# Analysis of the Origin of the Threshold Voltage Change Induced by Impurity in Fully Silicided NiSi/SiO<sub>2</sub> gate stacks

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### 1. Introduction

Metal gate electrodes have been studied extensively to improve the current drive capability in future metal-oxide-semiconductor field effect transistors (MOSFETs). Fully silicided (FUSI) NiSi metal gate electrodes have received increasing attention due to their simple integration scheme and controllability of the threshold voltage (V<sub>th</sub>) by implanting the poly-Si gate electrodes prior to silicidation on SiO<sub>2</sub> [1]. It has been reported that the V<sub>th</sub> change is related to the impurity redistribution at the NiSi/SiO2 interface during silicidation [1]. Some reports propose the reason of the  $V_{th}$ change [1, 2]. It has also been reported that the  $V_{th}$  change for the NiSi/HfSiON gate stack is much smaller than that for the NiSi/SiO<sub>2</sub> gate stack [3]. However, the origin of the  $V_{th}$  change has not been identified. It is important to address the mechanism of the V<sub>th</sub> change in order to control the uniformity of V<sub>th</sub> and to reveal the reason for the suppression of the  $V_{th}$  change on the HfSiON dielectric.

Figure 1 shows the major factors to determine the  $V_{th}$  shift by impurity: (a) the change in work function of the electrode in vacuum ( $\phi_m$ ), (b) the fixed charge ( $Q_{fix}$ ) within SiO<sub>2</sub> and (c) the dipole moment ( $d_{inter}$ ) at the NiSi/SiO<sub>2</sub> interface. In this work, we investigated the origin of the  $V_{th}$  change by impurity for the NiSi/SiO<sub>2</sub> gate stack, using backside X-ray photoelectron spectroscopy (XPS) and electrical measurements. It was found that neither factor (a) nor (b) is a dominant factor to determine the  $V_{th}$ . The obtained results indicate that a possible origin of the  $V_{th}$ change is the dipole moment due to the substitution of impurity atoms for the Si and/or Ni atoms at the NiSi/SiO<sub>2</sub> interface.

### 2. Experimental

We fabricated P-doped, As-doped and Sb-doped FUSI-NiSi/SiO<sub>2</sub> (oxide thickness = 1.4 - 3nm) capacitors. The impurity concentrations in poly-Si were  $2 - 4.6 \times 10^{20}$  cm<sup>-3</sup>. The backside XPS measurement was performed to evaluate the change in  $\phi_m$  and the d<sub>inter</sub>. For the XPS measurement, the Si substrate was removed mechanically and chemically, as illustrated in Fig. 2. Photoelectrons from SiO<sub>2</sub> and NiSi were detected because the thickness of SiO<sub>2</sub> is less than 3 nm. The change in  $\phi_m$  of NiSi was determined from the shift of the binding energy (BE) of Si2p in NiSi, since the BE of Si2p was measured from the Fermi level of NiSi when NiSi was grounded (Fig. 3). The d<sub>inter</sub> was detected as the BE shift of O1s in SiO<sub>2</sub>, because the d<sub>inter</sub> induces voltage drop (V<sub>int</sub>) across the interface region, as shown in Fig. 4. The Q<sub>fix</sub> within SiO<sub>2</sub> was evaluated from the dependence of the flatband voltage (V<sub>FB</sub>) and the equivalent oxide thickness (EOT).

### 3. Results and Discussion

## (a) Work function of the electrode in vacuum

Figure 5 is the XPS spectrum of the Si2p of the NiSi electrodes. The spectrum of the Si2p for the impurity-doped samples was almost the same as that for the Non-doped sample. Figure 6 shows the relationship between the V<sub>th</sub> change and the BE shift of Si2p in NiSi. The figure shows that the BE for impurity-doped samples was almost the same as that for Non-doped sample within an experimental error (0.05 eV), although the V<sub>th</sub> change for the P-doped, As-doped and Sb-doped samples was 0.12-0.2 V, 0.2-0.3 V and 0.4 V, respectively. Therefore, we conclude that the change in the  $\phi_m$  of NiSi is not a dominant causal factor of the V<sub>th</sub> change.

### (b) Fixed charge within SiO<sub>2</sub>

Figure 7 shows the dependence of the  $V_{FB}$  on the EOT for the

Non-doped and P-doped samples. From the slope of the relationship between the  $V_{FB}$  and the EOT, the  $Q_{fix}$  within SiO<sub>2</sub> for both samples was estimated to be less than  $3 \times 10^{11}$  e/cm<sup>2</sup> (e: electronic charge), which results in weak dependence of the  $V_{FB}$  on the EOT. In Table I, the  $Q_{fix}$  is summarized. The  $Q_{fix}$  within SiO<sub>2</sub> for the As-doped and Sb-doped samples was as low as those for the Non-doped and P-doped samples. These results indicate that the  $Q_{fix}$ , within SiO<sub>2</sub> is not a dominant causal factor of the  $V_{th}$  change. However, the possibility that the  $Q_{fix}$  at the NiSi/SiO<sub>2</sub> interface causes the  $V_{th}$  change is not excluded, since the evaluated  $Q_{fix}$  does not include the  $Q_{fix}$  at the NiSi/SiO<sub>2</sub> interface.

#### (c) Dipole moment at the NiSi/SiO<sub>2</sub> interface

Figure 8 is the XPS spectrum of O1s in the SiO<sub>2</sub> dielectric. The BE of O1s for the impurity-doped samples was higher than that for the Non-doped sample. The higher BE of O1s indicates the existence of the d<sub>inter</sub>, which consists of the positive charge on the SiO<sub>2</sub> side and the negative charge on the NiSi side, as illustrated in Fig. 4. Figure 9 shows the relationship between the V<sub>th</sub> change and the BE shift of O1s in SiO<sub>2</sub>. The BE shifts were strongly correlated with the V<sub>th</sub> change. These results indicate that a dominant causal factor of the V<sub>th</sub> change is the d<sub>inter</sub> and/or the Q<sub>fix</sub> at the NiSi/SiO<sub>2</sub> interface, which results in the interface dipole that consists of the Q<sub>fix</sub> in SiO<sub>2</sub> and its image charge in NiSi.

#### (d) Origin of the $V_{th}$ change

The obtained results show that a dominant causal factor of the V<sub>th</sub> change is the  $d_{inter}$  and/or  $Q_{fix}$  at the NiSi/SiO<sub>2</sub> interface, which are induced by the impurity at the NiSi/SiO<sub>2</sub> interface. Figure 10 shows the XPS spectrum of the impurity atoms at the NiSi/SiO<sub>2</sub> interface for the P-doped and Sb-doped samples. The P2p and Sb3d<sub>5/2</sub> peaks consisted of two peaks (main-peak and sub-peak). The BE of the sub-peak was higher than that of the pure P and Sb substance, which indicates that a part of the impurity atoms is bonded to the O atoms at the NiSi/SiO<sub>2</sub> interface.

Considering the radius of the impurities (Table II), it is thought that the diffusion of P into  $SiO_2$  occurs more easily than that of Sb. However, the V<sub>th</sub> change for the P-doped sample is smaller than that for the Sb-doped sample at the same impurity concentration in the NiSi electrode (Fig. 11). Thus, it is convincing that the d<sub>inter</sub> rather than the Q<sub>fix</sub> at the NiSi/SiO<sub>2</sub> interface is the origin of the V<sub>th</sub> change.

A possible origin of the  $d_{inter}$  is the substitution of impurity atoms for the Si and/or Ni atoms at the NiSi/SiO<sub>2</sub> interface, as shown in Fig. 12. Since the electronegativity of impurity (X) is larger than that of Ni and Si (Table II), the charge +Q' on the impurity atoms is smaller than the charge +Q on the Ni and Si atoms. Thus, the dipole moment of the X-SiO<sub>2</sub> bond is smaller than that of the Ni/Si-SiO<sub>2</sub> bond, which results in the effective dipole moment, as illustrated in Fig. 12. We estimated the effective dipole moment based on the principle of electronegativity equalization [4] and calculated the V<sub>th</sub> change assuming that the dipole density equals the impurity density estimated from the XPS sub-peak. The calculated V<sub>th</sub> change for the Sb-doped sample (0.35 V) is similar to the experimental value (0.38 V). This implies that the interface dipole moment is a possible origin of the V<sub>th</sub> change.

#### 4. Conclusion

We investigated the origin of the  $V_{th}$  change by impurity in FUSI-NiSi gate electrodes on a SiO<sub>2</sub> gate dielectric, using electrical measurements and a direct analysis of the NiSi/SiO<sub>2</sub>

interface by XPS. The results indicate that a possible origin of the  $V_{th}$  change is the dipole moment due to the substitution of impurity atoms for the Si and/or Ni atoms at the NiSi/SiO<sub>2</sub> interface.

#### References



Fig. 1 Possible origins for the  $V_{th}$  change induced by impurity.



Fig. 5 XPS spectrum of Si2p in NiSi .





Fig. 11 Dependence of the  $V_{th}$  change on the impurity concentration in the NiSi electrode.

Fig. 2 Sample for the backside XPS measurement.



Fig. 6 Relationship between the  $V_{th}$  change and the binding energy (BE) shift of Si2p in NiSi.



Fig. 9 Relationship between the  $V_{th}$  change and the binding energy (BE) shift of O1s in SiO<sub>2</sub>.

Element	Electronegativity	Radius (nm)
Ni	1.94	0.121
Si	2.14	0.111
Р	2.93	0.106
As	2.68	0.119
Sb	3.04	0.138

Table II Electronegativity and covalent radius. The electronegativity of impurity is estimated by the calculation of charge transfer for Si-X (X : impurity) cluster.

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[2] K. Sano et al., SSDM 2004, pp.456-455 (2004).

[3] E. Cartier et al., VLSI 2004, pp.44-45 (2004).

[4] H. Z. Massoud, J. Appl. Phys. 63, p.2000 (1988).



Fig. 3 Evaluation of the change in metal work function  $\Delta \varphi_m$ . Since NiSi is grounded (Fig. 2), the binding energy (BE) of Ni2p and Si2p is measured from the Fermi level of NiSi. Thus, the change in BE corresponds to  $\Delta \varphi_m$ .



**EOT (nm)** Fig. 7 Relationship between the EOT and the  $V_{FB}$  for the Non-doped and P-doped NiSi/SiO<sub>2</sub> capacitors.





Fig. 4 Effect of the interface dipole moment  $(d_{inter})$  on the binding energy (BE) of Si2p and O1s in SiO<sub>2</sub>. The voltage drop (V<sub>int</sub>) across the interface region due to the dipole causes the BE shift of Si2p and O1s in SiO<sub>2</sub>.

Electrode	$Q_{\rm fix}$ (cm <sup>-2</sup> )
Non-doped	$0.7 X 10^{11}$
P-doped	$2.2 \times 10^{11}$
As-doped	0.3X10 <sup>11</sup>
Sb-doped	$2.0 \times 10^{11}$

Table I Fixed charges  $(Q_{\rm fix})$  evaluated from the slope of the relationship between the  $V_{\rm FB}$  and the EOT.







Fig. 12 Possible origin of the interface dipole. The substitution of impurity atoms for the Si and/or Ni atoms causes the effective dipole moment  $(d_{eff})$  due to the larger electronegativity of impurity atoms.