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Low Temperature Oxidation of Silicon by Microwave Discharged Oxygen Plasma

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Silicon dioxide growth in oxygen plasma has been investigated using newly developed microwave discharge equipment with electron cyclotron resonance. It is found that the Mott-Cabrera model rather than the Deal-Grove thermal oxidation model validly explains plasma oxidation kinetics. The mechanism of plasma oxidation is considered to be the drift motion of adsorbed oxygen atom ions across the oxide film under the influence of self-bias in the plasma. Etch rate measurement reveals that the degree of plasma oxide densification is similar to that of the thermally grown film.

1. INTRODUCTION

Low temperature film formation techniques have recently been considered to be a key process to realize the forthcoming ULSIs. Plasma oxidation, which utilizes a highly activated oxygen plasma, is one of the low temperature techniques to grow dielectric film on semiconductor surfaces. The most extensively investigated technique is plasma anodization(1), in which the specimen to be oxidized is biased positively to enhance ion diffusion.

However, plasma anodization has several disadvantages. For example, because the two electrodes used to apply a bias to the specimen are directly immersed in the plasma, it is difficult to avoid possible contamination caused by electrode sputtering. Also, heavy damage by irradiation of charged particles and UV light is unavoidable.

Similarly, plasma oxidation(2) which uses no external bias has also been investigated. Although its oxidation rate is smaller than that of the plasma anodization, it is considered that irradiation damage with plasma oxidation will be less because the external bias is not used to pull charged particles. In addition, it has been reported that magnetic field plasma confinement was effective in obtaining high density plasma and a high oxidation rate(3).

To enhance the advantages of plasma oxidation, we have developed discharge equipment using electron cyclotron resonance (ECR). This method achieves a high density plasma(4) which allows a low temperature oxidation of Si (below 650°C).

In this paper, plasma oxidation kinetics is mainly discussed.

2. PLASMA OXIDATION EQUIPMENT AND EXPERIMENT

The plasma oxidation equipment used in this study is similar to the plasma stream transport system proposed by Tsuchimoto(5) in 1967. A bird's eyes view of the equipment is shown in Fig.1.

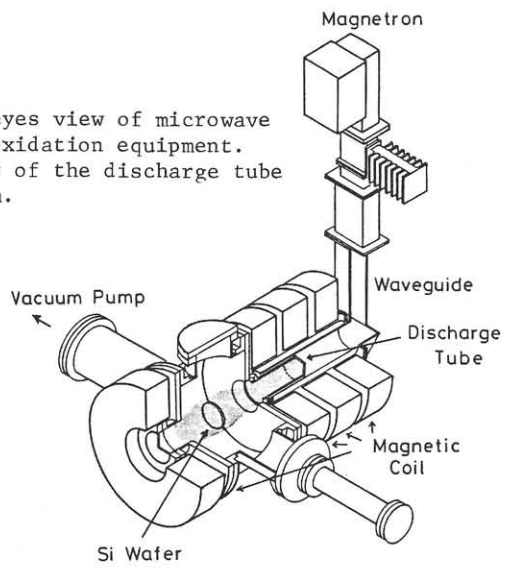

Fig.1
Bird's eyes view of microwave plasma oxidation equipment. Diameter of the discharge tube is 100mm.

Microwaves generated by a magnetron are guided to a quartz discharge tube filled with high purity oxygen gas. The discharge tube is surrounded by three magnetic coils and the magnetic field is set to meet an ECR condition.

Generated plasma is then transported to the specimen confined by the magnetic field as shown in Fig.2. One advantage of this equipment is that a low contamination plasma can be obtained, because the plasma is kept away from the metal chamber walls.

Oxygen pressure is 2.7×10^{-2} Pa. It is reported that a maximum plasma density ($\sim 10^{12}/cm^3$) can be obtained near this pressure.

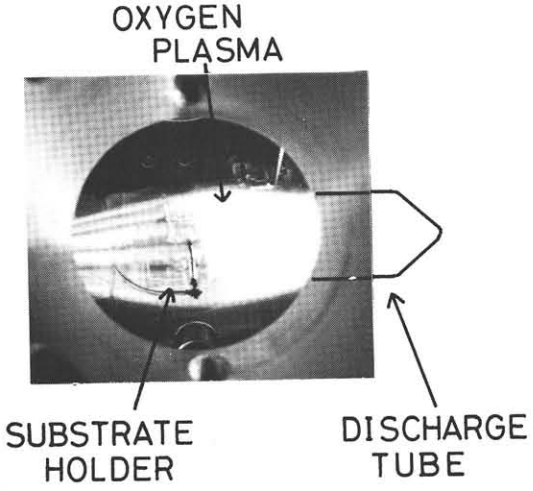

Fig.2 Side view of oxygen plasma. The plasma is confined by a magnetic field and transported to the specimen.

3. RESULTS AND DISCUSSIONS

3.1 Plasma Oxidation Kinetics

In order to discuss the plasma oxidation kinetics based on the proposed oxidation model, time and temperature dependences of oxide growth were investigated. The thickness of the SiO_2 film was measured by ellipsometer assuming a refractive index of 1.47. Since the thickness varies about 10%, the average of measurement taken at 9 points near the center of the specimen was used.

Figure 3 shows the relation between oxide thickness and oxidation time as a function of temperature. The results of thermal dry oxidation ($700^{\circ}C$, 1 atm) is shown as a dashed line. Even at just $640^{\circ}C$, plasma oxidation obtains an oxide thickness about 30 times greater than that with thermal oxidation.

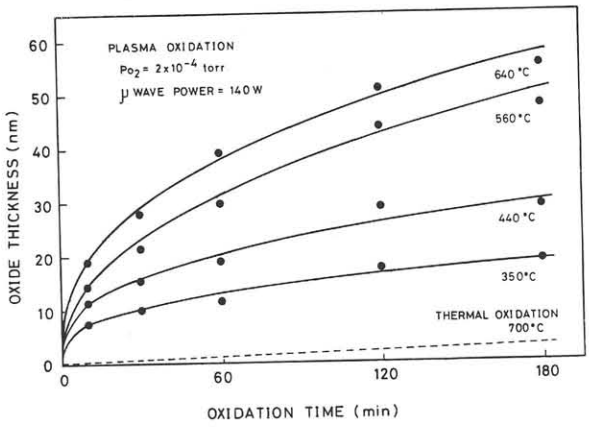

Fig.3 Oxide growth as a function of oxidation temperature. Dashed line shows thermal oxidation at 700°C, 1 atm.

Deal and Grove(6) proposed the linear-parabolic equation which is suitable for explaining thermal oxidation of Si (DG model). This model indicates that oxide thickness is linearly proportional to oxidation time when the oxide is thinner than 50nm. However, the oxide thickness is not linearly proportional to oxidation time in this plasma oxidation as shown in Fig.3. In addition, B/A constant including the reaction rate constant at the interface, which is obtained by fitting the data in Fig.3 to the linear-parabolic equation, becomes negative. These results clearly show that the DG model is not suitable to explain plasma oxidation kinetics.

On the other hand, Kamigaki et al.(7) and Horiuchi et al.(8) reported that the Mott and Cabrera model(9) (MC model) was adequate to explain the kinetics of thermal oxidation under low partial pressure. Also, Yamasaki et al.(10) showed that plasma anodization of GaAs was explained by the MC model.

In this model, the following oxidation rate equation was derived by assuming ion drift motion under the influence of potential across the oxide film,

$$\frac{dx}{dt} = 2u \cdot \sinh(X1/x) \cdots\cdots (1)$$

where X1 and u are the characteristic distance and velocity, respectively. X1 is proportional to the potential and u includes activation energy.

In order to obtain the oxidation rate (dx/dt), the measured data in Fig.3 is first fitted to the power law ($x^n=kt$) and then differentiated $\frac{dx}{dt} = k/nx^{n-1}$. The relation between dx/dt and x is calculated by directly fitting the data to Eq.(1). u and X1 are determined simultaneously to minimize error. The results are shown in Fig.4. The measured oxidation rate (closed circles) coincide well with the calculated curve.

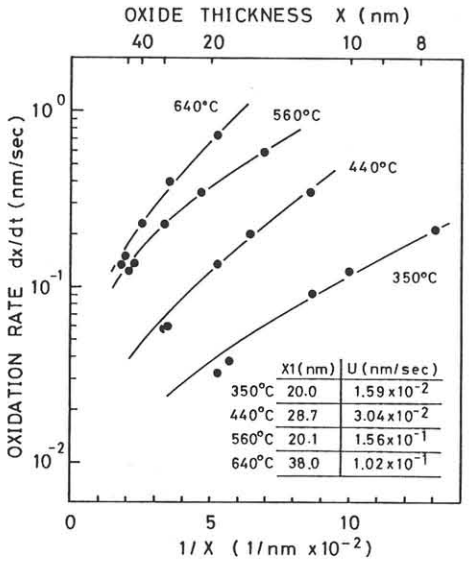

Fig.4 Mott-Cabrera analysis of oxidation rate. Solid lines are calculated curves.

Characteristic velocity u in Eq.(1) is closely related to activated processes such as diffusion. The Arrhenius plot of u is shown in Fig.5. Although it is peculiar that the data obtained at 540°C are greater than those at 640°C, a very small activation energy (0.37eV) can be obtained. Ray et al.(2) reported a considerably small activation energy (0.16eV) in his plasma oxidation using RF discharge. Details are subject to further study.

As mentioned above, the kinetics of plasma oxidation can be explained well by the MC model. However, the activation energy is much smaller compared with the previous results (1~2eV). This small activation energy seems to indicate that the diffusing species are small in size. Also, the diffusing species may be oxygen atom ions rather than oxygen molecules as in thermal oxidation or substrate atom ions as in plasma anodization.

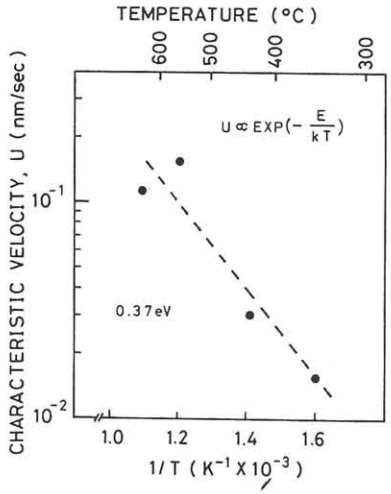

Fig.5 Arrhenius plot of characteristic velocity, u. Activation energy of plasma oxidation is 0.37eV.

So, a depth profile analysis of ^{18}O using SIMS was carried out to investigate the diffusing species. The specimen was first oxidized in a $^{16}O_2$ ambient and re-oxidized in a $^{16}O_2$ with a 20% $^{18}O_2$ ambient.

The SIMS depth profile is shown in Fig.6. Two solid lines denote intensities from ^{16}O and ^{18}O, respectively. The dashed line shows the ratio. From the ratio curve, it is found that ^{18}O exist throughout the oxide film and no pile up at the oxide surface is observed. This depth profile shows that the diffusing species are oxygen same as in thermal oxiation.

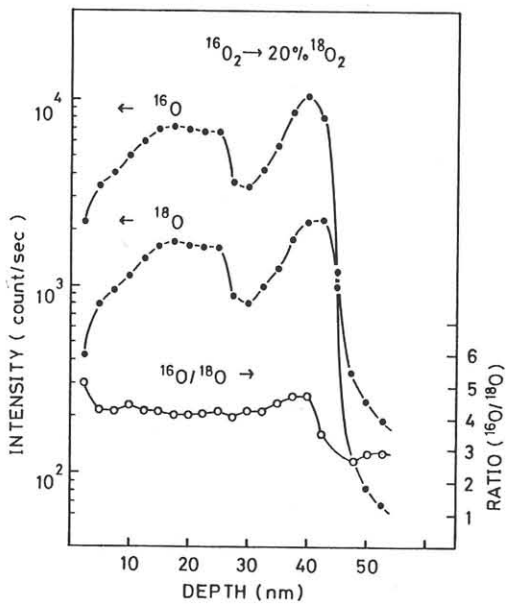

Fig.6 Depth profile of ^{16}O and ^{18}O in the plasma grown SiO_2. Open circles show the ratio ($^{16}O/^{18}O$).

From the above results, the mechanism of plasma oxidation is considered to be as follows. The diffusing species are considered to be oxygen atom ions produced in the plasma or on the specimen surface. These oxygen atom ions diffuse across the oxide due to the concentration gradient. The diffusion process should involve ion drift, since a built in potential that originated in the floating potential exists around the specimen.

3.2 Etch Rate Measurement of Plasma Grown SiO_2

The etch rate of plasma grown SiO_2 was measured to evaluate the degree of densification. A P-etch solution ($HF:HNO_3:H_2O=1.5:1:30$) was used.

Figure 7 shows the relation between etch rate and oxidation temperature. The dashed line shows the etch rate of thermally oxidized SiO_2 at 1000°C. The etch rate is a little faster than that of thermally oxidized film. Moreover, the lower the plasma oxidation temperature, the faster the etch rate.

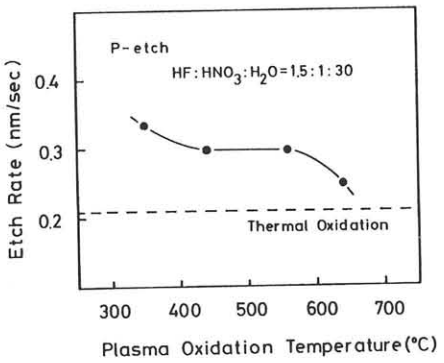

Fig.7 Relation between etch rate and oxidation temperature. Dashed line is the thermal oxide etch rate.

4. CONCLUSION

Microwave plasma oxidation equipment using ECR has been developed and silicon oxidation kinetics has been investigated.

It is found that plasma oxidation kinetics can be explained better by the Mott-Cabrera model rather than the Deal-Grove model. However, the activation energy obtained here is much smaller than any previous results. Also, the depth profile of ^{18}O in the plasma oxide clearly shows that the diffusing species are oxygen.

From these results, it is considered that the diffusion of oxygen atom ions are enhanced by the potential that originated in floating potential of the specimen.

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