface reaction processes along a progressive reaction time axis. E_x is photoexcitation energy. E_a, E_d, E_{th} and E_{sd} are activation energies for adsorption, desorption, thermal etching and surface diffusion, respectively.

sorption time). Reaction process Type II D' in Fig.3 corresponds to an extremely short reaction time.

Rate equations based on this reaction model are formulated as follows:

$$dN_s^*/dt = cqN_s\sigma - k_pN_s^*N_a^n - N_s^*/\tau_s \quad (1)$$

$$dN_a/dt = \Gamma - k_pN_s^*N_a^n - N_a/\tau_a \quad (2)$$

where c is light velocity, q is photon flux density, N_s is surface atomic density of the substrate, σ is an excitation cross section, n is a reaction order, k_p is a rate constant, Γ is the adsorption rate and N_a/τ_a is the desorption rate.

The etching rate R is given by the second term of (1) or (2),

$$R = k_pN_s^*N_a^n . \quad (3)$$

For the low pressure region, $R \ll \Gamma \propto N_g$ (N_g:gas molecule density), R is expressed according to some chemical kinetic considerations,

$$R \propto N_sN_g^n\tau_s \exp(-n(E_a-E_d+E_{sd})/kT) \quad (4)$$

where E_a, E_d and E_{sd} are activation energies of adsorption, desorption and surface diffusion, respectively (k:Boltzmann's constant, T:temperature). From experimental data of the 4th power dependence on the pressure (Fig.1), the reaction order n can be fixed on 4. This coincides with the suggestion that SiF_4 is the main product of the etching reaction. The observed substrate temperature dependence shown in Fig.2 is explained by Eq.(4) since it is reasonable to consider that $E_a-E_d+E_{sd}$ is negative and τ_s decreases with increasing temperature.

It is speculated that the observed differences in the etching rate among the materials correspond to the difference in the excited surface site density N_s^* or the lifetime τ_s.

The real etching reaction is probably a more complex one. These equations, however, effectively explain many of the observed results. Reaction models proposed here are considered to be a good approximation of true SR-stimulated etching mechanisms.

IV. Summary

SR-stimulated etching characteristics of Si and SiO_2 were investigated as a way of studying the reaction mechanism. Several unique phenomena were observed. Etching rates were found to be dependent on material properties. Substrate temperature dependence was quite different from that of plasma etching. It was also found that there exists a dependence on gas pressure and photon flux density.

Based on chemical kinetic considerations of the experimental results, it is concluded that a photostimulated surface reaction between adsorbed F and photoexcited substrate Si atoms, resulting in SiF_4 desorption, is a possible reaction model for the present SR-stimulated etching.

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