PLASMA ANODIZATION OF SILICON IN AN RF OXYGEN DISCHARGE

O. Takai and Y. Shinbo
Department of Materials Science, Faculty of Engineering,
The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

ABSTRACT

Plasma anodization of silicon in a tube-type rf glow discharge system has been investigated. The anodization was performed in the constant current mode. The oxidation rate was measured as functions of the anodic current density, the oxygen pressure, and the sample position. The oxide film can grow thick when the growth rate exceeds the sputtering rate.

1. INTRODUCTION

Plasma anodization in a low pressure discharge has been used widely for the low temperature and dry process preparation of insulating films with good dielectric and interface properties on semiconductors and metals (1,2). Plasma oxidation has several advantages over thermal oxidation: the oxidation both at lower temperature and at higher rate suppresses the generation of substrate defects and the variation of diffusion profiles, and also improves the interface properties. Many anodization techniques have been proposed using dc, rf, and microwave induced plasmas (1). The investigation on the detailed conditions necessary for the growth of oxide films and the mechanism of the plasma anodization is, however, still unsatisfactory. This paper reports the investigation on the method, the several oxidation conditions, and the oxidation mechanism for the anodic oxidation of Si in an rf induced oxygen plasma.

2. EXPERIMENTAL

The system for plasma anodization consisted of a quartz glass discharge tube whose inside diameter was 35 mm and length 1 m. This tube was supported by stainless steel holders at both ends. The system was evacuated to a pressure below 0.01 Torr (1.3 Pa) with a rotary pump and then back filled with 99.95 % oxygen gas to a final pressure between 0.02 Torr (2.7 Pa) and 0.3 Torr (40 Pa). The gas pressure was measured with a Pirani gauge. A 13.56 MHz generator of a maximum power of 1 kW supplied rf power which was transferred to the oxygen gas with an impedance-matching network terminating in an in-
ductively coupled copper coil around the tube. The coil was coaxial with the tube, water cooled, and placed at the position 48 cm apart from the left-hand tube holder.

The arrangement for plasma anodization is shown schematically in Fig. 1. A sample (anode) was placed in a quartz sample holder and was in contact with a platinum backing plate. The sample was exposed to a glow through a window of dimensions 5 mm × 5 mm. The sample position is indicated by the distance x from the center of plasma. Four kinds of sample positions were used and x was 3, 5, 7.5, or 10 cm. The deposition of SiO₂ by the sputtering of the quartz tube wall could be avoided at these positions (2). A variable constant-current dc power supply was used for the constant-current anodization. The left-hand tube holder was used for the cathode. A digital voltmeter of input impedance 10 MΩ was used to measure the open circuit voltage V₀c. The inductance of the lead wires and the stray capacitance affected V₀c. V₀c was used as a monitor for the plasma state. An rf filter was used to eliminate the rf interference to the monitoring equipments.

The samples used were (100)-oriented B-doped Si wafers with a carrier concentration (3 - 8) × 10¹⁴ cm⁻³, which were polished on one side. The wafers were cut into samples of dimensions 7 mm × 7 mm. They were degreased, etched, and finally rinsed in distilled water.

An ellipsometer at a wavelength of 5461 Å was used to determine the thickness and refractive index of the grown oxide. We analyzed the measured ellipsometric parameters Δ and Ψ using the usual three-layer (air/film/substrate) model. Reflection high energy electron diffraction (RHEED) was used to determine the crystal structure of the oxide film. Determination of the chemical composition and depth analysis were accomplished by simultaneous Auger electron spectroscopy (AES) and argon ion sputtering.

The electron energy and the positive ion density of oxygen plasma were determined by the floating double-probe method. The double probe consisted of cylindrical tungsten electrodes of diameter 0.8 mm, length 17.5 mm and separated by 15 mm, which were mounted in a Pyrex glass stem with insulating glass sheaths. The sample temperature was measured with a chromel-alumel thermocouple which was in contact with a sample surface.

3. RESULTS AND DISCUSSION

The oxidation was performed in the constant-current mode. We used the rf input power of 300 W throughout the experiment. The sample was placed at a distance of more than 50 cm from the cathode, and the contamination by the cathode sputtering could be avoided. The oxidation rate was measured as functions of the anodic current density Iₘ, the oxygen pressure P₀, and the sample position x.

Figure 2 shows the oxide thickness as a function of the oxidation time at P₀ = 0.05 Torr, Iₘ = 240 mA/cm², and x = 5 cm. Similar relationships were obtained under other oxidation conditions. The oxide growth was linear with time until the thickness reached about 5000 Å. As the oxide film grew thick, the growth rate decreased since the electric field in the ox-
ide dropped substantially because of the space charge effect in it (3). The oxide films were uniform in thickness except for the edge region of the quartz sample holder. The refractive index of the films was 1.47. The RHEED pattern showed a halo and the oxide was amorphous. AES measurements revealed that the composition was constant with depth and the interface region was sharp. The oxide was found to be SiO₂ by the ellipsometry and AES analyses.

The thickness of the oxide film anodized during 30 min is given in Fig. 3 as a function of Iₜ at P₀ = 0.05 and 0.1 Torr, and x = 5 cm. The oxide did not grow thick below 100 mA/cm². The growth rate is proportional to Iₜ above 100 mA/cm².

The growth rate was affected greatly by the oxygen pressure P₀. Figure 4 indicates the thickness of the oxide film grown during 30 min anodization as a function of P₀ at Iₜ = 120 and 240 mA/cm², and x = 5 cm. Similar relationships were also obtained under other conditions. The oxide film did not grow at the pressures both below 0.01 Torr and above 0.2 Torr. The oxidation rate was high at the pressures between 0.04 and 0.1 Torr.

The oxidation proceeds at both SiO₂/plasma and Si/SiO₂ interfaces (4). The growth rate is independent of the oxide thickness at the initial stage as shown in Fig. 2. The electric field intensity in the oxide film is larger than 10⁶ V/cm. Hence, the mass transport in the oxide is owing to not ionic diffusion but ionic drift (5). In this case, the ionic current Iᵢ under high electric field Eₒₓ is expressed as follows (6,7):

\[ Iᵢ = Iᵢ₀ \exp \left[ \frac{q}{kT} (-Wᵢ + ZbEₒₓ) \right] \]  

(1)

where q is the electric charge, k is the Boltzmann's constant, Iᵢ₀ is a constant or weakly dependent on a low power of the temperature T, qWᵢ is the zero-field activation energy for mobile ions jumping from one defect site to the next, qZ is the charge of the ions, and b is the half jump distance for the ions. The stoichiometry of the oxide was unchanged with the anodization conditions, which was revealed by the AES measurements. Hence, the growth rate K is proportional to the ionic current Iᵢ, which represents the rate of the mass transport, and given by the same form as Eq. (1),

\[ K = K₀ \exp \left[ \frac{q}{kT} (-Wᵢ + ZbEₒₓ) \right] \]  

(2)

where K₀ is a constant. The sample surface is, however, sputtered by the negative ions actually. Therefore, the observed oxide growth rate Kₖₒₜₜ is written by

\[ Kₖₒₜₜ = K - Kᵣₑᵥ \]  

(3)

where Kᵣₑᵥ is the sputtering rate. Therefore, the following conditions are necessary to raise the oxide growth rate from Eq. (3): (1) raise the sample temperature T, (2) raise the electric field Eₒₓ, (3) increase the constant K₀, or increase the negative oxygen ion density at the oxide surface, and (4) decrease the sputtering rate Kᵣₑᵥ.

The electron energy kTₑ and the positive ion density Nᵣ are shown in Fig. 5 as functions of P₀. Both kTₑ and Nᵣ vary a little with the pressure. The sample temperature T is
given in Fig. 6 as functions of $P_0$ and $x$. The change of $T$ with the pressure is also small. The electric field in the oxide $E_{ox}$ is constant because of the constant-current mode. The negative ion density was not measured in the present experiment. The negative oxygen ions will be born also at the sample surface on account of the reaction of neutral oxygen atoms with electrons. The negative ion density, and $K_0$ will increase with the pressure monotonously. Therefore, the change of the growth rate with the oxygen pressure $P_0$ depends on the sputtering rate.

Figure 7 shows the anodic current which flows at the zero bias voltage as a function of $P_0$. The fact that the the anode shows the negative voltage, means that the potential drop due to the electron sheath near the anode is large. This potential drop becomes maximum near 0.05 Torr. The pressure range which gives the negative potential corresponds well to the pressure range where the oxide film grows thick. The electron sheath formed in front of the anode becomes the barrier to the arriving negative ions and electrons, and the sputtering by the negative ions is reduced. In the pressure range where the electron sheath is formed, the oxide growth rate becomes high. The oxidation is, therefore, owing probably to the neutral oxygen atoms, which react with electrons on the sample surface, and not to the negative oxygen ions.

The oxide film can grow when the growth rate exceeds the sputtering rate.

Figure 8 represents the oxidation rate $K$, the electron energy $kT_e$, and the positive ion density $N_i$ as functions of the sample position $x$ at $P_0 = 0.05$ Torr and $I_s = 240$ mA/cm$^2$. We also obtained similar relations under other oxidation conditions. The growth rate is high at the position where both the electron energy and the positive ion density are high.

This phenomenon can be explained by assuming that electrons with higher energy have larger probability to be trapped by surface oxygen atoms and larger neutral oxygen atoms are generated at the higher positive ion density.

REFERENCES

Fig. 1. Schematic diagram of an arrangement for plasma anodization.

Fig. 2. Oxide thickness grown on Si in the anodization with constant current of 240 mA/cm² at the pressure of 0.05 Torr and the sample position of x=5 cm as a function of the oxidation time.

Fig. 3. Thickness of the oxide film grown on Si during 30 min in the constant-current anodization at the pressures of 0.05 and 0.1 Torr and the sample position of x=5 cm as a function of the anodic current density.

Fig. 4. Thickness of the oxide film grown on Si during 30 min in the anodization with constant currents of 120 and 240 mA/cm² at the sample position of x=5 cm as a function of the oxygen pressure.
Fig. 5. Electron energy and positive ion density for an oxygen plasma at the rf power of 300 W and the position of x=5 cm as functions of the pressure.

Fig. 6. Sample temperature in an oxygen plasma at the rf power of 300 W as functions of the sample position and the pressure.

Fig. 7. Anodic current flowed at the zero bias voltage at the rf power of 300 W and the sample position of x=5 cm as a function of the oxygen pressure.

Fig. 8. Oxidation rate in the anodization with constant current of 240 mA/cm², and the electron energy and the positive ion density for an oxygen plasma at the pressure of 0.05 Torr as functions of the sample position.