Interface properties and effective work function of Sb-predoped fully silicided NiSi gate

Takuji Hosoi,a,† Kosuke Sano,a,b Akio Ohta,b Katsunori Makihara,b Hirotaka Kaku,b Seiichi Miyazaki,b and Kentaro Shibaharaa,b

X-ray photoelectron spectroscopy (XPS) analysis of Sb-predoped fully silicided (FUSI) NiSi gate metal-oxide-semiconductor structure was carried out to evaluate the chemical bonding states and location of Sb pileup at NiSi/SiO₂ interface. The results reveal that Sb atoms encroach into the SiO₂ layer and that their pileup is formed at about 3 nm beneath the NiSi/SiO₂ interface. Direct measurement of the work function of Sb-doped FUSI NiSi gate by XPS suggests that the work function is identical to its original value without the Sb pileup located inside the gate oxide. Copyright © 2008 John Wiley & Sons, Ltd.

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Introduction

Metal gate technology is required for further scaling of complementary metal-oxide-semiconductor (CMOS) devices in order to solve the problems of the conventional polycrystalline Si (poly-Si) gate, such as gate depletion and boron penetration. To ensure compatibility with conventional poly-Si gate CMOS technology in terms of threshold voltage adjustment, dual gate work functions close to conduction and valence band edges of Si are required for n-MOS and p-MOS, respectively. Although there are several proposals for the integration of two different metals, they are more complicated than the conventional fabrication process flow used for the poly-Si gate devices. Therefore, the tuning of the work function of the metal gate has been widely studied. Ni fully silicided (FUSI) gate is one of the most promising candidates for a single-metal dual-work-function gate. As NiSi is already being used as a self-aligned silicide (SALICIDE) material for the current CMOS process, it is advantageous for process integration. In addition, it has been reported that the work function of the Ni-FUSI gate can be modulated by doping poly-Si before silicidation[3–9] and by controlling the composition of the silicide.[10] The impurities in the poly-Si layer are swept out toward the gate oxide during silicidation by the snowplow effect[11] and after complete silicidation, their pileup is formed at the NiSi/SiO₂ interface. The NiSi work function modulation is considered to originate from the impurity pileup.[3,4] Although the interfacial electric dipole induced by impurity pileup is considered as a possible origin of the work function shift, the detailed mechanism is not fully understood.

In this paper, we focus on the Sb-predoped FUSI NiSi gate on the SiO₂ dielectric, which is known to lead to the largest work function shift of about −0.40 eV.[3,5,7–9] The location of the Sb pileup and the chemical bonding states at the NiSi/SiO₂ interface were investigated by X-ray photoelectron spectroscopy (XPS). To discuss the role of the Sb pileup in an effective work function shift, the work functions of the FUSI NiSi gates were also directly evaluated by back-side XPS.

Experimental

FUSI NiSi gate MOS diodes were fabricated on p-type Si(100) substrates. A gate oxide with a thickness of 5 or 10 nm was grown by thermal oxidation, and poly-Si of 100 nm was deposited on it by low-pressure chemical vapor deposition. After gate patterning, 30 keV Sb ion implantation at a dose of 5 × 10¹⁵ cm⁻² was carried out, followed by rapid thermal annealing (RTA) in N₂ at 900 °C for 1 min for dopant activation and implantation-induced damage recovery. Then, a 60 nm Ni layer was deposited by d.c. sputtering, followed by in situ full silicidation annealing using sputtering stage heating in the chamber at 450 and 500 °C for 25 and 5 min, respectively. After silicidation, unreacted Ni was selectively etched away by wet etching, followed by post-metallization annealing in 20% H₂ at 400 °C for 30 min. The flatband voltages (VFB) of the fabricated MOS diodes were obtained from the capacitance–voltage (C–V) characteristics measurements. FUSI NiSi film structure and NiSi/SiO₂ interface properties were characterized by Raman spectroscopy and XPS.

† Present address: Course of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565–0871, Japan.

a Research Center for Nanodevices and Systems, Hiroshima University, 1-4-2 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8527, Japan.

b Graduate School of Advanced Sciences of Matter, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima 739-8530, Japan.
Results and Discussions

Effect of Sb-predoping on silicide formation

Figure 1 shows the measured $V_{FB}$ of the fabricated MOS diodes as a function of the gate oxide thickness. On the assumption that the fixed charge density in SiO$_2$ film is independent of the oxide thickness, the y-axis intercept of a linear fit provides an estimate of the gate work function. It was found that a work function shift of $-0.32$ eV was obtained by Sb-predoping in the case of silicidation at 450 °C. The Sb pileup formation at NiSi/SiO$_2$ interface was confirmed by back-side secondary ion mass spectrometry (SIMS) in our previous work.[7,8] However, an Sb-predoped specimen with 500 °C silicidation did not result in a work function shift. As reported previously, this difference was due to a lower peak concentration of the Sb pileup at the NiSi/SiO$_2$ interface formed at 500 °C than that formed at 450 °C.[7,8] This means that slower silicidation at a lower annealing temperature significantly enhances the snowplow effect, which leads to an increase in the Sb pileup concentration at the NiSi/SiO$_2$ interface. However, introducing the Sb gave rise to various changes in the FUSI NiSi film. Figure 2 shows the Raman scattering spectra for undoped and Sb-predoped FUSI NiSi MOS structures obtained from the NiSi surface. In the case of the undoped specimen, the NiSi phase is the predominant one in the FUSI layer. In contrast, the peak of the Ni$_2$Si phase was observed in an Sb-predoped sample. Since it is generally believed that the initially formed Ni$_2$Si phase transforms into the NiSi phase in a Ni–Si system, the existence of Sb atoms in the poly-Si layer is considered to retard the silicidation reaction. Furthermore, the peak of Si–Si bond was also found, indicating the existence of Si precipitation in the FUSI layer. In addition, void formation at Sb-predoped FUSI NiSi/SiO$_2$ interface was frequently observed, as shown in Fig. 3. These results suggest that the anomalous Si diffusion toward the surface during the silicidation is caused by Sb-predoping. Therefore, we can conclude that the silicidation kinetics is strongly affected by predoping.

XPS analysis of NiSi/SiO$_2$ interface

In addition to the effect on the formation of FUSI gates described in the previous section, we have previously reported that partial peeling of the Sb-predoped FUSI NiSi layer was frequently found.
after removal of the unreacted Ni. A similar problem was reported as due to a poor adhesion of Sb-predoped FUSI NiSi layer to underlying SiO₂ layer. This adhesion problem was applied to our sample preparation method for an XPS analysis of the NiSi/SiO₂ interface. By pulling apart a quartz plate glued onto the NiSi surface, an Sb-predoped NiSi/SiO₂/Si MOS structure was cleaved into the upper and lower specimens. This cleaving technique was not applicable to B-, P-, As- and In-predoped FUSI NiSi gate MOS structures as well as to the undoped one, even though voids were formed at the NiSi/SiO₂ interface. As shown in Fig. 4, the root mean-square (RMS) values of surface roughness obtained by atomic force microscopy (AFM) for both upper and lower parts were less than 0.4 nm, indicating that the cleaved faces were very smooth and flat. The NiSi/SiO₂ interfaces were characterized by XPS measurements for these specimens. The XPS measurements were taken using a monochromatic Al Kα source at 1486.6 eV with a takeoff angle of 90°. For the Si 2p spectra shown in Fig. 5(a) and (d), aside from the oxidized Si, metallic Si was detected slightly in the upper specimen, which was absent in the lower specimen. Since the escape depth of Si 2p photoelectrons in the SiO₂ layer is about 3.8 nm, the cleaved face is found to be about 3 nm away from the NiSi/SiO₂ interface. For the Sb 3d XPS spectra shown in Fig. 5(b) and (e), oxidized Sb was detected in both upper and lower specimens. This means that Sb atoms driven by the snowplow effect during silicidation encroached into the SiO₂ layer, and its encroachment length is considered to be about 3 nm or more. Although the metallic Sb peak is independent of the silicidation annealing temperature, the oxidized Sb peak for 450 °C silicidation is much larger than that for 500 °C. This temperature dependence of the Sb pileup agrees with the backside SIMS analysis. Although both the oxidized and metallic Ni peaks were found in the upper specimen, no Ni was detected in the lower one, as shown in Fig. 5(c) and (f). This indicates that the Ni atoms also encroached into the SiO₂ layer, and the Ni encroachment length was shorter than that of Sb.

In the XPS analysis of metals, both Fermi levels of the sample and detector are aligned, so the metal work function can be evaluated by measuring the cut-off energy for photoemission. However, since the XPS analysis was carried out at room temperature, the Fermi distribution of electrons must be considered for the precise evaluation. With this in mind, the effective work function of the Sb-predoped FUSI NiSi gate at the oxide interface was determined by fitting the Fowler function to the measured Fermi edge photoelectron spectra. Because the measurement is sensitive to the surface condition, specimens for work function measurement were lightly sputtered by Ar⁺ ions in order to remove carbon surface contamination. As shown in Fig. 6, the work function at the interface of the Sb-predoped FUSI NiSi formed by 450 °C silicidation was estimated to be 4.61 eV. The measurement of the FUSI NiSi surface yielded the same work function value. This work function value is different from that extracted from the C–V measurement, but is identical to that of the undoped
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Figure 5. Si 2p (a), (d), Ni 2p (b), (e) and Sb 3d (c), (f) core-level XPS spectra from the cleaved faces of Sb-predoped NiSi FUSI gate MOS structures formed by 450 and 500 °C silicidation. This figure is available in colour online at www.interscience.wiley.com/journal/sia.

Figure 6. Photoelectron spectra near the Fermi edge for the Sb-predoped NiSi/SiO2 interface formed by 450 °C silicidation. The effective work function was determined by fitting the Fowler function to the measured spectra.

FUSI NiSi gate. To clarify the reason for the discrepancy, the core-level XPS spectra were taken after the sputtering. The oxidized Sb peaks seen in the spectra in Fig. 5(b) disappeared despite no change being seen in the Si 2p core level spectra. These results indicate that the Sb atoms at the NiSi/SiO2 interface are mainly localized at the cleaved face, and their pileup in the SiO2 layer plays an important role in the work function shift.

Conclusions

We have investigated the interface properties of Sb-predoped FUSI NiSi gate MOS structures by XPS to investigate the origin of the effective work function shift. It has been found that the Sb atoms in the poly-Si layer encroach into the gate oxide after full silicidation, and their pileup located inside the SiO2 is considered to be related to NiSi gate work function shift. The existence of impurities in the poly-Si layer also retards the silicidation reaction and the anomalous Si diffusion toward the surface during silicidation, resulting in a nonuniform silicide phase and the void formation at NiSi/SiO2 interface.

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