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Metal-induced negative oxide charge detected by an alternating current surface photovoltage in thermally oxidized Fe-contaminated n-type Si (001) wafers

Hirofumi Shimizu *, Tomohiro Otsuki
College of Engineering, Nihon University, Koriyama, Fukushima 963-8642, Japan

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A B S T R A C T
The atomic-bridging type negative oxide charge in SiO₂ is investigated using the Fe-contaminated (001) surface of n-type Si wafers. The investigation is done on the basis of a chemical analysis and a method in which the frequency-dependent alternating current (AC) surface photovoltage (SPV) is measured. At room temperature, an AC SPV appears and gradually increases, saturating after approximately one day (with an Fe concentration on the Si surface of 4.0 × 10¹³ atoms/cm²). The AC SPV eventually becomes inversely proportional to frequency except at very low frequencies (< 10 Hz) corresponding to weak or strong inversion, indicating that the negative Fe induced oxide charge appears in the form of a (FeOSi)⁻ network. Also in Fe-contaminated n-type Si(001) surfaces thermally oxidized at between 550 and 650 °C for 60 min, strong inversion is unquestionably observed, proving that the (FeOSi)⁻ network survives and that most of the added Fe has segregated into the region closest to the surface of the thin SiO₂ film. At 850 °C and/or for long oxidation times, the AC SPV decreases and ultimately disappears, implying that the (FeOSi)⁻ network has collapsed and may have changed into Fe₂O₃. A model for the metal-induced negative oxide charge in the conventional oxide charge diagram is proposed.

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1. Introduction

An alternating current (AC) surface photovoltage (SPV) [1–11] appears when a depletion or inversion layer (negative charge on n-type Si or positive charge on p-type Si) is formed on a Si semiconductor surface by irradiating it with a chopped photon beam (PB). The depletion or inversion layer has been reported to be created either by an atomic-bridging formation in SiO₂ [metal-induced oxide charge (Qmi)] [12], such as (AlOSi)⁻ [13] or (FeOSi)⁻ [14] in n-type Si, or by a Schottky-barrier [15] on the bare Si surface, resulting in the appearance of an AC SPV.

The charge induced by Al in SiO₂ (silica) has been discussed and well documented in the field of glass electrodes. The trivalent Al ion, Al³⁺, replaces the tetravalent Si ion, Si⁴⁺ in silica, [16] and then, AlO₂⁻ is formed adjoining to the SiO₂. As is well known, SiO₂ has no charge, because Si⁴⁺ combines with two oxygen ions, 2xO²⁻. However, AlO₂⁻ must have a negative charge because one electronic bond from an O²⁻ ion is left unbalanced by the Al³⁺. Thus, the atomic-bridging charge state is written as (AlOSi)⁻ or, more intuitively AlO₂⁻. So, in thermally oxidized metal-contaminated n-type Si, when trivalent ions such as Al³⁺, Fe³⁺, Cr³⁺ replace the quadrivalent Si ion, Si⁴⁺, bonding networks of (AlOSi)⁻ [13], (FeOSi)⁻ [14], and (CrOSi)⁻ [18] are formed, and if the negative Qmi satisfies the equation Qmi > Q₀ (oxide charge) [19,20], an AC SPV appears in n-type Si(001) wafers. The surface of an n-type Si(001) wafer contaminated by an aqueous Fe solution (surface concentration of Fe: 2.7 × 10¹³ atoms/cm²) [14] exposed to air forms a (FeOSi)⁻ network, analogous to the (AlOSi)⁻ network model [13]. A wafer with this surface concentration of Fe shows strong inversion on the basis of frequency-dependent AC SPV measurements which show them to be inversely proportional to frequency. In the case of a lower concentration, 2.9 × 10¹² atoms/cm² [14], the AC SPV in the lower frequency region becomes flat, though it is inversely proportional to frequency in the higher frequency region. This indicates that the surface is weakly inverted or depleted [6,14]. The AC SPV vs. frequency curves are dependent on the Fe surface concentration. The critical concentration for strong inversion is of the order of 10¹³ atoms/cm². However, frequency-dependent AC SPVs have not been measured in thermally oxidized Fe-contaminated n-type Si. Also it has not yet been clarified whether the (FeOSi)⁻ network survives or not when the wafer is thermally oxidized. Therefore, it is worthwhile examining the behaviour of (FeOSi)⁻ networks in thermally oxidized Fe-contaminated n-type Si using the frequency-dependent AC SPV method as well as in native oxides [14].

In this work, we investigated the atomic-bridging type Fe-induced SPV in thermally oxidized Fe-contaminated n-type Si(001) wafers as well as the native oxide formed on exposure to air. The variation in the frequency-dependency of the AC SPV with time is examined and a chemical analysis of the contaminants is done using atomic absorption spectroscopy. In particular, our purpose is to prove the appearance of...
the negative $Q_{mi}$, [(Fe$\text{O}_2$)$_2$]$^-$ on thermally oxidized Fe-contaminated n-type Si, using the AC SPV method.

2. Experimental details

2.1. Sample preparation

Sample wafers (76 mm in diameter) were prepared from commercially available Czochralski-grown <100>-oriented Si wafers. The wafers were phosphorus-doped (n-type) with a resistivity of 3–6 $\Omega$ cm. The as-received wafers were rinsed in deionized water for 10 min in an ultrasonic bath, after which, they were treated with an aqueous hydrofluoric acid (HF) solution (HF:$\text{H}_2\text{O}=1:99$) for 5 min, and then rinsed in deionized water (18 $\Omega$ cm) for 5 min (the surface was hydrophobic) and in deionized water for 10 min in an ultrasonic bath. The wafers were then cleaned with RCA solution [21] (ammonium hydroxide/hydrogen peroxide/water; NH$_4$OH: $\text{H}_2\text{O}_2$: $\text{H}_2\text{O}=1:1:10$ in volume) at 85 ± 2 °C for 10 min followed by a wafer rinse for 10 min. Then, to deliberately contaminate the wafers with Fe, they were exposed to an aqueous Fe solution (10 $\mu$g/mL) using a spinner at a speed of 1000 rpm for 15 s. For the aqueous Fe solution, a standard Fe(NO$_3$)$_3$ solution (1000 ppm; 1 mg/ml) was used. Immediately after application, the Si wafers were dried by the spinner at a speed of 3000 rpm for 2 min. Some samples were thermally oxidized in a dry oxygen ambient (1 L/min) between 550 and 850 °C for 3 min, and then rinsed in deionized water (18 MΩ cm) for 10 min. Then, to deliberately contaminate the wafers with Fe, they were exposed to an aqueous Fe solution (10 $\mu$g/mL) using a spinner at a speed of 1000 rpm for 15 s. For the aqueous Fe solution, a standard Fe(NO$_3$)$_3$ solution (1000 ppm; 1 mg/ml) was used. Immediately after application, the Si wafers were dried by the spinner at a speed of 3000 rpm for 2 min. Some samples were thermally oxidized in a dry oxygen ambient (1 L/min) between 550 and 850 °C for 60 min. The samples were then exposed to air for various lengths of time before making measurements.

2.2. Chemical analysis of metal impurities on the wafer surfaces

The ion concentrations (Fe, Cr, Cu, Ni, Al, Zn, and Co) in the sample wafers were measured by atomic absorption spectroscopy (AAS: Hitachi Z-8270). The impurities were extracted using the pack extraction method (PEM), in which samples are immersed in 10 mL of solution (HF: HCl: HNO$_3$: $\text{H}_2\text{O}=1:1:1:95$) in a clean polypropylene bag ($<10^3$ atoms/cm$^2$) at 100 °C for 60 min. The extracted solutions (5 mL) were then analyzed by AAS.

2.3. AC SPV measurement

The AC SPV measurement relies on the change in surface potential of a semiconductor when it is illuminated. When n- or p-type Si is strongly inverted, the observed AC SPV is proportional to $1/f$ (frequency) [14]. As the surface approaches weak inversion and/or depletion, the AC SPV decreases at lower frequencies. In accumulation, the overall AC SPV cannot be detected [7]. In contrast, a Schottky-barrier has also been reported to cause an AC SPV [15] as previously described.

In the present experiment, the frequency-dependent AC SPV was measured with an instrument while illuminating the sample with light from a blue light-emitting diode (LED) in an off-on mode [14]. The wavelength peak of the LED was 470 nm and the optical power was of the order of microwatts. The instrument was developed in-house [14], based on the theory reported by Munakata et al. [5,6]. This instrument evaluates the charge state of the oxide and the Schottky-barrier by irradiating the wafer surface with a photon beam (PB). The incident PB power was adjusted to 2.5 $\mu$W. As a result, the electric field applied to the surface was negligible, and thus, no charge was created or annihilated on the surface.

2.4. Oxide thickness measurement

The oxide thicknesses of the thermally oxidized Fe-contaminated Si(001) wafers were measured using ellipsometry. The ellipsometer was equipped with a He–Ne laser (wavelength: 632.8 nm), with a measurement beam diameter of 1 mm at the wafer surface. The incident angle was 70° to the sample surface and a refractive index of 1.46 was used in the calculation. The thickness was measured at nine locations on each sample and averaged. The error in the thickness measurement was ±0.05 nm.

In order to examine the presence of Fe atoms in a thin SiO$_2$ film, the SiO$_2$ was etched in steps in aqueous HF solution (HF:$\text{H}_2\text{O}=1:99$). The frequency-dependent AC SPV of an Fe-contaminated n-type Si(001) wafer thermally oxidized at 650 °C for 60 min was measured after each etch step. Each steps of 15 s and then 45 s were done and the AC SPV vs. frequency was measured each time with the instrument developed in-house which has previously been reported [14].

3. Results and discussion

3.1. Concentrations of impurities on Si (001) surfaces

Table 1 shows the concentrations of metal impurities on the Si(001) surfaces for, (a) an Fe-contaminated wafer at room temperature, (b) Fe-contaminated wafers thermally oxidized at either 200 or 650 °C for 60 min. The concentration of the Fe contamination shown in (a) is $4.0 \times 10^{13}$ atoms/cm$^2$, which is one order of magnitude smaller than the atomic density of a Si(001) surface (6.78$ \times 10^{14}$ atoms/cm$^2$). In the samples oxidized at 200 and 650 °C for 60 min, no appreciable difference is observed. This indicates that for these samples, most of the Fe contamination is still contained in the SiO$_2$. The amounts of other impurities are equivalent to the background level in the experimental environment.

3.2. Variation of the frequency-dependent AC SPV with exposure time to air for an Fe-contaminated n-type Si wafer

Fig. 1 shows the frequency-dependent AC SPV of an Fe-contaminated n-type Si(001) wafer vs. exposure time to air at room temperature. The plot labelled RCA in Fig. 1 refers to a non-contaminated wafer rinsed in an RCA solution for which the AC SPV was very low, although very few impurities may be on n-type Si surface, as a result, very low AC SPV might appear [13].

In Fig. 1, except at very low frequencies (<10 Hz), the AC SPV for the Fe-contaminated n-type Si(001) wafer gradually approaches 1/f with increasing exposure time to air similar to the Al-contaminated case [12]. The AC SPV saturates after approximately one day exposure to air. This characteristic of the AC SPV shows without doubt that a negative charge has developed on the surface of the n-type Si wafer. When the native oxide was removed from Fe-contaminated wafers by dipping in HF, the observed AC SPV vanished. Thus, this negative charge is caused by Fe in the native oxide [14]. Analogous to the

Table 1

<table>
<thead>
<tr>
<th>Concentration ($\times 10^{11}$ atoms/cm$^2$)</th>
<th>Fe</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Al</th>
<th>Zn</th>
<th>Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-contaminated in aqueous solution</td>
<td>Room temperature</td>
<td>$4.0 \times 10^2$</td>
<td>&lt;1.8</td>
<td>&lt;1.2</td>
<td>&lt;1.1</td>
<td>&lt;1.0</td>
<td>&lt;4.5</td>
</tr>
<tr>
<td>Fe-contaminated and thermally oxidized</td>
<td>200 °C 60 min</td>
<td>$4.0 \times 10^2$</td>
<td>&lt;1.8</td>
<td>&lt;1.2</td>
<td>&lt;1.1</td>
<td>&lt;1.0</td>
<td>&lt;4.5</td>
</tr>
<tr>
<td>Fe-contaminated and thermally oxidized</td>
<td>650 °C 60 min</td>
<td>$3.4 \times 10^2$</td>
<td>&lt;1.8</td>
<td>&lt;1.2</td>
<td>&lt;1.1</td>
<td>&lt;1.0</td>
<td>&lt;4.5</td>
</tr>
</tbody>
</table>
formation of (AlOSi)− and/or AlO2− networks in Al-contaminated native oxides [13], trivalent Fe has replaced tetravalent Si in the SiO2 creating atomic-bridging by forming an (FeOSi)− network in the SiO2[16,17]. Thus, a negative oxide charge has appeared and it is postulated that this is the negative Qmi[12]. Thus, the incorporation of the trivalent Fe, O and Si (atomic bond), the so-called (FeOSi)− network, must have occurred as in the case with Al.

Munakata et al. [22] has already reported a clear deviation from the 1/f relationship in an electron beam (EB)-irradiated Si wafer due to the recombination of excess carriers at EB-induced traps. In eq. (4) of Ref. [14], the terms related to interface traps are thought to be dominant in the lower frequency region. However, strong inversion was clearly observed in Fe-contaminated Si wafers thermally oxidized at temperatures between 550 and 650 °C for 60 min, as shown later. The appearance of the negative charge is concluded to be due to the formation of the (FeOSi)− network. It is not clear at present whether the observed deviation in this Fe-contaminated case is caused by the interface traps or not.

3.3. Variation of frequency-dependent AC SPV in thermally oxidized n-type Si(001) wafer etched stepwise

Fig. 2 shows a plot of the frequency-dependent AC SPV in the n-type Si(001) wafer thermally oxidized at 650 °C for 60 min, labelled by (1), and the same sample etched stepwise in aqueous HF solution for 15 s, labelled (2), and 45 s, labelled (3), respectively. The data for (1) shows that the AC SPV is inversely proportional to frequency [5], indicating strong inversion. This shows that the Fe-induced negative oxide charge in the native oxide, the (FeOSi)− network, still survives after thermal oxidation at 650 °C. After 15 s etching in aqueous HF solution, the AC SPV, shown by (2), has decreased as a whole and has become flatter at lower frequencies, corresponding to weaker inversion. The oxide thickness etched after 15 s was 0.9 nm, indicating that most of the Fe contamination in the SiO2 had been etched away. After etching for 45 s, the AC SPV, shown by (3), has eventually fallen into low level, however a trace of negative charge may remain in the oxide. The oxide thickness etched after 45 s was 2.9 nm, demonstrating that the Fe had segregated into a layer close to the surface of the oxide film and that some of the Fe may have been in the form of a (FeOSi)− network. Based on these results, a negative Qmi model for (FeOSi)− networks in SiO2 was proposed as shown in Fig. 3, in addition to the oxide charge usually found [19,20].

3.4. The Fe-induced negative oxide charge in thermally oxidized Fe-contaminated n-type Si(001) wafers as a function of oxidation temperature

Fig. 4 shows the frequency dependence of the AC SPV for Fe-contaminated n-type Si(001) wafers thermally oxidized at temperatures between 550 and 850 °C for 60 min. At these temperatures, the AC SPV decreases in inverse proportion to frequency, indicating that the surface is strongly inverted in n-type Si surfaces due to the survival of the (FeOSi)− network contained in the Fe-contaminated native oxide.

Upon oxidation at temperatures between 700 and 750 °C for 60 min, the AC SPV in the lower frequency region decreases and becomes flat (<10 Hz), indicating that the surface was depleted and/or weakly inverted. At 850 °C, the AC SPV disappears (as low as the noise level), indicating that the negative oxide charge, (FeOSi)− network, has collapsed and has perhaps changed into Fe2O3. In this case, the growth of interface traps may not be related to the AC SPV vs. frequency.
4. Conclusion

The atomic-bridging type Fe-induced AC SPV in Fe-contaminated n-type Si(001) wafers was investigated. Chemical analysis using atomic absorption spectroscopy was done and frequency-dependent AC SPV measurements were made. At room temperature, an AC SPV appeared, which gradually increased over time and saturated after approximately one day (Fe concentration on the Si surface: $4.0 \times 10^{13}$ atoms/cm$^2$). The AC SPV was inversely proportional to frequency except at very low frequencies ($<10$ Hz) which corresponds to weak or strong inversion. This result shows that an Fe-induced negative oxide charge due to the formation of a (FeOSi)$^-$ network had appeared. The evaluation of Fe-contaminated Si(001) surfaces thermally oxidized between 550 and 650 °C by the AC SPV method combined with the chemical analyses indicated that the Fe-contaminated surfaces were strongly inverted and that most of the Fe had segregated into the region closest to the surface of the thin SiO$_2$ film, and also providing evidence that the Fe-induced negative charge had survived in the form of a (FeOSi)$^-$ network. As the oxidation temperature was increased, the AC SPV decreased as a whole, and finally at 850 °C disappeared, implying that the (FeOSi)$^-$ network had collapsed and had perhaps changed into Fe$_2$O$_3$. A model for the metal-induced negative oxide charge was proposed and added to the conventionally drawn oxide charge diagram.

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