## Native Oxides on Si-Surfaces of Deep-Submicron Contact-Hole-Bottoms

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Cleaning and treatments of deep-submicron contact-hole-bottom Si surfaces were investigated. Suboxide-rich native oxides are formed on dry-etch-damaged Si surfaces. The suboxide-rich layers still exist after APM and HPM cleaning and DHF dipping, resulting in high contact resistance. When chemical dry etching is performed, the dry-etch-damaged layers are removed and, after cleaning, native oxides of low suboxide densities appear. Such oxides are easily removed by DHF dipping resulting in low contact resistance.

#### I. INTRODUCTION

The down-scaling of current VLSI for such devices as 256Mega-bit DRAMs yields a minimum interconnection dimension of 0.2  $\mu$ m with high aspect ratios. It is necessary to solve problems in cleaning and treatment processes of contact-holes having such deep-submicron dimensions. The most essential subject for achieving low resistance and the reliability of contacts is the elimination of native oxides at the interface between contact-hole-bottom Si surfaces and plugging materials. It has previously been reported that chemical dry etching (CDE) improves the electronic properties of contacts by removing dry-etching damage on contact-hole-bottom Si surfaces.<sup>1,2)</sup>

In the present work, we reveal the variance of Si surface conditions under contact-hole processing, by using x-ray photoelectron spectroscopy (XPS) for non-patterned Si surfaces as concerns native oxides. Integrated contact-hole treatment processes, consisting of CDE and other dry and wet steps, is applied to the fabrication of deep-submicron contact-holes plugged with P-doped poly-Si.

#### **II. EXPERIMENTS**

Figure 1 shows a schematic diagram of treatment processes for contact-holes and for non-patterned Si surfaces. Arrays of 0.5  $\mu$ m-deep contact-holes with diameters ranging from 0.12  $\mu$ m to 0.4  $\mu$ m were fabricated on n<sup>+</sup> ion-implanted layers of Si. After several steps of treatments, the contact-holes were plugged with P-doped a-Si followed by annealing. Contact resistance of the arrays was measured.

Non-patterned Si surfaces of ion-implanted  $n^+$ ,  $n^-$ ,  $p^+$ , and  $p^-$  layers were treated in the same way as contact-holes after etch-back of HTO layers. The non-patterned Si surfaces simulate the properties of contact-hole-bottom Si surfaces.

Cleaning and treatments performed on both contact-holes and non-patterned surfaces were as

follows. O<sub>2</sub> plasma treatment and SPM (H<sub>2</sub>SO<sub>4</sub> / H<sub>2</sub>O<sub>2</sub> mixture) cleaning were used for the purpose of removing CF<sub>x</sub> contamination layers deposited during dry etching. CDE was used for removing dry-etch damaged layers. For the comparison, a part of samples was not treated by CDE. APM (NH<sub>4</sub>OH / H<sub>2</sub>O<sub>2</sub> / H<sub>2</sub>O mixture) and HPM (HCl / H<sub>2</sub>O<sub>2</sub> / H<sub>2</sub>O mixture) cleaning were used for removing particles and metal contaminations. DHF (diluted HF solution) dipping was used for the native oxide removal. The conditions of the processes are summarized in Fig.1.

In order to estimate the depth of dry-etch damaged layers, non-patterned dry-etched surfaces after  $O_2$  plasma treatment and SPM, and without CDE, were treated by long-time APM and DHF. The DHF dipping time required to make a surface hydrophobic was examined for the dry-etch damaged surfaces after various periods of APM cleaning. The conditions of APM and DHF are the same as those shown in Fig.1.



Figure 1 A schematic diagram of Si-surface treatment processes for contact-holes and non-patterned Si surfaces.

### **III. RESULTS AND DISCUSSIONS**

Figures 2(a) and (b) show compositions, analyzed by XPS, of non-patterned n<sup>+</sup> and p<sup>+</sup> layers after each treatment. Contaminations of C and F, which form  $CF_x$  polymers as indicated in C(1s) spectra, were removed after O<sub>2</sub> plasma treatment. The surfaces treated by CDE showed an increase in Si composition and a decrease in O composition after the last DHF-dipping step. These surfaces were hydrophobic. In contrast, the surfaces without CDE showed considerable O compositions even after DHF dipping, and were hydrophilic.

Fig.3 shows the dependence of contact resistance on contact-hole diameter for  $n^+$  layers with and without CDE. CDE lowered the contact resistance corresponding to the O composition decrease shown in Fig.2.

decrease shown in Fig.2. The effect of CDE was examined with Si(2p) XPS spectra, shown in Figs.4(a) and (b), for n<sup>+</sup> and p<sup>+</sup> layers. It has been reported that the Si(2p) chemical shift caused by Si-C bonds is about 0.3 eV for the C composition of 14%.<sup>3)</sup> In Fig.2, the C compositions on the Si surfaces after treatments are less than 10%. In addition the F compositions shown in Fig.2 are negligibly small after APM. Therefore chemical shifts shown in Fig.4, especially below APM, are mainly due to Si oxides. There may be some influence of Si-H and/or Si-OH bonds. The shifts in Fig.4 are deconvoluted to Si suboxide peaks.

Figures 5(a) and (b) show the addition of suboxide-peak intensities, Si<sup>2+</sup> and Si<sup>3+</sup>, after each treatment. The Si(2p) spectra for surfaces without CDE show the existence of the suboxides, as well as Si<sup>4+</sup>, after every treatment step. On the other hand, the CDE-treated surfaces show lower amounts of suboxides after APM and HPM, and show no oxides except Si<sup>1+</sup> after the last DHF dipping step.

the CDE-treated suffaces show lower amounts of suboxides after APM and HPM, and show no oxides except Si<sup>1+</sup> after the last DHF dipping step. Figure 4 shows that DHF dipping does not dissolve even Si<sup>4+</sup> on the suboxide-rich surfaces. It is indicated that the Si<sup>4+</sup> on non-CDE surfaces are mixed with suboxides, whose Si-Si bonds are not dissolved by DHF, and that the Si<sup>4+</sup> bonds located deeper than the suboxides cannot be dissolved by DHF dipping. It is considered that the existence of suboxide-rich layers is caused by dry-etching damage such as crystalline defects.

The depths of the dry-etch-damaged layers were estimated with non-patterned surfaces as follows. The damaged suboxide-rich Si surfaces are hydrophilic after short-period DHF dipping, while non-damaged surfaces easily become hydrophobic. DHF dipping for long periods removes the suboxiderich layers and changes the damaged surfaces from hydrophilic to hydrophobic. This is because F-ions penetrate into the layers and dissolve Si-O bonds. Thus whether the suboxide-rich layers exist or not can be inferred from the length of DHF-dipping required to make the surfaces hydrophobic. On the other hand, APM cleaning has the effect of Si surface etching, as well as oxidation for approximately 1 nm. According to damaged layer etching through APM cleaning, the damage-free regions become the surfaces, which contain native oxides of low suboxide

densities. The appearance of the damage-free surfaces can be examined by the DHF-dipping periods for achieving hydrophoby. Therefore the APM cleaning periods for forming the damage-free surfaces indicate the damaged-layer depths. Figure 6 shows the DHF dipping time for dryetch damaged Si surfaces without CDE to become hydrophobic, as a function of the time of APM cleaning prior to DHF dipping. The APM cleaning time, until the reduction of the DHF-dipping time saturates, is shorter for an n<sup>+</sup> layer (50 min) than for layers of n, p and p<sup>+</sup> (80 min). Figure 7 shows Si substrate etching depths as a function of APM cleaning time, measured by step-height change. The etching depth of the n<sup>+</sup> layer for 50 min is approximately 20 nm, while the etching depth of the n<sup>-</sup> and p<sup>+</sup> layers for 80 min are also approximately 20 nm. This indicates that the depth of the dry-etchdamaged layer, which influences the suboxide-rich layer formation, is approximately 20 nm independent of the type of ion-implanted layers. The DHF dipping time required to be hydrophobic are different between the surfaces; n<sup>+</sup> < n<sup>-</sup> < p<sup>-</sup> < p<sup>+</sup>. This tendency is caused by the existence of dopants on the surfaces.

Based on the above mentioned results, the contact-hole-bottom Si surface conditions are schematically described in Fig.8. After etching, the contact-hole-bottom Si surface contains CF<sub>x</sub> polymers on a dry-etch-damaged defect layer. The depth of the damaged layer is approximately 20 nm. After the removal of  $CF_x$  by  $O_2$  plasma treatment and SPM cleaning, the surface becomes suboxide-rich. CDE completely removes the damaged layer, resulting in a native oxide of a low suboxide density after APM and HPM cleaning. On the other hand, a surface without CDE still contains the damaged layer, whose top becomes the suboxide-rich native oxides. After the last DHF dipping step, the native oxide with a low suboxide density is dissolved and becomes hydrophobic, while the suboxide-rich native oxide stays on the surface of the damaged layer and retains hydrophilic.

# **IV. CONCLUSION**

Cleaning and treatments of contact-hole-bottom Si surfaces were investigated. Suboxide-rich native oxides are formed on dry-etch-damaged Si surface layers of approximately 20 nm-thick. The suboxiderich native oxide layers still exist after APM and HPM cleaning and DHF dipping, resulting in high contact resistance. When CDE is performed, the dryetch-damaged layers are removed and, after cleaning, native oxides of low suboxide densities appear. Such oxides are easily removed by DHF dipping. Thus low contact resistance is achieved. These results can be effectively applied to designing the integrated processes of contact-hole treatments, from dry etching to contact-hole plugging, in the fabrication of deepsubmicron contacts for 256M and larger DRAMs.

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Figure 2 Variance of composition on  $n^{\text{+}}\text{-}$  and  $p^{\text{+}}\text{-}\text{Si}$  surfaces through treatments.







Figure 6 DHF dipping time required to become hydrophobic for Si surfaces, without CDE, as a function of the time of APM cleaning prior to DHF dipping.



Figure 7 Si substrate etching depth as a function of APM cleaning time.



Figure 3 Contact resistance depending on contacthole diameter for  $n^+$  layers.



Figure 5 Variance of suboxide-peak intensities  $(Si^{2+} + Si^{3+})$  of Si(2p) spectra through treatments.



