

Quantitative Analyses of Negative Interface Trapped Charge in p-Type Si Wafer Studied by Frequency-Dependent Alternating Current Surface Photovoltage Technique

Hirofumi Shimizu

Department of Electrical and Electronic Engineering, College of Engineering, Nihon University, Tamura-machi, Koriyama, Fukushima, 9638642, Japan

shimizuh@ee.ce.nihon-u.ac.jp

Abstract- The conventionally defined oxide charge (Q_o) in thermally oxidized p-type Si(001) wafers is investigated by the frequency-dependent alternating current (AC) surface photovoltage (SPV). Upon etching the oxide layer, a minimum AC SPV was observed nearby SiO₂-Si interface. The reduction of AC SPV indicates the appearance of a negative charge. This strongly suggests that a fixed oxide charge (Q_f) and oxide trapped charge (Q_{ot}) might have been etched off. Then, the possible charge must be Q_{it} which is located to be approximately 2.7 nm from the SiO₂-Si interface. This explains that Q_f may be situated farther than Q_{it} from the SiO₂-Si interface. The Q_{it} density (D_{it}) is calculated to be $9 \times 10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ by analysing the AC SPV vs frequency relationship which is in good agreement with the previous result. The HF solution-etched p-type Si surface can be positive possibly because Si dangling bonds capture holes from p-type Si substrate. This positive charge may not have the same characteristic as positive Q_f . It is because Q_f is stable in air exposure at room temperature, in contrast, the positive charge on HF solution-dipped p-type Si surface decreases gradually with air exposure time in the measurements of frequency-dependent AC SPV as previously reported.

Keywords- Si; Oxidation; Fixed Oxide Charge; Interface Trapped Charge; Surface Photovoltage

I. INTRODUCTION

With continuing miniaturization of silicon (Si) ultra-large-scale-integrated (ULSI) devices, gate insulator has been replaced with high- k thin film such as Hf- and La-based materials upon scaling down to 22 nm technology nodes and beyond. However, such high- k materials reduce electron mobility, resulting in using ultra thin SiO₂ film between high- k materials and Si substrate. Thus, the research and development of ultra thin SiO₂ films are still important [1-3].

In thermally oxidized p-type Si, it is well known that an oxide charge (Q_o) might consist of a fixed oxide charge (Q_f), an interface trapped charge (Q_{it}), an oxide trapped charge (Q_{ot}), a mobile charge (Q_m) [4-6]. These charge states have been detected conventionally by capacitance-voltage (C-V) method, and recently by an alternating current (AC) surface photovoltage (SPV) method [7-14].

Historically, Q_o due primarily to structural defects (ionized Si) at the SiO₂-Si interface, has been determined to be positive in thermally oxidized p-type Si in terms of C-V method. However, based on AC SPV method, positive charge has also been reported to appear on hydrofluoric acid (HF) solution-dipped p-type Si(001) surface [15]. HF solution-dipped Si surfaces are postulated to be hydrogen terminated [16]. In the previous study [15], the appearance of positive charge may be due to dangling bonds which capture holes (abundant

majority carriers in p-type Si), whereas it is neutralized by electrons in n-type Si(001) during natural oxidation at room temperature and/or thermal oxidation [17].

In the radiation-damaged SiO₂ layer, a negative oxide charge appears on n-type Si wafers as Q_{it} , which is analyzed on the basis of AC SPV method [18]. Simultaneously, in the previous report [17], the negative charge which is located nearby SiO₂-Si interface is postulated to be Q_{it} . However, the AC SPV was measured only at a frequency of 2 kHz [17]. So far, quantitative analyses are not conducted to determine charge characteristics of SiO₂ film layer such as an interface trapped density (D_{it}) [19, 20]. Therefore, the measurements by using frequency-dependent AC SPV are worthy to investigate and analyze physical parameters related to oxide charge.

This paper describes supplementary experimental and analytical results that expand on the previous study [17] examining a negative Q_{it} in thermally oxidized p-type Si(001) wafers by the frequency-dependent AC SPV method. In order to identify the Q_{it} nearby the SiO₂-Si interface and analyze quantitatively, the thermal oxide is etched stepwise and subsequently measured by AC SPV method [16]. Simultaneously, based on half-sided junction model [10], D_{it} is evaluated in p type Si wafer etched stepwise by analyzing the frequency-dependent AC SPV [19, 20].

II. EXPERIMENTAL PROCEDURES

A. Sample Preparation

Sample wafers (125 mm in diameter) used were commercially available Czochralski-grown (001)-oriented Si ones. The wafers were boron-doped (p-type) at a resistivity of $10 \pm 1.5 \text{ } \Omega \cdot \text{cm}$. The incoming wafers were first treated with RCA solution [21] (ammonium hydroxide/hydrogen peroxide/water; $\text{NH}_4\text{OH}:\text{H}_2\text{O}_2:\text{H}_2\text{O}=1:1:10$ in vol%) at $97.5 \pm 2.5 \text{ } ^\circ\text{C}$ for 10 min followed by water (18 M $\Omega \cdot \text{cm}$) rinse for 10 min. Then, the wafers were rinsed with HF aqueous solution (HF: $\text{H}_2\text{O}=1:99$ in vol%) for 10 min, and then rinsed in pure water for 10 min. The wafers were thermally oxidized at $850 \text{ } ^\circ\text{C}$ for 30 min in dry oxygen ambient.

B. Oxide Layer Thickness Measurement

The oxide layer was stepwise etched in HF solution with a thickness step of 0.8-4.6 nm. After the etching, the oxide thickness was measured with ellipsometer (Mizojiri Optical: DVA-36VW) which 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. A refractive index of 1.46 was used in the calculation. Oxide thicknesses were measured at nine locations per wafer and the mean thickness was evaluated. In every case, the standard deviation on the mean thickness was within 0.05 nm.

C. Principle and Measurement of AC SPV

The SPV is the change in surface potential when a semiconductor is illuminated with a photon beam (PB) [7-13]. The SPV excited with a chopped PB is termed AC SPV. AC SPV has already been proposed for nondestructive evaluation of semiconductor wafers [10, 11, 22]. AC SPV appears in case that a depletion and/or inversion layer is formed on the wafer surface, due to either a positive charge in p-type Si or a negative charge in n-type Si, when the Si surface is irradiated with a chopped PB [7-13]. In the strong-inversion state, AC SPV is inversely proportional to frequency ($1/f$, f : frequency) [10]. In accumulation, when the surface charge is positive in n-type Si, the photovoltage is practically zero. As a result, the charge separation between excess electrons and holes is not sufficiently distinctive in accumulation, and AC SPV is thereby too small to be detected.

In the present experiment, frequency-dependent AC SPV was measured with an instrument developed in-house [14], based on the system reported by Munakata and coworkers [10, 11], while illuminating the sample with light from a blue-light-emitting diode (LED) in the on-off mode [14]. The wavelength peak of the LED was 470 nm. This instrument enables the evaluation of the metal-induced negative oxide charge newly postulated [23] and Schottky barrier [24] by irradiating wafer surface with a chopped PB. The incident PB power was adjusted to 2.5 μ W. As a result, the electric field applied to the surface was negligible, and thus no charge was created or annihilated on the surface [14, 22].

III. RESULTS AND DISCUSSION

Fig. 1 shows frequency-dependent AC SPV curves of the p-type Si(001) wafer which was thermally oxidized at 850 °C for 30 min and was etched stepwise to bare Si surface state. The initial SiO₂ film thickness was 9.8 nm and then the film was etched stepwise to final value (0.1 nm). Subsequently after every etching, the AC SPV was measured. The broken line shows a theoretically determined strong-inversion state in which AC SPV is proportional to $1/f$ [10]. In Fig. 1, circles seem to become very akin to the strong-inverted state.

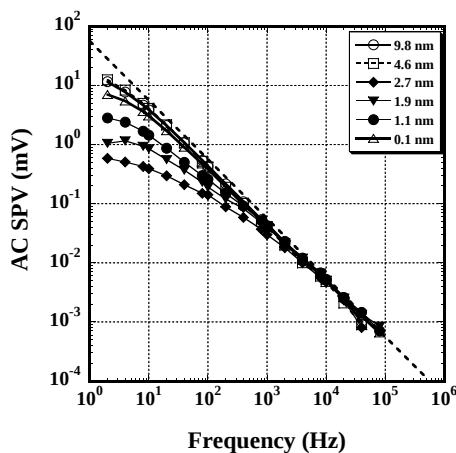


Fig. 1 AC SPV vs frequency relationship of p-type Si(001) wafer oxidized at 850 °C for 30 min in dry oxygen ambient, of which sample was stepwise etched and subsequently measured by the AC SPV method. The residual SiO₂ thicknesses are denoted in the figure. The broken line shows a theoretically determined strong-inversion state

This AC SPV vs frequency relationship is caused by a positive Q_f due to an oxidation of p-type Si. When the oxide surface came close to the SiO₂-Si interface by etching, the AC SPV in the lower frequency region was once reduced to a minimum value, which corresponds to a weakly-inversion state [11]. Then, the AC SPV increased again at the oxide thickness of 0.1 nm, although the AC SPV did not reach the initial one (9.8 nm: open circles). This is because the origin of Q_f and the positive charge may be different. This will be discussed later.

Fig. 2 shows the AC SPV variation at frequencies of 10 and 100 Hz plotted as a function of the oxide thickness on the basis of Fig. 1. Upon etching the oxide layer, the AC SPV kept the same level approximately until 5 nm in thick, indicating that the positive Q_f was prevalent ($Q_f \gg Q_{ot} + Q_{it}$) [18]. When the SiO₂ film thickness was reduced to 2.7 nm, a minimum AC SPV was observed. The reduction of AC SPV indicates the appearance of a negative charge. As the inequality of $Q_f \gg Q_{it}$ has been reported [19], the appearance of the negative charge strongly suggests that Q_f and positive Q_{ot} might have been etched off. Then, the possible charge must be Q_{it} which is located nearby at the SiO₂-Si interface. This explains that Q_f may be situated farther than Q_{it} from the SiO₂-Si interface. Thus, the Q_o is thought to appear as a dip in AC SPV vs oxide thickness curves. This explains that an occurrence of a negative charge (Q_{it}) compensated for the positive Q_f .

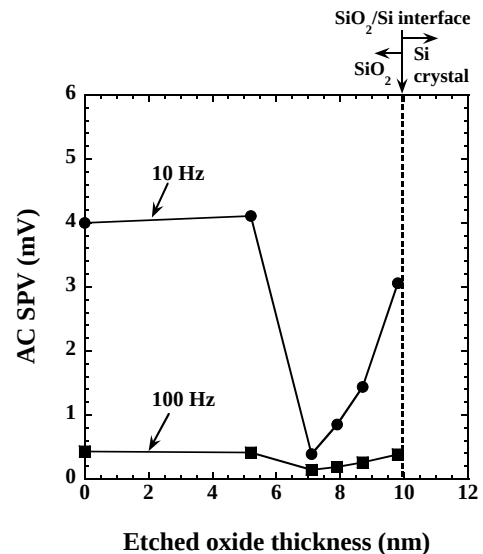


Fig. 2 AC SPV at frequencies of 10 and 100 Hz as functions of the etched thickness of SiO₂ from the oxide surface

After a Si(001) wafer was immersed in HF solution for 30 min, the native oxide thickness was measured to be 0.1 nm on the basis of subpeaks, corresponding to Si¹⁺ and Si²⁺ suboxides, in the Si 2p main peak in X-ray photoelectron spectroscopy (Termo ESCALA220i) profiles [15]. Thus, the surface may correspond to a state of oxygen adsorption onto a Si dangling bond, thereby the bare Si surface may be partially exposed. Based on the observed frequency-dependent AC SPV, HF solution-etched p-type Si surface can be positive possibly because the Si dangling bonds capture holes (abundant majority carriers in p-type Si substrate). However, the positive charge on HF dipped surface is not the same as Q_f itself [15]. It is because Q_f is stable in the air exposure at room temperature, in contrast, the positive charge in HF dipped surface decreased gradually with air exposure time in the

measurements of frequency-dependent AC SPV as previously reported^[15]. More detailed investigation is needed to identify the mechanism of the positive charge on HF solution-dipped p-type Si surface.

Quantitative calculation method based on the AC SPV vs frequency relationship^[19] has suggested to estimate charge density in SiO₂ film, for example, the Cr-induced negative oxide charge density was already reported to be calculated as shown in ref. [25]. Fig. 3 shows the AC SPV vs frequency relationship of the sample etched for 7.9 nm (denoted by closed reverse triangle), indicating flat- and 1/f-dependency regions^[19]. As a result, a cutoff frequency f_c can be obtained by finding the intersection point shown in Fig. 3^[19]. The f_c was found to be 48.3 Hz in this case. According to the previous paper^[19], f_c is given as

$$f_c = \frac{1}{2\pi} \frac{g_{mj}}{c_{dp}}. \quad (1)$$

g_{mj} and c_{dp} are given by equations of (1) and (5) of ref. [19]. Thus, a surface potential ψ_s was calculated to be 0.475 eV. Following Fig. 5 of ref. [19], the best fit of D_{it} was determined to be $9 \times 10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ which is in good agreement with that by Watanabe^[26].

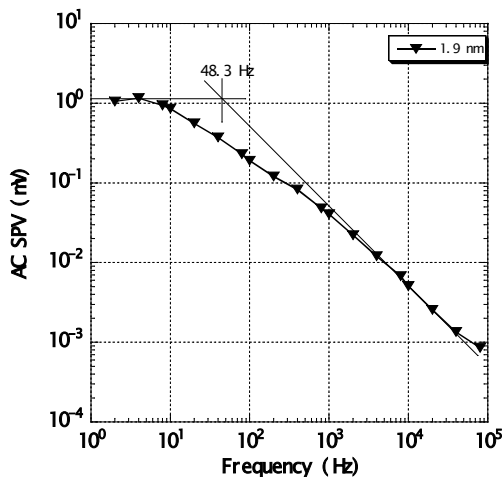


Fig. 3 Determination of the cutoff frequency of the sample of which residual oxide thickness is 1.9 nm. Reverse closed triangles indicate observed values

IV. CONCLUSIONS

Upon etching the oxide layer thermally oxidized at 850 °C for 30 min (oxide thickness: 9.8 nm), a minimum AC SPV was observed nearby SiO₂-Si interface. The reduction of AC SPV indicates the appearance of a negative charge, strongly suggesting that Q_f and Q_{ot} might have been etched off. Then, the possible charge must be Q_{it} which is located to be approximately 2.7 nm nearby the SiO₂-Si interface. This explains that Q_f may be situated farther than Q_{it} from the SiO₂-Si interface. Furthermore, the Q_{it} density (D_{it}) is calculated to be $9 \times 10^{10} \text{ cm}^{-2} \cdot \text{eV}^{-1}$ by analyzing the AC SPV

vs frequency relationship which is in good agreement with the previous result. The positive charge on the bare p-type Si(001) surface had similar features as Q_b but may not be the same as Q_f itself. The HF solution-etched p-type Si surface can be positive possibly because Si dangling bonds capture holes from p-type Si substrate. Simultaneously, Q_f is stable in air exposure at room temperature, in contrast, the positive charge on HF solution-dipped p-type Si surface decreases gradually with air exposure time by frequency-dependent AC SPV measurements as previously reported.

ACKNOWLEDGMENTS

This work was supported by a grant from Nihon University. The author is indebted to Dr. M. Ikeda for his diligence in assisting with the AC SPV measurement and to Mr. H. Hagiwara for his diligence in assisting with calculating D_{it} .

REFERENCES

- [1] M. L. Green E. P. Gusev, R. Degraeve and E. L. Garfunkel, J. Appl. Phys. 90, 2057 (2001).
- [2] H.R. Huff and D.C. Gilmer, High Dielectric Constant Materials-VLSI MOSFET Applications Springer, Berlin (2004).
- [3] E. Martinez, C. Leroux, N. Benedetto, C. Gaumer, M. Charbonnier, C. Licitra, C. Guedj, F. Fillot & S. Lhostis, J. Electrochem. Soc. 156, G120 (2009).
- [4] B. E. Deal, M. Sklar, A. S. Grove, and E. H. Snow, J. Electrochem. Soc. 114, 266C (1967).
- [5] B. E. Deal, J. Electrochem. Soc. 121, 198C (1974).
- [6] B. E. Deal, IEEE Trans. Electron Devices 27, 606 (1980).
- [7] A. M. Goodman, J. Appl. Phys. 32, 2550 (1961).
- [8] R. S. Nakhmanson, Solid-State Electron. 18, 617 (1975).
- [9] E. Kamieniecki, J. Vac. Sci. & Technol. 20, 811 (1982).
- [10] C. Munakata, S. Nishimatsu, N. Honma, and K. Yagi, Jpn. J. Appl. Phys. 23, 1451 (1984).
- [11] C. Munakata and S. Nishimatsu, Jpn. J. Appl. Phys., 25, 807 (1986).
- [12] J. Lagowski, P. Edelman, M. Dexter, and W. Henley, Semicond. Sci. Technol. 7, A185 (1992).
- [13] L. Jastrzebski, W. Henley, and C. J. Nuese, Solid State Technol. 35, 27 (1992).
- [14] H. Shimizu, R. Shin, and M. Ikeda, Jpn. J. Appl. Phys. 44, 3778 (2005).
- [15] H. Shimizu and Y. Sanada, Jpn. J. Appl. Phys. 50, 111301 (2011).
- [16] T. Takahagi, I. Nagai, A. Ishitani, H. Kuroda, and Y. Nagasawa, J. Appl. Phys. 64, 3516 (1988).
- [17] C. Munakata and H. Shimizu, Semicond. Sci. Technol. 15, 40 (2000).
- [18] C. Munakata and T. Mizutani, Jpn. J. Appl. Phys. 43, L290 (2004).
- [19] H. Shimizu, K. Kinameri, N. Honma, and C. Munakata, Jpn. J. Appl. Phys. 26, 226 (1987).
- [20] C. Munakata and K. Watanabe, Semicond. Sci. Technol. 6, 612 (1991).
- [21] W. Kern and D. A. Puotinen, RCA Rev. 31, 187 (1970).
- [22] K. Kinameri, C. Munakata and K. Mayama, J. Phys. E.; Sci. Instrum. 21, 91 (1988).
- [23] H. Shimizu: J. Electrochem. Soc. 144, 4335 (1997).
- [24] H. Shimizu, and Y. Sanada, Jpn. J. Appl. Phys. 50, 085701 (2011).
- [25] H. Shimizu, S. Nagase, and M. Ikeda, Appl. Phys. A 104, 929 (2011).
- [26] K. Watanabe: Semicond. Sci. Technol. 11, 1713 (1996).