Nondestructive Characterization of Surface Contaminants in Silicon Wafers Using AC Surface Photovoltage Method

Hirofumi Shimizu* and Chusuke Munakata**†

*Semiconductor & Integrated Circuits Division, Hitachi, Ltd., Josuihon-cho, Kodaira, Tokyo 187, Japan

**Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan

A scanning photon microscope (SPM), based on the imaging of ac surface photovoltages (SPVs), has been developed and used for nondestructive detection of impurities in silicon (Si) wafer surfaces rinsed with various solutions. When aluminum (Al), iron (Fe) and copper are incorporated into native oxide on Si surfaces, they induce a negative charge by forming a network of $(\text{AlOSi})^-$ or $(\text{FeOSi})^-$. For n-type Si, this negative charge gives rise to an appreciable ac SPV, while a positive charge due to phosphorus in the form of $(\text{POSi})^+$ causes an ac SPV in p-type Si. Thus, once contaminated ions are known on the basis of chemical analysis, the resulting ac SPV features can provide nondestructive information on the content and distribution of the contaminants on the Si wafer surfaces. This is what we demonstrate in the present paper.

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I. Introduction

As the scale of integrated circuits in silicon (Si) devices continues to shrink, there is an increasing demand for Si wafers with perfect surfaces. This is because the surface contaminants and irregularities of Si wafers affect the device characteristics⁽¹⁾. Wafer cleaning procedures in Si device fabrication usually use a combination of RCA (Radio Corporation of America) solution (alkaline and acid)⁽²⁾ and aqueous hydrofluoric acid (HF) solution. Prior to 1987, Pyrex glass containers were commonly used for the RCA alkaline rinsing procedure and relatively high concentrations of aluminum (Al) were detected in the native oxide on Si⁽³⁾. In the current cleaning processes, Pyrex glass has been replaced with much less contaminated glass. However, a small concentration of impurities (10^{14} – 10^{15} atoms/m²)-possibly from both the quartz container and chemical solutions such as hydrogen peroxide-sometimes degrades the device characteristics such as gate oxide integrity. The effectiveness of wafer cleaning is therefore a major concern in device fabrications, and extensive investigations are being conducted worldwide.

AC surface photovoltage (SPV), which is excited by a chopped photon beam in semiconductor wafers, has been proposed as a tool for conducting nondestructive evaluation of Si wafers^{(4)–(11)}. AC SPV arises when a depletion or inversion layer is formed at the wafer surface. Such a layer is caused by the charge-induced surface potential due to the positive charge in a p-type Si wafer or the negative charge in an n-type Si wafer^{(7)–(9)}. Based

on the image formed by the ac SPV distribution⁽⁷⁾⁽⁸⁾, a scanning photon microscope (SPM)⁽¹²⁾⁽¹³⁾ has been developed to evaluate interface traps⁽¹⁴⁾ and bulk defects in processed wafers⁽¹⁵⁾. Using this SPM method, we have already confirmed that a fairly large ac SPV is observed when n-type Si wafers are rinsed with RCA alkaline solution in Pyrex glass container, indicating an appearance of a negative charge at wafer surfaces⁽¹⁶⁾⁽¹⁷⁾. It has been reported that Al incorporated into the native oxide is one of the species for the negative charge⁽¹⁷⁾⁽¹⁸⁾. If a trivalent Al ion, Al^{3+} , replaces the quadrivalent Si ion, Si^{4+} , in silica, AlO_2 is partially formed, causing the negative charge in the form of $(\text{AlOSi})^-$ ⁽¹⁹⁾ or $(\text{SiAlO}_4)^-$ ⁽²⁰⁾.

Various physical and chemical analytical methods can be used for analyzing the impurities on wafer surface layers. Many are inherently destructive, time-consuming and require skilled operation. From a technological viewpoint, a non-destructive impurity detection technique is most useful. The ac SPV method using an SPM is considered to be promising for evaluating surface imperfection because it can quickly identify the charge polarity in an oxide layer and interface traps.

The present report describes how the SPM can be used to detect surface contaminants nondestructively, focusing at its application to quality control in device processing. The mechanisms by which impurities such as Al, Fe, and phosphorus (P) generate charges in the native oxide are also reported.

II. Experimental Procedure

1. Sample preparation

Si wafers 125 mm in diameter were prepared from Czochralski-grown <001>-oriented crystals. The wafers

† Present address: Department of Electronics, Tohoku Institute of Technology, Taihaku-ku, Sendai 982, Japan.

were phosphorus (P)-doped (n-type) or boron (B)-doped (p-type) to a resistivity of $100 \pm 5 \text{ m}\Omega \cdot \text{m}$ (P concentration; $\sim 4 \times 10^{20} \text{ atoms/m}^3$, B concentration; $\sim 1.6 \times 10^{21} \text{ atoms/m}^3$).

Figure 1 shows the flow chart of three different sample wafer treatments. First, experiments were done to evaluate wet cleaning processes. The wafers were subjected to rinses combining a modified RCA alkaline solution (ammonium hydroxide/hydrogen peroxide/water) at $360.5 \pm 2.5 \text{ K}$ for 900 s in both Pyrex glass and quartz glass containers, an acid solution (hydrochloric acid/hydrogen peroxide/water) in quartz container⁽²⁾, and aqueous HF dipping. Second, to clarify the effect of impurities on the generation of ac SPVs, some of the wafers were treated with a metal-contaminated RCA alkaline rinse made by adding 10^{-6} m^3 of a standard 1000 ppm (1 kg/m^3) solution containing $\text{Al}(\text{NO}_3)_3$, $\text{Fe}(\text{NO}_3)_3$, $\text{Zn}(\text{NO}_2)_2$, or $\text{Ni}(\text{NO}_2)_2$ to 10^{-2} m^3 of the alkaline solution in a quartz glass container. The added ion concentration in each solution was 10^{-4} kg/m^3 . After this treatment, the wafers were rinsed in deionized running water (semiconductor grade) for 900 s. In the typical cleaning processes, wafers finished with RCA or HF aqueous solutions are subjected to a water rinse—yet another source of contamination. Therefore, the third sample preparation was also performed to utilize the SPM technique for identifying impurities at wafer surfaces that had been rinsed with metal (including phosphorus)-contaminated waters ($5 \times 10^{-3} \text{ kg/m}^3$) and dried in air.

2. AC SPV measurements using SPM

Figure 2 shows a schematic prediction of the generation of ac SPV in both depletion/inversion and accumulation regions in Si wafers^{(7)–(9)}. As previously reported, the ac SPV is high enough to be detected when a wafer with a depletion or inversion layer is irradiated by a photon beam with power of μW order.

Figure 3 shows the schematic diagram of the SPM, which was developed in order to obtain scanning photon images showing the distribution of ac SPV in wafers⁽¹²⁾⁽¹³⁾. The SPM uses capacitance coupling through an air gap between the wafer surface and a transparent electrode sus-

ended above the wafer. A focused blue or near-infrared photon beam scans the wafer through the transparent electrode, thereby exciting the ac SPV and forming a scanning photon image displayed on the cathode ray tube screen. Figure 4 shows, for example, the scanning photon image “HITACHI” created on a Si wafer which was previously scratched with a diamond cutter and alkaline rinsed. Scratches and other damage on wafer surfaces create interface traps, causing excited carriers to recombine there. These surface irregularities show up as dark areas in the displayed image⁽¹⁴⁾. As reported previously, sulfuric ammonia crystallized from SO_4^{2-} in

Fig. 2 Prediction of the generation of ac SPV in both the depletion/inversion and accumulation regions in silicon.

Fig. 1 Sample preparation for measuring ac SPV. The first experiment is to evaluate cleaning processes of Si wafers, the second is to identify the effect of metal in the native oxide rinsed with RCA solution on ac SPV, and the third is to confirm the contamination effect.

Fig. 3 A scanning photon microscope developed for detecting contaminants and damages at silicon wafer surfaces.

Fig. 4 A scanning photon image on silicon wafer which was created by scratching with diamond cutter and then rinsing with alkaline solution.

NH_4OH ambient on the wafer also creates interface traps, and as a result, the ac SPV is reduced, like that an electron-beam-irradiated wafer⁽²¹⁾ exhibits a reduction in ac SPV, the magnitude of which is dependent on the SO_4^{2-} concentration on the wafer⁽¹⁴⁾.

The ac SPVs and hence their scanning photon images on Si wafers were observed by using the SPM with a blue photon beam (with a wavelength peak at 448 nm) that was chopped at 2 kHz⁽¹²⁾⁽¹³⁾. A photon beam of diameter 0.4 mm was projected onto the wafer surface with a penetration depth of about 0.4 μm . This penetration depth is determined by an inverse of the optical absorption coefficient depending on the photon energy⁽¹³⁾. The incident photon beam power was 4 μW . The ac SPV profiles along the wafer diameter were obtained from the scanning photon image, and their average value (excluding those in regions of 10 mm from the wafer edge) is referred to as the observed ac SPV in this paper. This SPM method does not apply a high electric field in the oxide, and thereby does not produce charges or push charges out of the oxide. The time required to examine each wafer was 300 s in the normal operation mode and 60 s in the rapid mode.

3. Chemical analysis of metal impurities in wafer surface layers

The ion concentration (Al, Fe, Cu, Ni, Zn, Co and P) in the wafers was measured mainly by ion chromatography. A flameless type of atomic absorption spectrometry, total reflection X-ray fluorescence spectroscopy (TRXF), and secondary ion mass spectrometry (SIMS) were used for complementary analysis. In ion chromatography, the impurities were extracted using 10^{-5} m^3 of the solution ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O}=1:1:1000$) at about 368 K for $1.8 \times 10^3 \text{ s}$. During the extraction, the wafer surface was etched away to a depth of about 0.1 μm .

Table 1 The surface concentration of metal impurities on silicon wafers treated with various solutions.

Process	Concentration (atoms/ m^2)						
	Al^{3+}	Zn^{2+}	Cr^{2+}	Fe^{3+}	Cu^{2+}	Ni^{2+}	Co^{2+}
	$(\times 10^{15})$			$(\times 10^{13})$			
(A)	7.2	0.76	<1.9	8.8	<7.6	<8.4	<4.2
(B)	<2.0	<0.38	<1.9	<4.4	<7.6	<8.4	<4.2
(C)	<2.0	<0.38	<1.9	<4.4	<7.6	<8.4	<4.2
(D)	105	1.1	<1.9	20	19	21	<4.2
(E)	330	—	—	—	—	—	—

III. Experimental Results and Discussions

1. Evidence of the negative charge due to Al

Table 1 lists the concentration of metal impurities in wafer surfaces finished with different cleaning procedures, (A) modified RCA alkaline rinse in a quartz container, (B) RCA acid rinse in a quartz container, (C) HF dipping after the RCA alkaline rinse, (D) Al-contaminated RCA alkaline rinse (10^{-4} kg/m^3), and (E) modified RCA alkaline rinse in Pyrex glass container. In the solution (A), Al is a major impurity and its concentration is higher than that of other impurities. The wafers intentionally contaminated with Al had Al concentration about two orders of magnitude higher than the wafers finished with process (A). In acid rinse (B), the Al and Fe were drastically reduced⁽²⁾. The HF dipping (C) removed the native oxide, reducing impurities such as Al and Fe. Thus, the Al concentration follows the order, $\text{E} > \text{D} \gg \text{A} > \text{B}$. Complementary analysis revealed that $\text{B} > \text{C}$.

Figure 5 shows how ac SPVs change with exposure time when n-type Si wafers are finished with cleaning solutions of A, B, C or D⁽¹³⁾. The observed ac SPVs in n-type Si demonstrate an appearance of a negative charge at wafer surfaces. The ac SPVs have a close relationship with the order of Al concentration which was shown in Table 1. This proves that Al contributes to the generation of a negative charge⁽¹⁴⁾⁽¹⁵⁾. The S shaped curves may be at-

Fig. 5 AC SPV of n-type silicon wafers treated with (A) modified RCA alkaline solution, (B) RCA acid solution, (C) HF dipping after RCA alkaline rinse, (D) Al-contaminated RCA alkaline solution, and (E) modified RCA alkaline solution in Pyrex glass container.

tributed to the native oxide growth, which is probably layer by layer growth. The increasing of ac SPV are particularly prominent for process (D), and it levels off after about 6×10^5 s to nearly the same level as in the Pyrex glass case. This high ac SPV implies that the surface layer is strongly inverted in n-type wafers to a resistivity of $100 \pm 5 \text{ m}\Omega \cdot \text{m}$. If the Al-contaminated native oxide was removed by HF dipping, then the ac SPV vanished, indicating that the negative charge disappeared. This disappearance is consistent with Al residing in the native oxide and acting as the negative charge before HF dipping.

Figure 6 illustrates our proposed mechanism by which trivalent and pentavalent atoms induce charges in native oxide on Si. In quartz each Si atom is surrounded tetrahedrally by four oxygen atoms, occupying the corner points of a tetrahedron, to which it is bound by electron pair bonds. The charge appearance mentioned above is then thought to be due to Al introduced into the native oxide. When the Si atoms are substituted by Al atoms, a network of $(\text{AlOSi})^-$ would be formed. This mechanism is also consistent with the results on native oxide formed on mirror-polished Si, which show that about 4% of Al in the native oxide contributes to the negative charge⁽²²⁾. Similarly, Fe is also expected to give rise to a negative charge in the native oxide, because Fe is easily incorporated into the native oxide. Moreover, it is speculated that replacement by the pentavalent P atom might induce a positive charge in SiO_2 , but this possibility is currently under investigation.

2. Variation of the ac SPV for wafers rinsed with metal-contaminated RCA alkaline solution

Table 2 lists the analyzed metal concentrations at wafer surfaces prepared in the second treatment shown in Fig. 1. Each added metal (Al, Fe, Zn and Ni) was confirmed to be intentionally incorporated into the native oxide on the order of 10^{17} atoms/ m^2 .

Fig. 6 Mechanism by which trivalent and pentavalent atoms induce charges in native oxide on silicon.

Table 2 Metal concentrations at wafer surfaces rinsed with alkaline solutions to which small quantities of metal contaminants were added.

Process	Concentrations (atoms/ m^2)					
	Al^{3+}	Fe^{3+}	Zn^{2+}	Ni^{2+}	Cu^{2+}	Co^{2+}
	$(\times 10^{15})$				$(\times 10^{13})$	
RCA	<9.1	0.09	1.1	<0.08	<7.6	<4.2
RCA/Al	105	0.09	<0.38	<0.08	15	<4.2
RCA/Fe	<9.1	46	<0.38	<0.08	<7.6	<4.2
RCA/Zn	<9.1	0.18	81	<0.08	11	<4.2
RCA/Ni	<9.1	0.18	1.5	58	12	<4.2
RCA/HF	<2.0	0.04	<0.38	<0.08	<7.6	<4.2

Figure 7 shows the variation of ac SPVs with air exposure time when n-type Si wafers were subjected to the clean and metal-contaminated RCA alkaline rinses. Open triangles correspond to the ac SPVs that appeared after the clean alkaline rinse, open circles show the ac SPVs after the Al-contaminated alkaline rinse, and squares show those after the Fe-contaminated alkaline rinse. The ac SPVs for the Fe-contaminated wafers increased with air exposure time and after about 6×10^5 s leveled off at a value higher than that for wafers subjected to the clean alkaline rinse. This reveals that Fe, as well as Al, induces a negative charge in the native oxide. The saturated ac SPV for Fe contamination was lower than that for Al, probably because the ionization rates of Fe and Al might be different from each other and also the concentration of Fe was lower than that of Al. The fact that nickel and zinc had little effect on the ac SPVs may imply that they neither create negative nor positive charge or they don't influence the density of Dit, as a result, causing not an appreciable net charge.

3. Variation of the ac SPV for wafers rinsed with metal-contaminated water

The chemical analysis data of the wafers rinsed with water intentionally contaminated by Fe, P, Cu, Ni, Zn, Cr ($5 \times 10^{-3} \text{ kg}/\text{m}^3$) for 900 s at room temperature are

Fig. 7 AC SPV of n-type silicon wafers treated with metal-contaminated RCA alkaline solutions. Triangles correspond to the ac SPVs that appeared after clean alkaline rinse.

shown in Table 3, together with the data for the cleaned reference wafer (ref).

Figures 8 and 9 show the ac SPVs for n- and p-type Si wafers rinsed with metal-contaminated deionized water, respectively. The ac SPV is higher for Fe and Cu-contaminated n-type wafers than for the reference wafer that was treated with a clean RCA alkaline solution, although it was not detected for the metal-contaminated p-type Si wafers. On the other hand, the ac SPV for P-contaminated n-type Si was almost null, whereas that for p-type Si wafers was significantly enhanced. These results indicate that Fe and Cu create a negative charge and P causes a positive charge.

The concentration of Fe and Cu in oxide on Si strongly depends on surface finish (hydrophilic or hydrophobic) and dipping time and, as expected, the ac SPV is proportionally enhanced as the concentration increases. The negative charge induction of Cu is not clear at present. If Cu ions replace Si atoms in SiO_2 and/or Cu atoms move into interstitial sites, the bonding between Si and oxygen might be disturbed, then causing unbridged bonds and possibly leading to the creation of a negative charge. When the Si wafer surface is hydrophobic, Cu ions should get electrons and settle at the Si surface as atoms, as described by $\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$. Cu-Si contact might create a depletion layer, thereby causing the ac SPV. Further experiments are necessary to clarify the charge induction mechanism. Generally nickel and zinc seem to have little effect or less on charge induction. No negative nor positive charge appears in wafers rinsed with Cr-contaminated aqueous solution. In the field of silica chemistry⁽²⁰⁾, it is reported that the chromite ion is not easily formed as the aluminate ion, AlO_2^- . The Cr^{3+} ion is much larger than Al^{3+} and cannot fit into the SiO_2 lattice to yield stable anions such as $(\text{SiAlO}_4)^-$ ⁽²⁰⁾. Thus, Cr^{3+} is thought not to create a negative charge in the native oxide. The ac SPV method is, therefore, only applicable for the identification of impurities such as Al, Fe, Cu, and P on wafer surfaces.

IV. Conclusion

A scanning photon microscope (SPM), based on the image monitor of ac surface photovoltages (SPVs), has been developed to characterize silicon (Si) wafer surfaces

Table 3 The surface concentration of impurities on silicon wafers rinsed with impurity-contaminated pure deionized water.

Group	Added element	Concentrations (atoms/ m^2)					
		Fe^{3+}	P^{5+}	Zn^{2+}	Cu^{2+}	Ni^{2+}	Cr^{3+}
III	Fe	185	<6	<0.38	<0.1	<0.1	<9.4
	P	0.1	220	<0.38	<0.1	<0.1	<9.4
	Cu	0.1	<6	<0.38	170	<0.1	<9.4
	Ni	0.2	<6	<0.38	<0.1	342	<9.4
	Zn	0.1	<6	172	<0.1	<0.1	<9.4
	Cr	0.1	<6	<0.38	<0.1	<0.1	338
	ref.	0.1	<6	<0.38	0.2	<0.1	<9.4

Fig. 8 AC SPV of the n-type silicon wafers rinsed with metal-contaminated deionized water.

Fig. 9 AC SPV of the p-type silicon wafers rinsed with metal-contaminated deionized water.

which were treated with RCA standard solutions (alkaline and acid), hydrofluoric acid dipping, and deliberately contaminated solutions. Aluminum, iron, and copper give rise to a negative charge in the native oxide, resulting in the appearance of ac SPV in n-type Si wafers by forming $(\text{AlOSi})^-$ and $(\text{FeOSi})^-$ networks. The ac SPV varies with the concentration of those impurities. Phosphorus acts as a positive charge in the form of $(\text{POSi})^+$, thereby causing an ac SPV in p-type Si wafers. Zinc, nickel, and chromium show little effect in inducing charge in the native oxide. The effect of charge induction by impurities suggests the possibility for detecting contaminants on wafer surfaces by the ac SPV method. Therefore, the SPM can successfully be used to diagnose contaminated Si wafers in quite a nondestructive manner.

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