Tuning of NiSi/Si Schottky barrier heights by sulfur segregation during Ni silicidation

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The Schottky barrier height (SBH) of NiSi on Si(100) was tuned in a controlled manner by the segregation of sulfur (S) to the silicide/silicon interface. S was implanted into silicon prior to silicidation. During subsequent Ni silicidation, the segregation of S at the NiSi/Si interface leads to the change of the SBH. The SBH of NiSi decreased gradually on *n*-Si(100) from 0.65 eV to 0.07 eV and increased correspondingly on *p*-Si(100). © *2005 American Institute of Physics*. [DOI: 10.1063/1.1863442]

Self-aligned silicidation is one of the key technologies in the state-of-art complementary metal-oxide-semiconductor (CMOS) process to make Ohmic or Schottky contacts at source/drain and gate. Amongst of them, NiSi silicide has emerged as a leading choice in Si nanometer electronics due to its low resistivity and high scalability. Recently, Schottky barrier source/drain metal-oxide-semiconductor field-effect transistors (MOSFETs) have been receiving a lot of attention because of the lower parasitic series resistance at source/drain, possible zero junction depth and simpler fabrication process.[1–4] However, for a typical Schottky barrier (SB) MOSFET, the on-current is limited by the tunneling through the Schottky barrier at the source. If a very low or a negative SBH could be realized, the on-current of SB-MOSFET could be increased substantially.[4] NiSi has an experimental SBH of 0.65 eV on *n*-Si(100). This high SBH value hinders the application of NiSi in SB-MOSFETs. If we can lower the SBH of silicides to very low value, the device exhibits the same intrinsic performance as conventional MOSFET but also benefits from the advantages of SB-MOSFETs mentioned above.

In an ideal metal-semiconductor system the Schottky–Mott theory suggests that the SBH (Φ_B) is simply determined by the difference between the work function of the metal (ϕ_M) and the electron affinity of the semiconductor (χ_S) ($\Phi_B = \phi_M - \chi_S$).[5] In practice, however, the presence of interface states leads to the SBH being less dependent on the metal work function. Dangling bonds at the semiconductor surface can be eliminated by valence-mending adsorbates.[6] S and Se are two possible valence-mending candidates for the Si(100) surface.[6] Lacharme *et al.*[7] reported that surface states on Si can be removed by S exposure at room temperature. Tao *et al.*[8–10] have used a monolayer of Se to eliminate the surface states on the Si(001) surface by terminating dangling bond and relaxing strained bonds. Pure metals, like Mg, Al, Cr, and Ti, on Se-passivated *n*-Si(001) showed very low and even negative SBH values which can be predicted by the Schottky–Mott theory.[8–10] However, deposition of these elements seems inappropriate for silicide contacts on Si due to the suppression of silicide formation.[10] In order to benefit from advantages of silicides in state-of-art MOSFET technology, methods to tune the SBH of silicides on Si are required. In this paper we show an effective method to tune the SBH value of NiSi on both *n*- and *p*-type Si(100). A small dose of S ions was implanted into Si before Ni deposition. During subsequent Ni silicidation, the segregation of S at the NiSi/Si interface tunes the SBH.

n-type Si(100) with a resistivity of 2.5–8.5 Ω cm, and *p*-type Si(100) with a resistivity of 7–21 Ω cm were used in the experiments. 250 nm thermal SiO_2 was grown by wet thermal oxidation. After removal of the SiO_2 on the backside by HF wet etching, P and B with a dose of $3\times10^{15}/cm^2$ were implanted into the backside of *n*-Si(100) and *p*-Si(100), respectively. The backside dopants were activated by rapid thermal annealing (RTA) in N_2 at a temperature of 1050 °C. Schottky diode windows were opened by photolithography and dry-etching of the SiO_2 layers on the front side. Then S ions at an energy of 15 keV in a dose range from 1×10^{13} to $2\times10^{14}/cm^2$ were implanted into the exposed Si diode areas using photoresist as the implantation mask. After removal of the photoresist and standard cleaning of the S-implanted samples, the native oxide on the Schottky diode areas was removed by an HF-dip and subsequently a 30 nm Ni and a 10 nm Ti (cap) layer were deposited using e-beam evaporation at room temperature. Ni silicidation was carried out by RTA at 550 °C for 1 min in forming gas (90% N_2+10% H_2). The Ti cap-layer and unreacted Ni were removed using $H_2SO_4:H_2O_2$.

NiSi layers formed by RTA at 550 °C for 1 min with and without S implantation prior to Ni deposition were investigated using cross-sectional transmission microscope (XTEM). Figure 1 shows an XTEM image of the NiSi layer formed on a Si(100) substrate implanted with S^+ at an energy of 15 keV with a dose of 2×10^{14} S/cm^2 prior to Ni deposition. The NiSi layer has a thickness of 62 nm with a high uniformity. The sheet resistance is 2.7 Ω/square measured

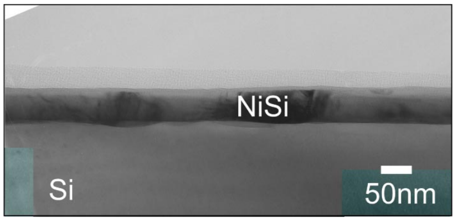

FIG. 1. XTEM image of a NiSi layer formed at 550 °C for 1 min on the n-Si(100) substrate implanted with 15 keV, 2×10^{14} S^+/cm^2 prior to Ni deposition.

by Van der Pauw measurements. It is known that Se deposition suppresses the silicidation,[10] but we found that S implantation in a dose range from 1×10^{13} to $2\times10^{14}/cm^2$ does not affect the layer structure, layer thickness and the resistivity.

The Schottky diodes with and without S implantations were characterized using current–voltage ($I-V$) measurements. The Ohmic contacts were made on the wafer backside using 200 nm Au. Figure 2 shows the $I-V$ characteristics of the NiSi/n-Si(100) Schottky diodes. With increasing S dose, the SBH of NiSi decreases. At a dose of 2×10^4 S/cm^2, NiSi shows a perfect Ohmic contact to the n-Si(100). The SBH values on the n-Si(100) have been measured by activation-energy [current–temperature ($I-T$)] measurements. Figure 3 shows the plot of I/T^2 versus $1/T$ at different forward bias (V_f) for the sample with 15 keV 2×10^{14} S/cm^2 implantation. The SBH values are determined from the slopes of the curves.[11] The slope of the curve in Fig. 3 is not constant. The reason is that when the thermal energy of the carriers is comparable to the SBH, the barrier apparently disappears. In this case, the SBH value can be determined using the low temperature data.[9] The SBH values were in the range between 0.04 eV to 0.09 eV depending on the forward bias. The average SBH value is 0.07 eV which is much lower than the conventional SBH of 0.65 eV for NiSi on n-Si(100).

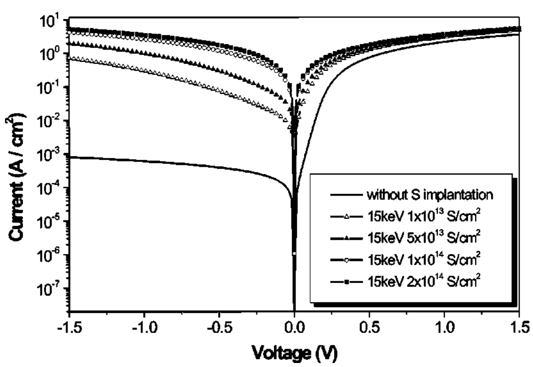

FIG. 2. $I-V$ characteristics of NiSi/n-Si(100) Schottky diodes with and without S implantations.

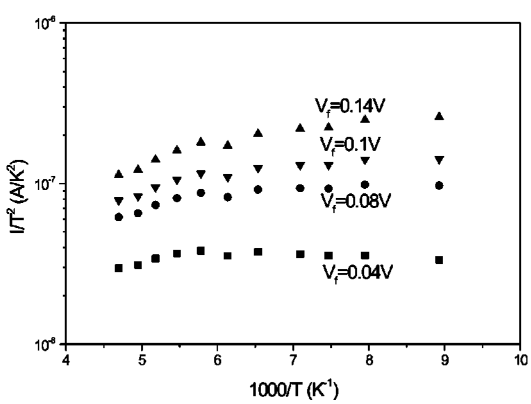

FIG. 3. Activation-energy measurements for the SBH determination of the NiSi diode formed on n-Si(100) implanted by 15 keV, 2×10^{14} S^+/cm^2 prior to Ni deposition.

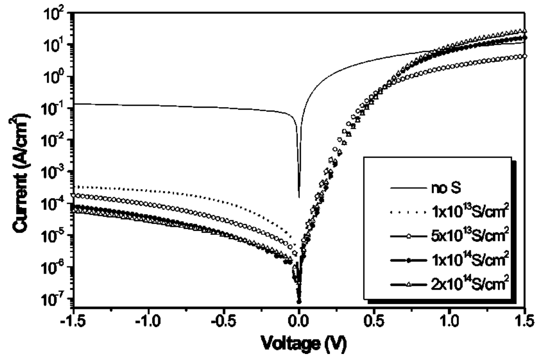

FIG. 4. $I-V$ characteristics of NiSi/p-Si(100) Schottky diodes with and without S ion implantations.

The effect of S implantation on the Schottky barrier of NiSi on p-Si(100) was also investigated. The $I-V$ characteristics of NiSi/p-Si(100) Schottky diodes are shown in Fig. 4. Without S implantation, NiSi has an SBH value of 0.45 eV on p-Si(100) extracted from the $I-V$ curve in Fig. 4 using thermal emission theory.[11] The SBH values of NiSi/p-Si(100) increase with S implantation dose, which is indicated by the reduction of the reverse currents. A small dose of 1×10^{13} S/cm^2 leads to a significant increase of the SBH to 0.68 eV. For a larger dose of $1\times10^{14}/cm^2$, the SBH is 0.75 eV. Theoretically, the sum of the SBH on n-Si(100) (Φ_{bn}) and the SBH on p-Si(100) (Φ_{bp}) equals approximately to the band gap of silicon (~1.1 eV). For samples without S implantation, $\Phi_{bn}+\Phi_{bp}=1.1$ eV. But for samples with S implantation, $\Phi_{bn}+\Phi_{bp}<1.1$ eV. A higher dose of S implantation results in a smaller $\Phi_{bn}+\Phi_{bp}$. Prokopyev *et al.*[12] pointed out that when the SBH is large (>0.7 eV), the extraction of SBH using $I-V$ methods is not correct because of minority-carrier (electrons in p-Si) injections at metal contacts, and the errors increase with Φ_{bp}. For a higher SBH, the leakage currents from the surface and edges of the diode also induce a large error. Therefore, other methods and Schottky diodes with guard-rings to reduce the leakage currents are necessary to measure the high SBH (>0.7 eV) values.

In order to understand the effect of sulfur implantation on SBH, secondary-ion mass spectrometry (SIMS) was used to measure the S distribution after Ni silicidation, as shown in Fig. 5. The NiSi/Si interface is marked by the dashed line at the depth of 62 nm. The mean depth of 15 eV S implantation in Si is 25 nm, corresponding to a depth of 33 nm in NiSi after silicidation, which can be seen from the peaks at a depth of 33 nm in Fig. 5 for higher doses. The peak of the S distribution near the NiSi/Si interface indicates the segregation of S during silicidation at 550 °C. The concentration of the segregated S increases with the fluence of S implantation. After silicidation, the whole original S implanted region was converted to NiSi. Therefore, the S distribution near the NiSi/Si interface is caused by segregation of S during silicidation. Predominantly, the S is found in the silicide and near the interface, considering the small solubility of S in Si

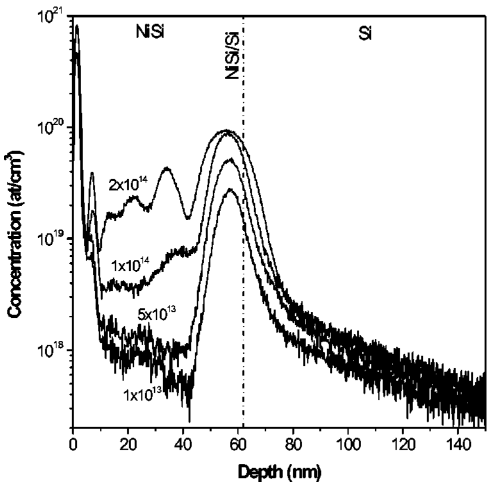

FIG. 5. SIMS depth profiles of S for various S fluences after Ni silicidation at 550 °C.

($<10^{15}$ cm^{-3}).[13] The sluggish exponential decrease of the S depth profiles deeper in the Si substrate shown in Fig. 5 could be due to interface effects and the sensitivities of the SIMS method. Because of the low energy (1 keV Cs^+) of the sputtering ions, the "knock-on" effects by the ion beam during SIMS measurements do not influence the S distributions. Further investigations will be done to study the S diffusion in the Si substrate. The segregation of S at the NiSi/Si(100) interface leads to the change of SBH. Figure 6 shows the SBH values of NiSi on *n*-Si(100) as a function of the S concentration at the interface. The SBH drops very quickly from the original 0.65 eV to 0.34 eV at a S concentration of $1.38\times 10^{19}/\mathrm{cm}^3$, and then decreases approximately linearly with the S concentration at the interface.

The segregation of S at the NiSi/Si(100) interface leads to a large change of the SBH and allows SBH tuning in a wide range. A model of the S passivation of the Si surface has been proposed by Saiz-Pardo *et al.*[14] They showed that the effect of S-passivation is to modify the Fermi level position by moving it in the higher (lower binding) energy direction, leading to an Ohmic contact with the Fermi level pinned right at the semiconductor conduction band minimum. The Fermi level shift is basically due to the interaction between the metal and the local density of the states associated with the passivating layer.[13] After passivation of the Si surface by a Se monolayer, the SBH values of Ti, Cr, Al, and Mg on Se passivated Si reached the values of the Schottky–Mott theory. However, in our present work, the lowest SBH value of NiSi on *n*-Si(100) is much smaller than the Schottky–Mott theoretical value if one assumes a work function of NiSi of 4.68 eV.[15] During NiSi formation by solid-reaction of Ni with Si substrate, chemical bonds are formed at the NiSi/Si interface. These interface bonds influence the SBH value. We suggest that the tuning of NiSi SBH values by S segregation at interfaces is mainly due to two effects. First, the formation of chemical bonds between S and NiSi changes the work function of the NiSi, and second, the segregation of S at interfaces form a dipole layer at the NiSi/Si interface. Further investigations are needed to clarify the detailed mechanism. As compared to the deposition of a Se monolayer between the metal and Si to change the SBH of the metal,[8–10] this method has several advantages. Self-aligned silicidation combined with S ion implantation can be easily used to fabricate nanometer MOSFETs. Diodes with different SBHs on one wafer can be made by the use of different ion fluences. Investigations using Se ion implantation and other silicides, and applications of this method in devices are in process.

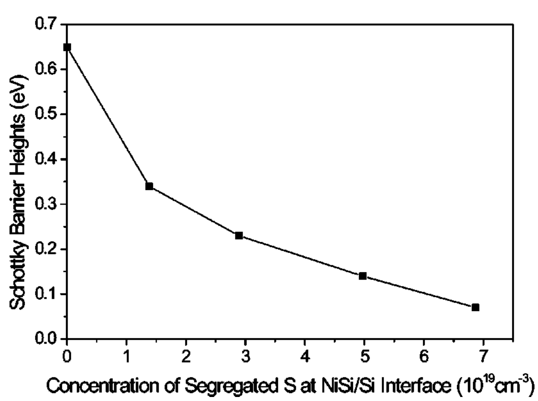

FIG. 6. SBH values of NiSi on *n*-Si(100) as a function of the concentration of the S atoms segregated at the NiSi/*n*-Si(100) interface.

In summary, a method to tune the Schottky barrier height of NiSi on Si(100) substrates by segregation of S was investigated. The SBH value of NiSi on *n*-Si(100) substrates decreases by increasing the dose of S implantation prior to Ni deposition. The SBH was reduced from 0.65 eV to 0.07 eV on S implanted *n*-Si(100), while the SBH on *p*-Si(100) increases by S implantation.

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