Silicide doping technology in formation of TiSi$_2$/n$^+$p shallow junction by salicide process

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The fabrication of a shallow n$^+$p junction by diffusing arsenic atoms from the As$^+$-implanted TiSi$_2$ into the underlying silicon has been developed. The amendment of the radiation damage and the activation of impurities can be fulfilled in one annealing process in conjunction with the dopant drive-in. The junction depth below the TiSi$_2$/Si interface is about 0.11 $\mu$m, and is insensitive to the values of implanted ion energy and the annealing condition as long as the dopants remain in the TiSi$_2$ film. The dopant concentration near the surface in the n$^+$ region can be added up to $2 \times 10^{19}$/cm$^3$ for an implanted dose of $5 \times 10^{15}$/cm$^3$.

I. INTRODUCTION

Recently, a silicide doping technique has been developed for the fabrication of shallow WSi$_2$/n$^+$p junctions by directly applying the chemical vapor deposition (CVD) of silicides. Unfortunately, it is not applicable to the self-aligned silicide (salicide) process. Until now, only a few works concerning the connection between the salicide process and silicide doping technology have been reported. The combination of these two processes can surmount many obstacles in salicide processing of metal-oxide-semiconductor (MOS) devices with shallow junction. First, since each angstrom of metal will consume 2–4 $\AA$ of the Si layer during salicide formation, the source and drain contacts and the polysilicon gate are made simultaneously. The shallow junction will be destroyed during the thick salicide formation of the gate. Second, when the silicide film is in contact with the As-doped silicon, significant amounts of arsenic will diffuse outward from silicon during high-temperature annealing, resulting in high contact resistance. To doped silicide, the dopants are first ion implanted into the silicide and then they drive-in the underlying silicon by annealing. Post-silicide formation implies a flexible profile margin in very large-scale integration (VLSI) devices. Since most of the heat treatment is carried out before the drive-in process, it can minimize spoiling of the dopant profile. Furthermore, because the diffusivity of As in most silicide is much higher than in silicon, it is possible to form the required junction depth with low ion-energy implantation.

Because TiSi$_2$ has the lowest resistivity among all the metal silicides, the salicide process by TiSi$_2$ has attracted much attention in the fabrication of high-performance MOS devices. Recently, many authors have reported that arsenic atoms only redistribute in the TiSi$_2$ layer and do not diffuse into the underlying polysilicon, which is contrary to the results declared by Van Ommen, Van Houtum, and Theunissen. In this work, we have fulfilled the salicide process for the TiSi$_2$ on (100) silicon substrate. The dopant redistribution, segregation, and electrical behavior as functions of implanted ion energies, and annealing temperatures and times are presented.

II. PROCESS DESCRIPTION

The fabrication procedures of TiSi$_2$/n$^+$p diodes are depicted in Fig. 1. The p-type silicon substrates of 1–10 $\Omega$ cm in (100) orientation are oxidized at 1100 $^\circ$C for 60 min to a thickness of 5500 $\AA$. The backside of the wafers are boron implanted to p$^+$ to ensure good electrical contact. The photolithographic method is implemented to open the windows on the oxide to define a diode area of $650 \times 650 \mu$m$^2$. A titanium film of 500 $\AA$ was electron-gun deposited at 2 $\AA$/s. The metallization is carried out by rapid thermal annealing (RTA) at 650 $^\circ$C for 30 s in Ar ambient gas. The C49-TiSi$_2$ phase is formed as examined by the transmission electron microscope (TEM) diffraction pattern. The unreacted Ti on SiO$_2$ is chemically removed by an etchant composed of...
H$_2$SO$_4$ and H$_2$O$_2$ (30%) in a 2:1 volume ratio at 80 °C. The selective wet etchants only etch Ti metal and do not attack TiSi$_2$ or SiO$_2$.

After chemical etching, the silicide is annealed by RTA at 1000 °C for 10 s to form the stable C54-TiSi$_2$, which has the lowest resistivity of all silicides. Arsenic ions with energies ranging from 80 to 160 keV were implanted into the TiSi$_2$ window at a dose of $5 \times 10^{15} \text{ cm}^{-2}$ followed by RTA or vacuum isothermal annealing (VIA) at temperatures between 800 and 1100 °C for durations of 5 s–30 min.

III. RADIATION DAMAGE IN TiSi$_2$

The radiation damages in TiSi$_2$ are inspected by the TEM technique, as shown in Fig. 2. After implantation at a dose of $5 \times 10^{15} \text{ cm}^{-2}$, many clusters are observed through the cross-sectional view of TEM. The damages are limited to no more than 700 Å from the surface for the samples with implanted ion energies below 100 keV. The Auger spectra of TiSi$_2$ films before and after ion implantation are depicted in Figs. 3(a)–3(c). For the unimplanted sample, the oxygen trace rapidly diminishes with depth, and reaches the background level, whereas the Si/Ti ratio almost keeps a constant value under a rather long depth. If the ion energy increases to 130 keV, the disturbed regions may extend to the underlying silicon. Significant amounts of oxygen atoms are incorporated into the heavily implanted film and the same Ti atoms are knocked into the underlying silicon. However, the chaotic state and the incorporated oxygen can easily be removed by annealing at 900 °C for 20 s. The knocked-in Ti atoms can be released by the fast diffusion of Ti in silicon during TiSi$_2$ regrowth. The Auger profile of Fig. 3(d) is similar to that in Fig. 3(a) except that the annealed films appear with an extremely uniform profile distribution of Ti and Si atoms. The zigzag Auger signals of the unannealed sample [Fig. 3(c)] are due to voids and displacements of the Ti and Si atoms from their regular positions by implantation and are not due to oxygen noise, since the signal integration time in taking Figs. 3(c) and 3(d) is the same. The SiO$_2$ layer intrinsically grown on the Ti/Si interface during Ti deposition will inhibit the formation of TiSi$_2$. Ion implantation will admit the Ti and Si atoms$^{12}$ and assist in forming TiSi$_2$, resulting in a more uniform profile regrowth.

The effect of ion implantation on the electrical resistivity of TiSi$_2$ films is also examined. Figure 4 shows the temperature dependence on the resistivity of TiSi$_2$ with various heat treatments. The smooth appearance of $p$-$T$ curves indicates that the resistivity follows Matthiessen’s rule as a normal metal which shows

$$
\rho(T) = \rho_s + \rho_l(T),
$$

(1)

where $\rho_s$ is the residual resistivity due to collision of carriers with mechanical imperfections and impurities in the lattice, and $\rho_l(T)$ is the resistivity caused by thermal phonons with the implication of phonon-mode structure. It can be seen that all the curves are almost parallel to each other which implies that the implantation only introduces lattice damages and interstitial impurities which results in a drastically increasing residual resistivity.

However, if we compare the slopes of these curves in detail, a slight reduction of the slope with the increase of $\rho_s$ can be observed. This is a famous phenomenon in the disorder metal system referred to as the Mooij correlation.$^{13}$ As the defect density becomes greater than $1/1^2$, where $l$ is the mean free path, the electrical resistivity cannot be properly described by the Boltzmann transport equation. The carriers are localized and the conductivity is written as

$$
\sigma(T) = \sigma_s(0) \left( 1 - \frac{3}{(K_l l_e)^2} \right) + \frac{e^2}{\pi^2 \hbar} \left( \frac{1}{L_e(T)} - \frac{(K_l l_e)^2}{3l_e(T)} \right),
$$

(2)

where $\sigma_s(0)$ is the Boltzmann conductivity, $l_e$ is the elastic mean free path, $L_e$ is the inelastic diffusion length as defined by $L_e = (3/2 l_e)^{1/2}$, with $l_e$ the inelastic mean free path. The first term in the above equation is the quantum corrected conductivity due to localization, and the second term represents the competition between the degradation of inelastic scattering due to quantum interference and thermal excitation. The conductivity increases as the temperature increases owing to the overwhelming of the phonon-induced inelastic scattering.

The electrical resistivity of the film increases with an additive amount of 60 $\mu \Omega$ cm after 100 keV of implanted As$^+$ at a dose of $5 \times 10^{15} \text{ cm}^{-2}$ is annealed out at 900 °C for 20 s. To reduce the extent of radiation damage and to avoid the knocking of atoms into the junction, the dopants can be tailored to reside in the silicide, which is then annealed at high temperatures to redistribute and diffuse into the silicon.

IV. DOPANT DRIVE-IN AND DEVICE PERFORMANCES

We use Biersack and Ziegler model$^{14}$ to calculate the projected range $R_p$, projected stragggle $\Delta R_p$, and lateral stragggle $\Delta R_L$ for arsenic implantation in TiSi$_2$. The calculated data as shown in Fig. 5 indicate that the dopants can survive in the silicide film of 1250 Å if the ion energy is below 150 keV, which is congruent with Rutherford backscattering spectra (RBS), as shown in Figs. 6(a) and 6(b). This can be confirmed by calculating the spreading thickness of As atoms in TiSi$_2$, which is given by
implanted As retain their original implanted positions and only a few segregate at the TiSi₂/Si interface for annealing below 700 °C. The diffusion coefficient $D$ of arsenic in TiSi₂ is very high and of the order of $10^{-13}$ cm²/s (Ref. 11) at 600 °C, which is about four to five orders of magnitude larger

\[ t_{\text{As}} = \frac{\Delta E_{\text{As}}}{(e)_{\text{TiSi₂}} N_{\text{TiSi₂}}} = 1.12 \times 10^{-5} \text{ cm}, \tag{3} \]

where $\Delta E_{\text{As}} = 82.9$ keV is the As channel width, $(e)_{\text{TiSi₂}} = 3.168 \times 10^{-13}$ eV cm² is the As-stopping cross-section factor in TiSi₂ matrix, and $N_{\text{TiSi₂}}$ is the molecular concentration of TiSi₂. The observation of the redistribution and segregation of arsenic in the TiSi₂/Si structure after annealing is also examined by RBS and shown in Fig. 6(c). Most of the

FIG. 3. Auger depth profile of silicide films for (a) without implantation, (b) with 80-keV As⁺ implanted at a dose of $5 \times 10^{15}$ cm⁻², (c) with 130-keV As⁺ implanted at a dose of $5 \times 10^{15}$ cm⁻², and (d) after annealing.

FIG. 4. Resistivity vs temperature of TiSi₂ for various implanted ion energies and annealing conditions.

FIG. 5. Theoretical calculations of range parameters for As in TiSi₂ as functions of incident ion energies.
than that in the silicon. Consequently, the diffusion of arsenic in silicon is limited by the available source at the TiSi₂/Si interface.

The arsenic diffusion profiles in the underlying silicon are performed by the spreading resistance (SPR) method. As shown in Fig. 7, the inadequately annealed samples will lead to a lack of surface concentration. The measured junction depth below the TiSi₂/Si interface is about 0.11 ± 0.015 μm.

FIG. 8. Current-voltage characteristics of a TiSi₂/p Schottky diode and a TiSi₂/n⁺ p diode fabricated by implanting 80-keV As⁺ at a dose of 5 × 10¹⁵ cm⁻² into TiSi₂ films followed by 900℃, 20-s RTA.
μm with the surface concentration up to $2 \times 10^{19}$ cm$^{-2}$ for a dose of $5 \times 10^{15}$ cm$^{-2}$. The quantitative estimation of the As spectra, as shown in Fig. 6(c), invokes a fact that part of the implanted doses are lost by evaporation after annealing at 800 °C for 30 min. RTA can be immunized from dopant loss due to evaporation, however, there is no significant difference in surface concentration between RTA and RTA due to evaporation, however, there is no significant difference in surface concentration between RTA and RTA. This is not surprising, because numerous arsenic atoms can diffuse into silicon for long-time annealing, whereas the loss of arsenic atoms by thermal evaporation at elevated temperatures will decrease the available diffusion source.

TiSi$_2$ Schottky diodes fabricated on p-type silicon have a typical turn-on voltage of about 250 mV, which is about 400 mV smaller than that of a n$^+$ p junction diode, implying a higher reverse current in the Schottky diode. It is easy to specify whether the TiSi$_2$/n$^+$ p structure has been formed by silicide doping technology or not. Typical results on the I-V characteristics of the sample by an arsenic implantation with a dose of $5 \times 10^{15}$ cm$^{-2}$ at 80 keV are found following annealing at 900 °C, 20 s. RTA are shown in Fig. 8. The sharp contrast with the undoped TiSi$_2$/p Schottky diode means that a TiSi$_2$/n$^+$ p structure can be easily well formed without tedious heat treatment. Table I summarizes the electrical measurements of the TiSi$_2$/n$^+$ p diode produced by different implanted energies and various annealing conditions. For high-energy implanted samples, the radiation damage and interstitial Ti atom introduced in the junction will lead to trap levels resulting in an excess of leakage current (see samples Nos. 7 and 11). Prolonging the annealing time can remarkably reduce the leakage current (see samples Nos. 8–10 and sample 12). For samples without adequate heat treatment, the junction depth is very shallow and the surface concentration is too low to fulfill the requirement of VLSI technology (see sample No.1).

### V. CONCLUSION

In this work, we find the diffusion coefficient of arsenic in TiSi$_2$ is much larger than that in silicon which can be exploited to obtain a very shallow n$^+$ p junction. The junction depth below the TiSi$_2$/Si interface is insensitive to the implanted ion energy, the annealing condition, and possibly the TiSi$_2$ thickness. These advantages provide a potential for process modeling in VLSI fabrication. In the silicide doping technology, the necessary n$^+$ layer is obtained from the segregation or redistribution of arsenic atoms during heat treatment. With RTA above 900 °C, the interface segregation is more pronounced and leads to a high surface concentration. However, the segregation of doped As$^+$ disappears while the dopants redistribute over the TiSi$_2$ film after annealing at 800 °C for 30 min. The problems involved, including the amendment of radiation damages in TiSi$_2$ and Si, and the removal of unnecessary impurities in TiSi$_2$ (such as oxygen) and Si (such as Ti), can be fulfilled in one dopant drive-in process. This work concludes that the TiSi$_2$/n$^+$ p structure fabricated by silicide doping technology can be satisfied by the requirements of VLSI devices.

### ACKNOWLEDGMENTS

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TABLE I. Junction depth ($x_j$), maximum carrier concentration ($n_{\text{max}}$), reverse current ($J_R$), and ideal factor of the TiSi$_2$ (125 Å)/n$^+$ p diode at an arsenic-implanted dose of $5 \times 10^{15}$ cm$^{-2}$ for various ion energies and annealing conditions.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Ion energy (keV)</th>
<th>Anneal conditions</th>
<th>$x_j$ (μm)</th>
<th>$n_{\text{max}}$ ($10^{19}$ cm$^{-2}$)</th>
<th>$J_R$ (V)</th>
<th>Ideal factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>800 °C, 20 s</td>
<td>0.090</td>
<td>0.03</td>
<td>1128</td>
<td>2.13</td>
</tr>
<tr>
<td>2</td>
<td>80</td>
<td>900 °C, 20 s</td>
<td>0.115</td>
<td>1.12</td>
<td>80</td>
<td>1.26</td>
</tr>
<tr>
<td>3</td>
<td>80</td>
<td>1000 °C, 20 s</td>
<td>0.115</td>
<td>1.20</td>
<td>46</td>
<td>1.18</td>
</tr>
<tr>
<td>4</td>
<td>80</td>
<td>800 °C, 30 min</td>
<td>0.12</td>
<td>1.88</td>
<td>72</td>
<td>1.05</td>
</tr>
<tr>
<td>5</td>
<td>80</td>
<td>900 °C, 30 min</td>
<td>0.125</td>
<td>2.00</td>
<td>44</td>
<td>1.20</td>
</tr>
<tr>
<td>6</td>
<td>80</td>
<td>1100 °C, 5 s</td>
<td>0.095</td>
<td>0.90</td>
<td>62</td>
<td>1.23</td>
</tr>
<tr>
<td>7</td>
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<td>900 °C, 20 s</td>
<td>0.12</td>
<td>1.20</td>
<td>138</td>
<td>1.24</td>
</tr>
<tr>
<td>8</td>
<td>130</td>
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<td>···</td>
<td>···</td>
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<td>1.22</td>
</tr>
<tr>
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<td>0.90</td>
<td>48</td>
<td>1.20</td>
</tr>
<tr>
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<td>···</td>
<td>40</td>
<td>1.16</td>
</tr>
<tr>
<td>11</td>
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<td>0.71</td>
<td>1701</td>
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</tr>
<tr>
<td>12</td>
<td>160</td>
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<td>···</td>
<td>67</td>
<td>1.10</td>
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