

Native Oxide Growing Behavior on Si Crystal Structure and Resistivity

Katsuyuki SEKINE, Geun-Min CHOI, Mizuho MORITA and Tadahiro OHMI

Department of Electronic Engineering, Faculty of Engineering,
Tohoku University, Sendai, 980-77, Japan
TEL:81-22-217-7124, FAX:81-22-263-9395

ABSTRACT

We have studied native oxide growing behavior on various surfaces by X-ray photoelectron spectroscopy (XPS) and revealed that the oxide thickness obtained after cleaning treatments widely varies on surface conditions: single crystal (c-Si), amorphous(a-Si) and undoped or highly phosphorous-doped polycrystalline silicon (poly-Si). Native oxide growing in sulfuric acid-hydrogen peroxide mixture (SPM, H₂SO₄ / H₂O₂ = 4:1) cleaning shows a critical point of silicon surface resistivity around 10⁻² Ω·cm. The native oxide thickness on a-Si after the SPM cleaning is thicker than that on c-Si, because the a-Si surface has many defect sites. The native oxide thickness grown during ultra pure water (UPW) rinsing after dilute hydrofluoric (DHF) cleaning relies on the resistivity but not the crystal structure.

1. INTRODUCTION

As semiconductor devices are scaled down to smaller dimensions, the control of native oxide growth on silicon surfaces is more and more important in the fabrication of ultralarge-scale integrated devices. The native oxide grown on c-Si substrates increases the contact resistance and degrades the precise control of the thickness and electrical properties of ultra-thin gate oxide films. Also, the native oxide is a source of contaminants such as oxygen and metallic impurities¹⁾. On continuous decreasing of device dimensions, the control of native oxide growth on poly-Si and a-Si in addition to c-Si surfaces is also important more and more, because the native oxide degrades the quality of films deposited on poly-Si and a-Si in the contact formation or the capacitor structure fabrication in DRAM processes. Thus, it is a key issue in the film deposition process how to control native oxide growth. Until now, a large number of studies have been made on the growth characteristics of native oxide on c-Si²⁻⁷⁾. However, the growth of native oxide on silicon surfaces except c-Si is not well understood yet. In this paper, we describe the growing behavior of native oxide on silicon substrates with different crystal structures or resistivities after hydrophobic or hydrophilic cleaning.

2. EXPERIMENTAL

The samples used in this study were prepared using a hot wall type of low pressure chemical vapor deposition (LPCVD) vertical system under conditions as summarized in Table 1. The samples were cleaned with an SPM solution for 10 min to remove carbonic compounds and metallic impurities from the silicon surface. The chemical oxide grown during the SPM cleaning was etched away by 1 min dip in a 0.5 % DHF solution. Finally, the samples were treated by the following hydrophilic or hydrophobic cleaning just before XPS measurements.

(1) hydrophilic cleaning

The samples were dipped in an SPM solution for 10 min, rinsed in UPW (resistivity : 18.2 MΩ·cm) for 10 min and dried by nitrogen gas blowing. The native oxide was grown in the SPM cleaning step and its thickness hardly increases in the UPW rinsing step.

(2) hydrophobic cleaning

After the SPM cleaning under the condition (1), the samples were dipped in a 0.5% DHF solution for 1 min. To study the native oxide growing behavior after hydrophobic cleaning, the UPW rinsing time was varied from 1 to 300 min. The native oxide was grown in the UPW rinsing step.

Table 1. Surface structure, film deposition condition and resistivity of silicon samples.

Split No.	Structure	Deposition condition	Resistivity
#1	Single crystal	-	9-10 Ω·cm
#2	Amorphous	510 °C deposition (Si ₂ H ₆ -based)	Intrinsic
#3	Polycrystalline	620 °C deposition (SiH ₄ -based)	Intrinsic
#4	Polycrystalline	620 °C deposition (SiH ₄ -based), 900 °C POCl ₃ doping	3.3x10 ⁻² Ω·cm
#5	Polycrystalline	550 °C deposition (SiH ₄ -based with PH ₃ in N ₂), 650°C N ₂ anneal (30 min, 1 atm)	1.6x10 ⁻² Ω·cm
#6	Polycrystalline	550 °C deposition (SiH ₄ -based with PH ₃ in N ₂), 650°C N ₂ anneal (30 min, 1 atm)	1.1x10 ⁻³ Ω·cm
#7	Polycrystalline	550 °C deposition (SiH ₄ -based with PH ₃ in N ₂), 650°C N ₂ anneal (30 min, 1 atm)	3.7x10 ⁻⁴ Ω·cm

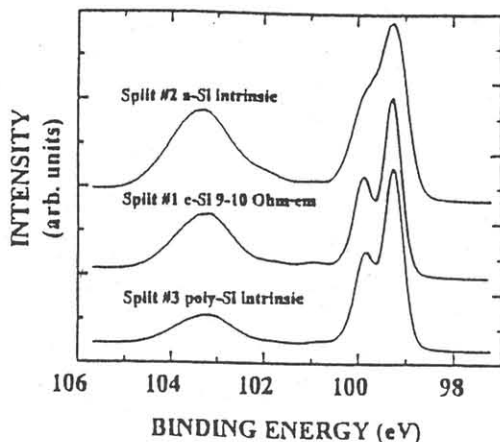


Fig. 1. Si2p XPS spectra of native oxide on silicon substrates after SPM cleaning.

The surface microroughness of the samples after the SPM cleaning was measured by an Atomic Force Microscope (AFM) in the contact mode. The resistivity of phosphorous-doped silicon films was evaluated by auto spreading resistance profile (ASRP). The microstructure and the orientation of silicon films were determined by X-ray diffraction (XRD) and reflection electron diffraction (RED). The XPS measurements were performed by a Scienta ESCA-300 system with a monochromatic Al-K α X-ray source. In order to enhance the sensitivity of native oxide thickness determination, the take-off angle was adjusted at 15 deg. and the counts per second of Si2p3/2 peak was at above 10^5 counts for all measurements. The native oxides formed by cleaning treatments were evaluated by known methods: the oxide thickness determination method using XPS calibrated by ellipsometry⁹⁾ and the characterization method of suboxide Si⁺¹, Si⁺², Si⁺³ and Si⁺⁴ reported by Himpsel⁸⁾.

3. RESULTS AND DISCUSSIONS

Figure 1 shows Si2p XPS spectra of native oxide on silicon substrates with different crystal structures after the SPM cleaning, where the height of Si2p3/2 peaks is normalized. The full width at half maximum (FWHM) values of bulk silicon and native oxide for a-Si is larger than that for c-Si and poly-Si. This indicates that the energy state of Si2p is broad because the bond length between a Si atom and the nearest neighbor Si atom is not constant in a-Si. The intensity of native oxide on a-Si is the highest among the three, while poly-Si shows the lowest oxide thickness as shown in Fig. 1.

Figure 2 shows the film thickness and the root mean square (RMS) value of surface microroughness of native oxide on Si substrates with different crystal structures after SPM cleaning. RED pattern and crystal orientation for silicon substrate surfaces are also shown in Fig. 2. The native oxide thickness on a-Si after the SPM cleaning is thicker than that on c-Si. It is supposed that the short-range-order structure and the elongated silicon bond⁹⁾ which forms many defect sites in a-Si surface enhances the growth rate of the native oxide.

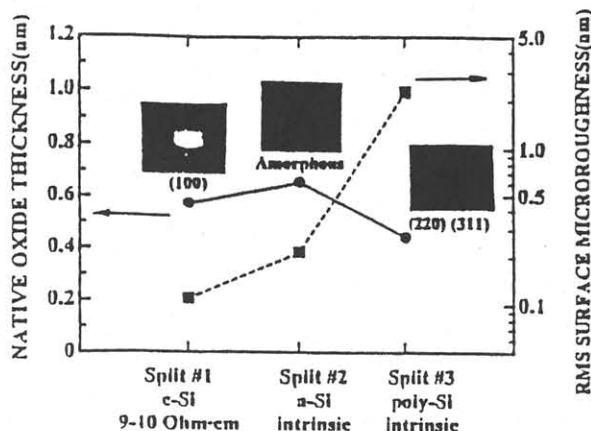


Fig. 2. Oxide thickness and RMS value of surface microroughness after SPM cleaning on silicon crystal structure. RED patterns and crystal orientations of silicon surface are also shown.

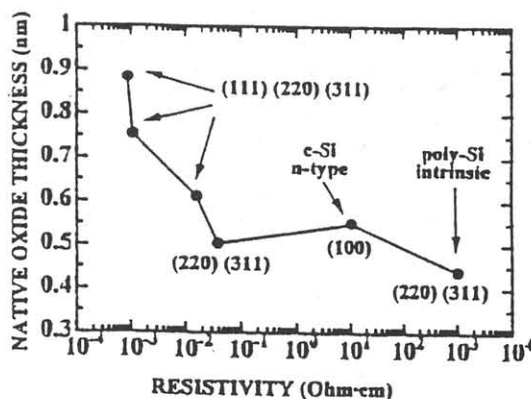


Fig. 3. Oxide thickness after SPM cleaning as a function of resistivity. Crystal orientations of silicon surface are also shown.

The native oxide thickness on undoped poly-Si is thinner than that on c-Si, while the RMS value of surface microroughness of undoped poly-Si is larger than that of c-Si, indicating that the poly-Si substrate has a larger effective surface area. These suggest that the oxide thickness on undoped poly-Si reflects the steric hindrance effect¹⁰⁾ of crystal structure on silicon oxidation.

Figure 3 shows native oxide thickness after the SPM cleaning as a function of the resistivity of silicon surface. The crystal orientation of silicon surface are also shown in Fig. 3. For high-resistivity level (above 10^{-2} Ω -cm), the native oxide thickness depends on the surface crystal structure regardless of the resistivity. This suggests that the oxide thickness predominantly reflects the steric hindrance effect on the crystal structure for high-resistivity surfaces. For low-resistivity (below 10^{-2} Ω -cm), the native oxide thickness after the SPM cleaning increases with a decrease of the resistivity of silicon surface. Native oxide thickness after the SPM cleaning for low-resistivity level mainly depends on the resistivity regardless of the crystal structure. This result shows that a relation between the native oxide thickness on poly-Si after cleaning treatments and the surface doping level is similar to that on c-Si¹⁰⁻¹¹⁾

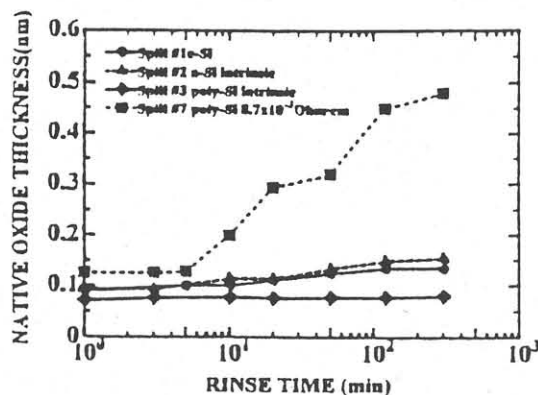


Fig. 4. Oxide thickness as a function of rinsing time in UPW after dilute HF etching. The resistivity of ultra pure water is $18.2 \text{ M}\Omega\cdot\text{cm}$.

From these results, it can be concluded that native oxide growing behavior on poly-Si in the SPM cleaning has a critical point of the resistivity around $10^{-2} \Omega\cdot\text{cm}$.

Figure 4 shows native oxide thickness as a function of the rinsing time in UPW after the DHF treatment. Thicker native oxide on the poly-Si surface with low-resistivity is grown even after 1 min rinsing in the UPW. The oxide thickness on a-Si and undoped poly-Si after the UPW rising is nearly same as that on c-Si, while the native oxide thickness on a-Si after the SPM cleaning is thicker than that on c-Si. This suggests that native oxide growing behavior in UPW rinsing strongly relies on the resistivity rather than the crystal structure. This means that the DHF-treated surface of a-Si, in terms of the oxidation during UPW rinsing time, is relatively more stable than poly-Si with low-resistivity surface. This result is very important for the double silicon deposition or the HSG (hemispherical grain) film deposition process, which are used for the contact formation of bit-line and the storage node or the capacitor structure fabrication of DRAM devices.

Figure 5 shows native oxide thickness formed in UPW rinsing as a function of the resistivity of silicon surface. The crystal orientation of silicon surface is also shown in Fig.5. The oxide thickness increases with decreasing of the resistivity. It can be concluded from Figs.4 and 5 that native oxide growing behavior in UPW rinsing after the hydrophobic cleaning strongly depends on the resistivity but not on the crystal structure.

4. CONCLUSION

We have studied that native oxide growing behavior on various silicon surfaces and revealed that the oxide thickness after cleaning treatments widely varies on silicon surface conditions: c-Si, a-Si and un-doped or highly phosphorous-doped poly-Si surfaces. After SPM cleaning, for low-resistivity silicon surface with below $10^{-2} \Omega\cdot\text{cm}$, the native oxide thickness strongly depends on the resistivity regardless of the crystal structure. The native oxide thickness for high-resistivity silicon surface with above $10^{-2} \Omega\cdot\text{cm}$ depends on the crystal structure rather than the resistivity of silicon surface.

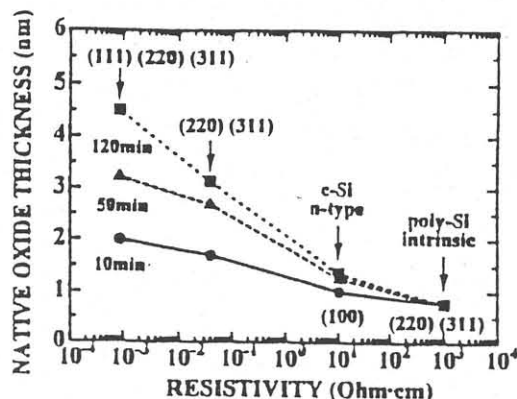


Fig. 5. Oxide thickness grown in UPW as a function of resistivity. Crystal orientations of silicon surface are also shown. The resistivity of ultra pure water is $18.2 \text{ M}\Omega\cdot\text{cm}$.

The native oxide thickness formed in UPW rinsing after the hydrophobic cleaning relies on the silicon surface doping level but not on the crystal structure.

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