Influence of Electrolyte Temperature on Anodic Oxidation of Single Crystalline Silicon in Ethylene Glycol Solution

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Anodic oxidation of single crystalline silicon was carried out in constant current and constant voltage modes using a solution of 0.04 N HNO₃ in an ethylene glycol at temperatures of 20 to 70°C. The current and voltage between an anode and a cathode were measured during the anodic oxidation process. The influence of anodic oxidation temperature on the growth process of silicon dioxide films was studied by current-time characteristics. The silicon dioxide films grown on silicon wafers were analyzed by XPS to study the influence of the electrolyte temperature and hydroxides content. The transition time when the voltage between the anode and cathode reaches the preset-up voltage had a maximum value at 45°C. The silicon dioxide film thickness and capacitance had a maximum and minimum, respectively, when the anodization was carried out at 45°C. Stoichiometric SiO₂ films could not be formed at this temperature. The XPS peak intensities of Si⁴⁺ and Si⁰⁺ in anodically oxidized films depended on the electrolyte temperature. The Si⁴⁺ peak appeared even in the substrate for the films anodized at 45°C. It was confirmed that the boundary region existed between the SiO₂ film and Si substrate. Furthermore, hydroxides existing within the film was concentrated at the silicon dioxide-silicon boundary at 45°C. The property of oxide films depends on the content of hydroxide, which is a function of the anodization temperature.

Key Words : Anodic Oxidation, Single-crystalline Silicon, Ethylene Glycol, X-ray Photoelectron Spectroscopy (XPS)

1 Introduction

Growth of silicon dioxide (SiO₂) film is a basic technique for integrated circuit technology. Usually, thermal oxidation process of silicon is carried out in a horizontal reactor at a high temperature over 1100°C. However, application of the thermal oxidation technique to device fabrication is limited, because it needs a high temperature. For example, hydrogen bonds in amorphous silicon are cut off over 400°C. A high temperature is not required to an anodic oxidation technique.¹⁾ However, there have been a few reports on anodic oxidation of single crystalline silicon,^{2, 3)} because thermally oxidized silicon films are generally superior in quality to anodically oxidized films. Particularly the influence of electrolyte temperature on anodic oxidation process of silicon has scarcely been reported, although it was examined in GaAs.⁴⁾

We studied the growth of SiO₂ films by anodic oxidation on Si wafers at around room temperatures and found that the quality of the SiO₂ films were considerably influenced by the electrolyte temperature previously.⁵⁾ This paper describes the influence of temperature on the oxide film growth in the anodic oxidation of single crystalline silicon at low temperatures. The quality of the anodically oxidized films will be discussed based on the results of XPS analysis.

2 Experimental

2.1 Anodic oxidation

The automatic monitoring system for the anodic oxidation is shown in Fig. 1, in which details of the anodic oxidation cell and the electrodes used in this study are illustrated. The cell was placed in a water bath, which is provided with a heater to control the temperature. The anode was an n-type single crystalline silicon wafer, whose resistivity was 10 Ω cm. The cathode was a platinum plate, whose purity was 99.9%. The silicon wafer was clung on the hollow holder by vacuum pumping with a trap. The electrolyte used in this study was a solution of 0.04 N HNO₃ in an ethylene glycol. The electrolyte temperature was kept constant in the range of from 20°C to 70°C. When a constant current was fed to the electrode by a DC power supply, a silicon dioxide film began to grow on the silicon wafer, and the thickness of oxide film increased with the elapse of time. The voltage and current between the anode and cathode were measured during the anodic oxidation process every ten seconds. The voltage in a standard resistance of 100 Ω was converted into the current. Both the voltage and current measured by a digital voltmeter were transferred to a personal computer through a GP-IB interface cable. When the voltage reached 200 V, the constant current mode was changed to the constant voltage electrolysis,

Fig. 1 The automatic measuring system of anodic oxidation process used in this study, and the cell configuration.

in which the current decreased with elapse of time, and the surface of silicon dioxide film was found to become smooth.

2. 2 XPS analysis

XPS analysis of SiO_2 film on Si substrate was carried out under the pressure of less than 10^{-7} Pa. The silicon dioxide film thickness and internal hydroxide contents were measured by the XPS depth profile. The surface of sample was sputtered by argon ions at 20 mPa to obtain the profile. It was confirmed that the depth of one sputter cycle was constant by the measurement of the standard sample. The observation was made on the SiO_2 film surface by using a CCD camera during the XPS analysis. The experimental condition of XPS analysis is summarized in Table 1. Finally, MOS structures were fabricated based on the silicon dioxide films by vacuum depositing an aluminum electrode of 1.23 mm^2 in area, and the capacitance of SiO_2 films was measured to study the effect of the electrolyte temperature on the SiO_2 thickness.

3 Results and Discussion

3. 1 Current-time characteristics

The change in current and voltage with the anodic oxidation time of the Si wafer at the electrolyte temperature of 35°C is given in Fig. 2, where the anodic oxidation begun at a constant current density of 100 mA cm^{-2} and the preset-up voltage was 200 V. In the constant current electrolysis, the voltage between the anode and cathode increased with an increase in thickness of growing SiO_2 film and reached the preset-up voltage, and then the anodic oxidation was changed to the constant voltage electrolysis, where the current decreased with elapse of time. The time when the voltage between the anode and cathode reaches the preset-up value of 200 V and the current begins to decrease is defined as transition time in this

Fig. 2 Changes in current density and voltage with anodic oxidation time of Si at 35°C .

paper. As described above, the electrolysis mode was changed from constant current to constant voltage at the transition time.

The current-time characteristics of the anodic oxidation are given in Fig. 3 for four choices of electrolyte temperature of 40, 45, 50 and 60°C at current densities of 50 and 100 mA cm^{-2} . In general, the transition time was long in the anodization at low current densities in comparison with high current densities. The transition time depended on the electrolyte temperature and was the longest at 45°C for both the current densities. Similar results were also obtained by the current interrupting method⁶⁾ on the analysis of anodic oxidation process of single crystalline silicon. These results suggest that oxidation process at 45°C may be different from those at other temperatures.

3. 2 XPS spectra of Si2p and O1s

To study the anodic oxidation of Si at 45°C in more detail, internal chemical states of the oxide films were analyzed by XPS with argon ions sputtering. XPS analysis was carried out every 30 s of sputtering. The depth profiles of the SiO_2 film on Si substrate by XPS analysis are shown in Fig. 4 for three choices of anodic oxidation at

Fig. 3 Changes in current density with anodic oxidation time of Si at 40, 45, 50 and 60°C .

Table 1 The experimental condition for XPS analysis.

X-ray	Filament	hν	Voltage	Power
	Mg	1253.6/eV	14/kV	400/w
Sputter	Beam	Emission	Pressure	Interval
	3/kV	25/mA	20/mPa	30/s

the electrolyte temperatures of 40, 45 and 50°C for 1 hour anodization. The ordinate and abscissa in the figure indicate the depth and the binding energy, respectively. The zero point on depth axis corresponds to the surface of the specimen. The height indicates the photoelectron counts. The photoelectron counts of the O1s peaks are referred to Fig. 6. The boundary between the SiO₂ and Si substrate was located at the depth of about 100 nm for all the specimens. The right two peaks are Si2p spectra, Si⁴⁺ corresponds to SiO₂, whose binding energy is about 108 eV, and the other peak Si⁰⁺ originates from single crystalline Si, whose binding energy is about 100 eV. The left peak is O1s, whose binding energy is about 538 eV.

The growth rate of oxide films in thermal oxidation

was reported.^{7, 8)} To compare the anodic oxidation with thermal oxidation, thermal oxidation of a Si wafer with the same resistivity was carried out at 1100°C for 3 hours in dry O₂ in this study, and the XPS analysis was made on the formed film. Results for the thermally oxidized specimen is also given at the top of Fig. 4. In the thermal oxidation, the Si⁴⁺ peak intensity was approximately constant up to the boundary from the surface and decreased rapidly associated with an increase in Si⁰⁺ peak intensity in the Si substrate. In contrast to the thermal oxidation of Si, the Si⁴⁺ peak intensity did not decrease so rapidly associated with an increase in Si⁰⁺ peak intensity beyond the boundary for the anodic oxidation at 40°C. This tendency was more predominant, the Si⁴⁺ peak intensity did not decrease even beyond 100 nm for the anodic oxida-

Fig. 4 Depth profiles of Si⁰⁺, Si⁴⁺ and O1s spectra by XPS analysis for specimens thermally oxidized at 1100°C and anodically oxidized at 40, 45 and 50°C.

tion at 45°C, where the Si^{0+} peak began to increase but not so strongly. However, the Si^{4+} peak intensity decreased rapidly and the Si^{0+} peak intensity increased strongly beyond the boundary for the anodic oxidation at 50°C, which were close to the results of the thermal oxidation.

On the other hand, change in depth profiles of the O1s at 538 eV, shown at the left side of Fig. 4, with the electrolyte temperature was similar to that of the Si^{4+} peaks, though the peak intensity was about five times of that of the Si^{4+} peaks. Change in the Si2p and O1s peaks with electrolyte temperature suggests that the anodic oxidation film formed at 45°C is the thickest among the three films formed at various temperatures at the same oxidized time. The O1s peak intensity was high at the surface for all the specimens, which can be attributable to oxygen adsorption on the surface. The small peak at around 529 eV is a satellite peak by Mg-K β , and the other small peak at around 542 eV may be hydroxide or moisture in the anodically oxidized film.

3. 3 Depth profiles of XPS analysis

Depth profiles of Si^{0+} and Si^{4+} are shown in Fig. 5 for the thermal and anodic oxidation. The zero point on the abscissa indicates the surface of a specimen. The concentration of Si^{0+} increased sharply around 100 nm and the concentration of Si^{4+} decreased sharply simultaneously in the thermal oxidation specimen. This result suggests that the thickness of the thermally oxidized layer is determined by the rising point of Si^{0+} concentration and the falling point of Si^{4+} in Fig. 5, where the thickness is about 100 nm. In Fig. 5, Si^{0+} of a small quantity which exists in the oxidized film consists of mostly a satellite peak and the back ground. Therefore, Si which was not oxidized through the anodization process may not be remained in the anodically oxidized film. Although the Si^{0+} and Si^{4+} concentrations begin to increase and decrease in the anodic oxidation respectively, at approximately the same depth as the thermal oxidation, the boundary of Si and SiO_2 is not so unambiguous as that except for the anodic oxidation at 50°C and 60°C. The decrease of Si^{4+} and the increase of Si^{0+} in the anodic oxidation are not so sharp comparing with those in the thermal oxidation. The boundary of the SiO_2 film on Si substrate is not definite any more in the anodic oxidation at 40°C. In other words, the boundary between the SiO_2 film and Si substrate is ambiguous in the anodic oxidation at 40°C. This result suggests that considerable amount of oxygen diffuse into the Si region and anodize Si existing in the boundary territory for the anodic oxidation at 40°C.

Further diffusion of Si^{4+} was confirmed for the anodic oxidation at 45°C as shown in Fig. 5(d). The boundary region broadened most widely at 45°C. The existence of excess oxygen was confirmed by the quantitative analysis from the comparison of O1s and Si^{4+} peak area at this temperature. In this case, stoichiometric SiO_2 film was not formed because of excess oxygen. The excess oxygen influences the insulating properties of the film. As a result, the film insulation becomes improper in the anodic oxidation at 45°C. However, the boundary became clear again in the anodic oxidation at over 50°C as shown

in Figs. 5(e) and (f). Because of deterioration of insulating ability of SiO_2 insulation, the transition time when the voltage reaches the preset-up value becomes long where the thickest oxide film is formed at 45°C.

Depth profiles of the peak intensity of main O1s peak and O1s originated from oxygen in the hydroxide are shown in Fig. 6 for the anodic oxidation at various temperatures. In Fig. 6, the main peak at about 538 eV is originated from the oxygen bound with Si, while the peak at 542 eV from the oxygen of hydroxide. The O1s peak located at the SiO_2 -Si boundary is sharp except for the anodic oxidation at 45°C, and the O1s intensity decreases rapidly in the Si substrate. The peak intensity of the part of hydroxide is smaller than those of O1s, and the depth profile of the hydroxide intensity changes obviously with electrolyte temperature. The O1s peak intensity in the oxide films was constant for the thermal oxidation, and any trace of hydroxide peaks did not appear as shown in Fig. 4. The sum of the intensities of main O1s peak and O1s originated from oxygen in hydroxide becomes constant for the anodic oxidation and without excess oxygen. On the other hand, the sum is not constant at the boundary of the SiO_2 film and Si substrate, which suggests existence of excess oxygen in the films.

When the anodic oxidation at 30 and 35°C proceeds, the hydroxide is distributed uniformly inside the SiO_2 film. When the electrolyte temperature rises to 40°C, however, the distribution of hydroxide begins to lean around the SiO_2 -Si boundary. This result suggests that stoichiometric SiO_2 films can not be formed, because the reaction proceeds so rapidly^{9,10)} at the vicinity of the boundary. The activation energy for reaction changes suddenly⁶⁾ at the temperature, and excess oxygen is formed, resulting in deterioration of insulating properties of the film. Particularly at 45°C, the hydroxides are concentrated only vicinity the boundary, and no hydroxide appear at the surface as shown Fig. 6(d). If oxygen does not perfectly bind with Si, excess oxygen may disturb ion movement. Usually the resistance of Si decrease with an increase in temperature, but it increases temporarily in such a case.⁶⁾ This condition relates to the increase in film thickness at 45°C. Furthermore, the amount of hydroxide is small for the anodization at 45°C. When much water is contained in the electrolyte, the growth ratio of the anodically oxidized films becomes small.¹¹⁾ The electrolyte used in this experiment did not contain any water. However, the film capacity increased when water was contained in the electrolyte. In addition, the capacity of films formed in an electrolyte with some water decreased when water was removed by the annealing at over 300°C. These results indicate that the hydroxide in the film promotes the increase in film thickness. Because the amount of hydroxide is small at 45°C, the thickness of a SiO_2 film is larger than those anodized at other temperatures. In other words, changes in both the oxide film thickness and the transition time with electrolyte temperature depend on both the total amount and distribution of hydroxide in the film. The reaction rate decreases at higher than 50°C and the hydroxide distribution becomes uniform again as shown in Figs. 6(e) and (f).

Such change in oxidation behavior occurred in the anodic oxidation at 45°C did not appear in amorphous Si formed the current interrupting method.¹²⁾ The specific oxidation behavior of Si at 45°C may be correlated with crystallinity of Si, although the detailed mechanism is

ambiguous at this moment.

The thickness and capacitance of the anodically oxidized films as a function of electrolyte temperature are given in Fig. 7. The former was determined by the rising point of Si^{0+} concentration in Fig. 5 and the maximum

Fig. 5 Depth profiles of Si^{0+} and Si^{4+} concentration determined by XPS analysis. (a) thermal oxidation at 1100°C, (b) anodic oxidation at 25°C, (c) anodic oxidation at 40°C, (d) anodic oxidation at 45°C, (e) anodic oxidation at 50°C, (f) anodic oxidation at 60°C.

point of O1s in Fig. 6, both were close with each other, and the latter was determined by capacitance measurements on MOS structures fabricated from the anodically oxidized films. The thickness and capacitance are maximum and minimum when anodized at 45°C respectively.

This is reasonable because the capacitance is inversely proportional to oxidize film thickness. In addition, a blue interference color on the surface of Si wafer was uniform under any conditions. The dielectric constant of films obtained from film thickness and capacitance may suggest

Fig. 6 Depth profiles of main O1s peak and O1s originated from oxygen in hydroxide determined by XPS analysis for anodic oxidation specimens. Anodic oxidation temperatures are as follows.

(a) 30°C, (b) 35°C, (c) 40°C, (d) 45°C, (e) 50°C, (f) 55°C.

Fig. 7 Thickness and capacitance of the anodically oxidized films as a function of electrolyte temperature.

change in dielectric phase. This result also suggests that the film surface is flat and the measurements are correct. The results in Fig. 7 are consistent with those in Figs. 5 and 6.

In conclusion, the behavior of films anodically oxidized at 45°C may be explained as follows. Because of deterioration of insulating ability of SiO_2 film, the film thickness increases and the transition time becomes long at this temperature. The film thickness is influenced by the amount of hydroxide in the film. Although the insulation property of the film oxidized at 45°C is not good, the film characteristics change greatly at about 45°C. These results suggest that the film property can be controlled by the anodization temperature. Oxidized films of a good quality may be obtained by the anodization at a temperature higher than 45°C.

4 Conclusion

The anodic oxidized of single crystalline silicon was

carried out by applying a DC voltage in ethylene glycol solution at various temperatures. It can be concluded that the anodically oxidized film thickness has a maximum at the electrolyte temperature of 45°C. The distribution of hydroxides inside the film, which was confirmed by XPS analysis, leans around the SiO_2 -Si boundary at the same temperature. The capacitance of anodically oxidized film had a minimum value at the electrolyte temperature of 45°C. Changes in both the oxide film thickness and the transition time with electrolyte temperature depend on both the total amount and distribution of hydroxide in the film. The property of anodically oxidized films depends on the anodization temperature and is changed drastically at the vicinity of 45°C, where the thickest oxide film is formed.

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