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ANALYSIS OF THE ANODIC OXIDATION OF SINGLE CRYSTALLINE SILICON IN ETHYLEN GLYCOL SOLUTION

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Abstract

Silicon dioxide films were prepared by anodizing silicon wafers in an ethylene glycol+ HNO_3(0.04 N) at 20 to 70℃. The voltage between silicon anode and platinum cathode was measured during this process. Under the constant current electrolysis, the voltage increased with oxide film growth. The transition time at which the voltage reached the predetermined value depended on the temperature of the electrolyte. After the time of electrolysis reached the transition time, the anodization was changed the constant voltage mode.

The depth profile of oxide film/Si substrate was confirmed by XPS analysis to study the influence of the electrolyte temperature on the anodization. Usually, the oxide-silicon peaks disappear in the silicon substrate, however, this peak was not small at 45℃ in this region.

Key words : *Anodic Oxidation, Silicon Wafers, Ethylene Glycol, X-ray Photoelectron Spectroscopy, Depth Profile of Oxide Film*

1. INTRODUCTION

Anodic oxidation of single-crystalline silicon is a basic technique for integrated circuit technologies. The growth of a silicon dioxide layer at room temperature is desirable, but anodization of silicon at room temperature has not been studied in detail yet. This paper describes the influence of temperature on the oxide film growth rate in the anodization of a single-crystalline silicon at low temperatures.

2. EXPERIMENTAL

Anodization of silicon wafers were carried out by applying a dc voltage in an ethylene glycol solution. The anodization cell used in this study is illustrated in Fig. 1[1]. The anode was an n-type silicon wafer, and whose resistivity is 10Ω·cm. The silicon wafer was clung with the hollow holder by vacuumization, and the cathode was a platinum plate. The cell was placed in a water bath, and the temperature of the

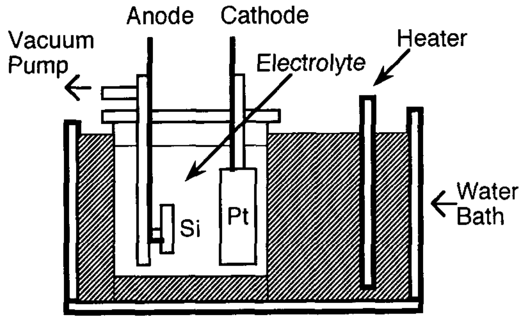


Fig. 1 Anodization cell and electrode configuration

electrolyte was changed from 20℃ to 70℃.

The anodization was carried out in the following mode. First, the anodization was begun at a constant current of 100 mA, where the voltage between the anode and the cathode increased with an increase in thickness of growing oxide films, then the anodization was changed to the constant voltage mode beyond the predetermined voltage of 200V, where the current decreased with elapse of time. The transition time, at which the electrolysis mode was changed, was measured to study the influence of electrolyte temperature. The current and voltage during the anodization were measured by a digital voltmeter and sent to a personal computer by a GP-IB interface.

When the current decreased enough to small by the anodic oxidation process, the surface of silicon dioxide films became smoother. XPS analysis was carried out on this sample, then we obtained the depth profiles of the oxide film/Si substrate.

3. RESULTS AND DISCUSSION

Changes in cu::rrent and voltage with time during the anodization of the silicon wafer are given for four choices of the electrolyte temperature lower than 45℃ in Fig. 2 (a). The transition time, at which the adnodization mode was changed from constant current to constant voltage, was found to depend on the temperature of electrolyte[2]. As the electrolyte temperature in}creased, the transition time became shorter.

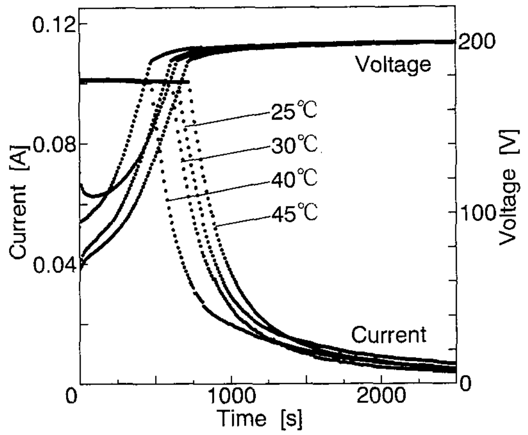


Fig. 2(a) Changes in current and voltage with time during anodization of Si at 25, 30, 40 and 45℃

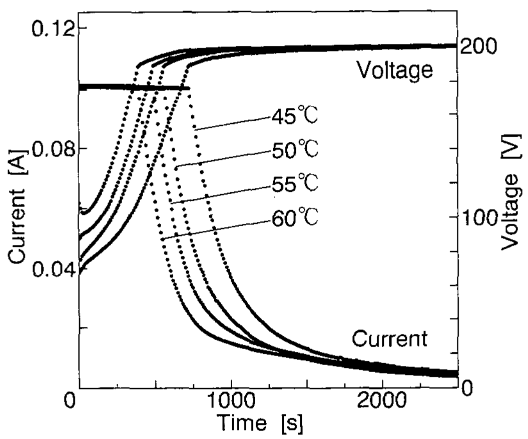


Fig. 2(b) Changes in current and voltage with time during anodization of Si at 45, 50, 55 and 60℃

However, the transition time was the longest at 45℃.

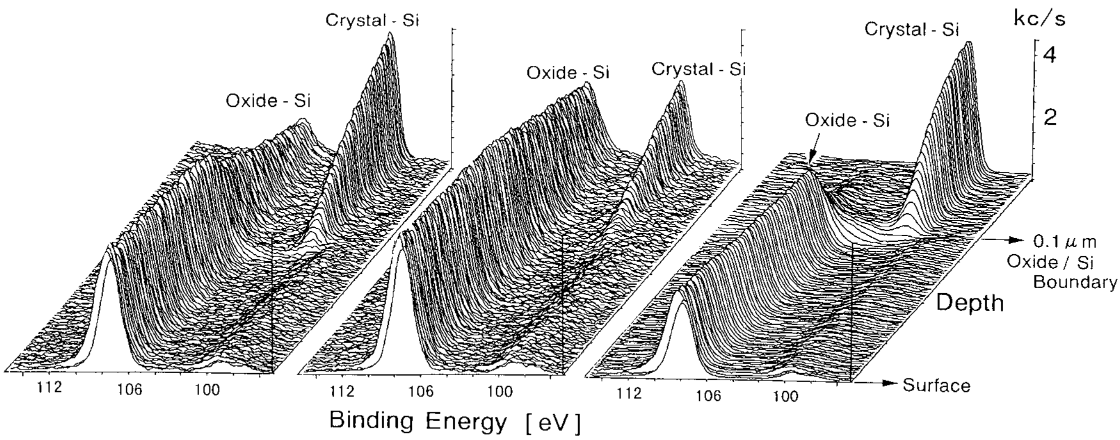
The variation of the current and voltage with temperature over 45℃ is given in Fig. 2(b). When electrolyte temperature increased, this transition time decreased in the temperature range of 45~60℃. Figures 2(a) and (b) indicate that the transition time has the maximum value at 45℃.

XPS analysis was carried out on the oxide film /Si substrate to study the influence of electrolyte temperature on the silicon anodization. The condition of X-ray source is summarized in Table 1, along with the argon ion gun condition. The X-ray source was magnesium standard. The etching rate by one cycle sputter was about 1.6 nm.

The depth profiles of the oxide film/Si substrate by XPS analysis are shown in Fig. 3. The depth of the boundary between the silicon dioxide and silicon substrate was about 0.1㎛. The single crystalline Si peak is strong to deep boundary, while, the oxide Si peak is small at the electrolyte temperature of 30℃. However, the oxide silicon peaks didn't become small in the silicon substrate at 45℃. In the case the anodization at 60℃, the oxide silicon peaks decreased in this region. The Si2p peak suggests that the anodic oxide film formed at 45℃ is the thickest among the three films formed at various temperatures. In addition, the capacitance of anodic oxide film was found to be minimum at the anodization temperature of 45℃[2]. It can be concluded that steady oxide films are grown by the anodization at a controlled electrolyte temperature.

Table 1. The condition of XPS analysis

(X-ray source) Filament X-ray Voltage	 Mg 14kV
(Ion gun) Ar pressure Emission current Beam voltage Sputter interval Raster size	 20 mPa 25 mA 3kV 30 s 2.5×2.5㎜ square



(a) 30℃ (b) 45℃ (c) 60℃

Fig. 3 Depth profile of XPS Si2p spectra for specimens anodized at (a)30℃, (b)45℃ and (c)60℃

4. CONCLUSION

Anodization of single crystalline silicon was carried out in ethylene glycol+HNO_3 solution at various temperatures. It can be concluded that the anodization rate is maximum at the electrolyte temperature of 45℃. And then, we could grow steady oxide films by anodization at a low temperature.

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