New Ti-SALICIDE Process Using Sb and Ge Preamorphization for Sub-0.2 μm CMOS Technology

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Abstract—A new process for thin titanium self-aligned silicide (Ti-SALICIDE) on narrow n⁺ poly-Si lines and n⁺ diffusion layers using preamorphization implantation (PAI) with heavy ions of antimony (Sb) and germanium (Ge) has been demonstrated for application to 0.2-μm CMOS devices and beyond. Preamorphization enhances the phase transformation from C<sub>49</sub>Ti<sub>51</sub>Si<sub>2</sub> to C<sub>54</sub>TiS<sub>2</sub> and lowers the transformation temperature by 80 °C so that it occurs before conglomeration in narrow lines. Preamorphization by Sb and Ge implantation yields better results than that by As. The sheet resistance of TiS<sub>2</sub> on heavily As doped poly-Si lines are 3.7 Ω/□ and 3.8 Ω/□ for the samples preamorphized by Ge and Sb implantations even with line width down to 0.2 μm. There is less leakage in the Ti-SALICIDE diode with preamorphization than without it. The probable reasons and mechanisms are discussed.

Index Terms—MOSFET’s, semiconductor device fabrication, semiconductor device ion implantation, silicon compounds.

I. INTRODUCTION

SELF-ALIGNED silicide (SALICIDE) technology with low series resistance in poly-Si and source/drain diffusion layer has become an essential technology for high-speed CMOS logic VLSI circuits. Ti, Co, Pt, and Ni are well-known refractory metals for SALICIDE processes. Ti-SALICIDE is the most common silicide technology due to its temperature stability and low resistivity.

The main difficulty of using conventional Ti-SALICIDE for future deep submicron dimensions is Si consumption during silicide formation on extremely shallow junctions. If the silicide–silicon interface approaches the junction depth, there is an increase in junction leakage or even shorts due to inhomogeneous silicidation or the formation of spikes. Therefore, as the device size shrinks down to deep submicron, shallow junction technology requires thinner Ti film and extremely homogeneous silicidation. The conventional Ti-SALICIDE process has encountered the following problems related to thin film thickness and narrow lines.

1) Rate of phase transition from C<sub>49</sub>Ti<sub>51</sub>Si<sub>2</sub> (high resistivity) to C<sub>54</sub>TiS<sub>2</sub> (low resistivity) slows remarkably [1], [2].
2) Agglomeration temperature of TiS<sub>2</sub> decreases to a point that is lower than the phase transition temperature [3], [4].

3) TiS<sub>2</sub> formation is suppressed on heavily As doped n⁺ poly-Si and n⁺ diffusion region [5]. These problems make the resistivity of narrow TiS<sub>2</sub> lines increase dramatically in the sub quarter-micron device and degrade the stability of TiS<sub>2</sub>

To overcome these difficulties, several proposals for process enhancement have been published, such as LD-SICRON process [6] (Silicidation after Ion Implantation through Contamination Restrained-Oxygen-free LPCVD Nitride layer in a Light Doped diffusion layer); PASET process [7] (Pre-Amorphization before Ti film deposition and SEquential Two step sintering); SEDAM process [8] (SElective silicon Deposition and subsequent pre-Amorphization); high-temperature sputtering of Ti [9]; and Si ion beam mixing [10]. Among these proposals, PAI with As has been found to be particularly attractive. To avoid As counter-doping, which increases R<sub>sd</sub> of PMOS and its suppression of TiS<sub>2</sub> formation [5], we propose PAI with Sb or Ge. Because Sb differs out of the Si substrate totally during Ti-SALICIDE process [11], and Ge is a neutral species. Furthermore, Sb is much heavier than As, therefore it produces a sharper amorphous/crystal interface so that the defects can be removed by annealing with a lower thermal budget. Also its big size makes the amorphization more efficient. Ge may enhance dopant activation and reduce contact resistance with metal. In this paper, a new Ti-SALICIDE process is proposed for the application to a 0.2-μm CMOS device and beyond using preamorphization implantation (PAI) with Sb and Ge instead of As [7] before Ti film sputtering. Under the optimum condition, low (<4 Ω/□) and uniform sheet resistances of TiS<sub>2</sub> are obtained on n⁺ diffusion layer and n⁺ poly-Si lines with 0.2 μm line width with large process windows. The junction leakage current is also improved. These advantages are attributed to the ability of the new process to facilitate uniform reaction between Ti and Si and to reduce the temperature of the phase transformation of C<sub>49</sub>Ti<sub>51</sub>Si<sub>2</sub> to C<sub>54</sub>TiS<sub>2</sub>. The smoother and more uniform TiS<sub>2</sub> film is beneficial to reducing the leakage current.

II. EXPERIMENT

A. Process Sequence

P-type (100) silicon wafers with 30–50 Ω-cm resistivity were used as the substrates. The main process steps are listed as follows.

- Gate oxidation.
- Poly-Si deposition (250 nm).
- Poly-Si doping with phosphorus (70 keV, 5 × 10<sup>15</sup> cm<sup>-2</sup>) and annealing.
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Fig. 1. Sheet resistance of Ti-SALICIDE over unpatterned As⁺ doped diffusion layer with and without preamorphization ion implantation (PAI) as a function of RTA temperature. Ti is 30 nm, PAI energy is 60 keV, and dose is $3 \times 10^{14}$ cm⁻². RTA time is 10 s.

- Photolithography with $I$-line stepper.
- Fluoridation pretreatment.
- RIE etching of poly-Si.
- Oxide spacer formation.
- As implantation for S/D and poly-Si doping (50 keV, $4 \times 10^{15}$ cm⁻²).
- RTA for As activation (990 °C).
- Preamorphization implantation (PAI) for poly-Si and S/D diffusion regions with As, Sb, and Ge at dosage of $3 \times 10^{14}$ cm⁻² and various energies of 40, 60, and 80 keV.
- HF dip and Ti sputtering (30 nm).
- First RTA 670 °C, 20 s, N₂.
- Selective etching.
- Second RTA up to 880 °C, up to 20 s, N₂.

B. Analysis of Samples

The amorphous layer depths formed by PAI were determined by Rutherford back scattering spectroscopy (RBS). The microstructure and thickness of TiSi₂ film formed were analyzed by plane-view transmission electron microscopy (TEM) and cross-section TEM, respectively. The phase transformation from C_{51}TiSi₂ to C_{54}TiSi₂ was investigated with both X-ray diffraction (XRD) and the measurement of sheet resistance, which sharply drops after annealing at the transformation temperature. The surface microroughness of the Ti-SALICIDE films was studied with the atomic force microscope AFM. The sheet resistance of TiSi₂ on an unpatterned wafer were measured with a standard four-point probe, and that on a patterned n⁺ poly-Si lines were measured with the semiconductor parameter analyzer HP4145A. The surface topographies of TiSi₂ fine lines were observed by SEM. The leakage currents of salicided junctions were measured with the semiconductor parameter analyzer HP4145A.

![Fig. 1](https://example.com/f1.png)

![Fig. 2](https://example.com/f2.png)

III. RESULTS AND DISCUSSIONS

A. Sheet Resistance of TiSi₂ over Unpatterned n⁺ Diffusion Layer

Fig. 1 shows the sheet resistance of Ti-SALICIDE over an n⁺ diffusion layer without and with PAI by Sb, Ge, and As at an energy of 60 keV and a dose of $3 \times 10^{14}$ cm⁻² as a function of RTA temperature. Here, Ti film sputtered is 30 nm. It shows that PAI facilitates the phase transformation of C_{51}TiSi₂ to C_{54}TiSi₂. At 800 °C (10 s) RTA, the sheet resistance of the samples with PAI by Sb, Ge, and As are down to their lower stable values: 4.8, 4.4, and 5.4 Ω/□, respectively; meanwhile, the Ti-SALICIDE sample without PAI exhibits much higher sheet resistance and reaches its lower sheet resistance value only after 880 °C RTA. These data show that the sample without PAI has 80 °C higher phase transformation temperature (880 °C versus 800 °C). PAI with Sb, Ge, and As can all enhance the phase transformation from C_{51}TiSi₂ to C_{54}TiSi₂. PAI with Sb and Ge can achieve lower sheet resistance than with As.

Fig. 2 shows the effect of PAI energy on the sheet resistance of Ti-SALICIDE over n⁺ diffusion layer at various temperatures of RTA. In the case of RTA at 800 °C (10 s), there is a threshold energy of 60 keV for phase transformation. When the energy is equal to or larger than the threshold energy, the sheet resistance is down to their lower stable values. In the case of RTA at 850 °C (10 s), the threshold energy is 40 keV. Apparently, the phase transition temperature lowers with an increasing degree of amorphization, which is attained at an increasing implant energy.

The X-ray diffraction technique is used to examine the composition and structure of the Ti-SALICIDE film. Fig. 3 shows the X-ray diffraction patterns of the samples without and with Ge PAI. Fig. 3(a) is for the sample without PAI and shows the four characteristic peaks corresponding to Ti₅Si₃.
and Ti$_5$Si$_4$, i.e., C$_{49}$Ti$_2$Si$_2$ phase. This sample has a high sheet resistance of 16.3 $\Omega/\square$. Fig. 3(b) is for the sample with PAI by Ge at an energy of 60 keV and a dose of $3 \times 10^{14}$ cm$^{-2}$. It shows the three characteristic peaks corresponding to TiSi$_2$, i.e., C$_{54}$TiSi$_2$ phase. The sheet resistance is 4.4 $\Omega/\square$. Fig. 3(c) is for the sample with Ge PAI at an energy of 40 keV and a dose of $3 \times 10^{14}$ cm$^{-2}$. It can be seen that six characteristic peaks corresponding to both C$_{49}$ (Ti$_5$Si$_3$, Ti$_5$Si$_4$) and C$_{54}$TiSi$_2$ are present. The corresponding sheet resistance is 10.7 $\Omega/\square$.

The results of X-ray diffraction prove that at 800 °C RTA for 10 s, the phase transformation from C$_{49}$ to C$_{54}$ is complete for the sample with PAI by Ge at the energy of 60 keV, incomplete for that with PAI by Ge at the energy of 40 keV, and totally absent in the sample without PAI.

After PAI, depending on the mass and energy of the implanted atoms, the first hundreds of Angstroms of silicon is amorphized. It is important to understand the dependence of the amorphous layer formation on the implantation parameters.
since the thickness of the TiSi₂ formed is affected by the amorphous layer depth. Rutherford backscattering spectroscopy (RBS) was employed to determine the thicknesses of the amorphous layers formed by Sb, Ge, and As ion implantation. In Fig. 4, the flat peaks indicate complete amorphization in all cases. It can be seen that the thickness of the amorphous layer increases with the increase of energy at fixed dose of $3 \times 10^{14}$ cm$^{-2}$ and it is about $R_p + 2\Delta R_p$ ($R_p$ is the project range, and $\Delta R_p$ is the standard deviation) as shown in Table I.

Fig. 5 gives the TEM cross-section of TiSi₂ over n$^+$ diffusion layer. The thickness of the sputtered Ti film is 30 nm and the samples are processed with two step RTA process (670 °C/20 s and 880 °C/20 s). Here the TEM cross sections are doublets formed from two regions of the same sample. Fig. 5(a) is a sample without PAI, and the thickness of TiSi₂ is about 510 Å; Fig. 5(b)–(d) show samples with Sb PAI at the energy of 40, 60, and 80 keV, respectively. The SALICIDE thickness from these and other cross-section TEM’s are also summarized in Table I.

From Table I, it can be seen that with the increase of the depth of the amorphous layer in certain range the thickness of TiSi₂ formed also increases. This indicates that the thickness of TiSi₂ formed is affected by the depth of the amorphous layer. It can be also seen that for Sb implanted samples with the energy $\leq$ 80 keV and Ge implanted samples with the energy $\leq$ 60 keV, the thickness of TiSi₂ formed are thinner than that without PAI. It suggests that for these samples processed with

### Table I

<table>
<thead>
<tr>
<th>sample</th>
<th>$R_p$(Å)</th>
<th>$\Delta R_p$(Å)</th>
<th>depth of amorphous layer(Å)</th>
<th>thickness of TiSi₂ formed(Å)</th>
<th>$R$ (Ω·cm)</th>
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<tr>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>510</td>
<td>6.29</td>
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<tr>
<td>Sb$^+$ 40keV PAI</td>
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<td>71</td>
<td>380</td>
<td>360</td>
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<tr>
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<td>310</td>
<td>96</td>
<td>500</td>
<td>395</td>
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<tr>
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<td>385</td>
<td>118</td>
<td>630</td>
<td>450</td>
<td>4.20</td>
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<tr>
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<td>102</td>
<td>500</td>
<td>395</td>
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<tr>
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<td>140</td>
<td>650</td>
<td>450</td>
<td>4.20</td>
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<tr>
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<td>177</td>
<td>820</td>
<td>520</td>
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<tr>
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<td>99</td>
<td>480</td>
<td>/</td>
<td>4.90</td>
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<tr>
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<td>374</td>
<td>136</td>
<td>650</td>
<td>510</td>
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<tr>
<td>As$^+$ 80keV PAI</td>
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<td>172</td>
<td>760</td>
<td>/</td>
<td>4.90</td>
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</tbody>
</table>

Spotted Ti film thickness is 30nm, dose of PAI is $3\times10^9$ cm$^{-2}$. Annealing condition is 670°C for 20 sec (the first RTA) and 880°C for 20 sec (the second RTA).
Fig. 6. Sheet resistance of Ti-SALICIDE on heavily As doped Poly-Si lines as a function of the line width without and with preamorphization after second RTA at 880 °C for 20 s. PAI dose is $3 \times 10^{14}$ cm$^{-2}$.

PAI the sputtered Ti film is not completely converted into silicide. In other words, for these samples, the reaction between Si and Ti mainly occurs in the amorphized silicon layer. It seems that the transition region at the amorphous-Si/crystal-Si interface retards the Ti–Si reaction. From Table I, it can be noted that PAI with Sb, Ge, or As can all enhance the phase transformation from $C_{49}$ to $C_{54}$, which makes the resistivity much lower than that of conventional SALICIDE (32.1 $\mu \Omega$-cm). The reason is that PAI before Ti sputtering makes the grains of TiSi$_2$ film formed during the first RTA finer, as shown in the next section and in Fig. 8. Finer grains increase the density of $C_{54}$ nucleation sites that are located at triple grain boundaries [12]. This promotes the nucleation of $C_{54}$ and phase transition. From Table I, it can also be seen clearly that the sample with PAI by Sb at an energy of 60 keV and a dose of $3 \times 10^{14}$ cm$^{-2}$ has only the lowest resistivity of 17.4 $\mu \Omega$-cm but also a small film thickness of TiSi$_2$ of 395 Å. This is beneficial to ultra shallow junction as shown in Section III. At the same PAI energy and dose, the resistivities are 18.9 $\mu \Omega$-cm and 22.6 $\mu \Omega$-cm for Ge and As PAI, respectively. These show that the samples with PAI by Sb and Ge have better results than that by As, and the best is that by Sb. The probable reasons are discussed below.

$C_{54}$TiSi$_2$ has a different structure from $C_{49}$Ti$_2$Si$_x$. $C_{49}$Ti$_2$Si$_x$ is base-centered orthorhombic and $C_{54}$ is face-centered orthorhombic. The transformation from $C_{49}$Ti$_2$Si$_x$ to $C_{54}$TiSi$_2$ can be considered as a recrystallization process in which nucleation and regrowth of a new phase ($C_{54}$TiSi$_2$) occur. This originates from a reconstruction of the original phase($C_{49}$Ti$_2$Si$_x$). Earlier study shows that Sb starts to diffuse through the Ti$_2$Si$_x$/Ti layer at 600 °C, and at 900 °C, practically no Sb is left in silicon [11]. Sb incorporated in the $C_{49}$Ti$_2$Si$_x$ film could make the reconstruction easier due to its big size, which distorts the $C_{49}$Ti$_2$Si$_x$ lattice so that the energy barrier for the phase transformation from $C_{49}$Ti$_2$Si$_x$ to $C_{54}$TiSi$_2$ is lowered. Because As in Si suppresses TiSi$_2$ formation inherently [5], the result of PAI by As is not as good as Sb and Ge.

Impurities ($O$, $C$, and $N$) can also influence the phase transformation temperature; however, the Ti films and the $n^+$ diffusion layers used for all these experiments were processed in the same run.

B. Sheet Resistance of TiSi$_2$ on Patterned $n^+$ Poly-Si Lines

Fig. 6 shows the sheet resistance of TiSi$_2$ on As doped $n^+$ poly-Si lines as a function of line width after the second RTA (880 °C for 20 s). The thickness of the sputtered Ti film is 30 nm. The length of the poly-Si line is 1000 μm. It can be seen that the sheet resistance of the sample without PAI increases dramatically as line width decreases down to 0.2 μm due to the difficulty of phase transformation and the occurrence of agglomeration before phase transition. This sheet resistance is much different from that of unpatterned $n^+$ diffusion layer shown in Fig. 1 owing to the narrow line width here. On the other hand, the sheet resistances of the samples with PAI by Ge, Sb, and As at an energy of 60 keV and a dose of $3 \times 10^{14}$ cm$^{-2}$ are 3.7, 3.8, and 4.0 $\Omega$/$\square$, respectively, are insensitive to the line width even for line width down to 0.2 μm. This is
because low-resistivity $C_{54}\text{TiSi}_2$ is formed on the $n^+$ poly-Si lines with PAI. Experiments also show that the increment of sheet resistance is about 14% with PAI by Ge at an energy of 40 keV (fixed dose), while it is about 10% with PAI by Sb at the same energy and dose. Fig. 7(a) shows the SEM micrograph of a sample without PAI after the second RTA (880 °C for 20 s). The agglomeration phenomena are observed for TiSi$_2$ on 0.2 μm $n^+$ poly-Si line. Fig. 7(b) is for a sample with Sb PAI at an energy of 60 keV and a dose of $3 \times 10^{14}$ cm$^{-2}$ after the same second RTA. TiSi$_2$ on 0.2 μm $n^+$ poly-Si line is excellent [other samples with PAI over the energy range of 40 to 80 keV have the same results as that shown in Fig. 7(b)].

The microstructure of $C_{49}\text{TiSi}_2$ film is analyzed by plane-view TEM to clarify why PAI facilitates phase transition from $C_{49}$ to $C_{54}$. Fig. 8 shows the plane-view TEM micrographs of the Ti$_2$Si$_x$ film over $n^+$ poly-Si without and with PAI. These samples were subjected to the first RTA (670 °C, 20 s, N$_2$) and then the selective etching step. Fig. 8(a) is for a sample without PAI, and the grain size of Ti$_2$Si$_x$ film is in the range of 170–220 nm. Fig. 8(b) is for that with PAI at an energy of 40 keV, and the grain size is in the range of 60–100 nm. Fig. 8(c) is for that with PAI at an energy of 60 keV, and the grain size is in the range of 40–70 nm. It is evident that PAI reduces $C_{49}$ grain size remarkably, leading to low sheet resistance even for line width down to 0.2 μm. The finer grained structure has a larger grain boundary area per unit volume and increases the density of nucleation sites that are located at triple grain boundaries [12]. This enhances the nucleation of $C_{54}$ and promotes the transformation of $C_{49}$ to $C_{54}$. For the case of the sample without PAI, the grain size in the range of 170–220 nm is comparable to the line width of 0.2 μm, and the grains span nearly the whole line width and few triple grain boundaries would be present. The slow rate of phase transformation allows agglomeration to occur for the 0.2 μm lines as shown in Fig. 7(a).

Fig. 9 shows the AFM images of the surface microroughness of Ti-SALICIDE on $n^+$ poly-Si after the first RTA and selective etching for the samples without and with PAI. Fig. 9(a) is for the sample without PAI. AFM indicates a RMS roughness of 6.2 nm. Fig. 9(b) is for that with PAI by Ge at an energy of 60 keV and the RMS roughness is 4.1 nm. This shows that PAI can enhance the uniformity of TiSi$_2$ growth. This is beneficial to the reduction of leakage current of very shallow junction.

C. Junction Leakage

The leakage measurements show that PAI with Sb, Ge, and As at an energy $\leq$80 keV and a dose of $3 \times 10^{14}$ cm$^{-2}$ does not increase the diode leakage current.

Fig. 10 shows the leakage current of Ti-salicided diodes after annealing in forming gas (H$_2$:N$_2$ = 1:10) at 400 °C for 30 min. It shows that the annealing greatly improves the leakage current of the diodes, especially for the PAI samples, probably because of residual damage removal, stress relief, and elimination of interface states.

Leakage measurements also show that diodes without PAI have increased leakage current when $V >$ 4 V, while diodes with PAI by As, Ge, and Sb at the energy of 40 keV have increased leakage current only at $V >$ 5, 7, and 11.5 V, respectively. Diodes with PAI by As, Ge, and Sb at the energies of 60 and 80 keV all have low leakage current at 10 V. These data indicate that the leakage current of the diodes can be reduced by suitable PAI process. The reason is that the PAI process enhances the uniformity of TiSi$_2$ growth by increasing the density of nucleation sites and makes the silicide film smoother and more uniform and reduces the incidence of spikes that cause local high field regions.

IV. Conclusion

A new process for thinner Ti-SALICIDE on narrow and heavily As doped $n^+$ poly-Si lines and $n^+$ diffusion layers using preamorphization implantation (PAI) with heavy ions of antimony (Sb) and germanium (Ge) before Ti film sputtering deposition has been developed for the application to the
Fig. 9. AFM images of Ti-SALICIDE on n⁺ poly-Si without and with preamorphization after the first RTA and selective etching: (a) without PAI and (b) with Ge PAI at energy of 60 keV.

Fig. 10. Leakage current of Ti-SALICIDE diodes after annealing in forming gas (H₂ : N₂ = 1 : 10) at 400 °C for 30 min versus PAI energy with As, Sb, and Ge, respectively, measured at V = 5.0 V.

0.2-μm CMOS device and beyond. It has been found that the phase transformation temperature decreases by 80 °C in preamorphized samples and thus makes possible the phase transformation from C₁₂₅TiₓSiₓ to C₅₄TiS₁₂ before agglomeration in narrow lines. The experiment has also shown that PAI by Sb and Ge produces better results than that by As, and the best is that by Sb. This is due to its bigger size and its diffusion out from silicon substrate into Ti₋₅Siₓ during the SALICIDE process, which distorts the Ti₋₅Siₓ lattice and lowers the energy barrier for phase transformation. As in Si suppresses TiS₁₂ formation inherently [5]. The sheet resistance of TiS₁₂ on heavily As doped n⁺ poly-Si lines are 3.7, 3.8, and 4.0 Ω/□ for the samples with PAI by Ge, Sb, and As respectively, even with line width down to 0.2 μm. Without PAI the agglomeration of TiS₁₂ on n⁺ poly-Si lines occurs
before phase transition as line width approaches 0.2 μm. There is less diode leakage in PAI salicided diodes because the TiSi₂ films are more uniform and smoother than that without PAI. As indicated by plane-view TEM, the grain size of the C₄₉ film of the sample processed at the optimum condition is in the range of 40–70 nm, much less than the line width of 0.2 μm, while that of the sample without PAI is about 170–220 nm. The finer grain size structure of the C₄₉ film enhances the phase transition from C₄₀TiₓSiₓ₂ to C₄₃TiₓSi₂ owing to a higher density of C₄₃ nucleation sites. We conclude that Sb and Ge are better choices as PAI species than As, not only for their lower resistivity, thinner TiSi₂ formed, and lower leakage current, but also for the fact that the source/drain conductivity is not changed, because Ge is a neutral species and Sb diffuses out of the Si substrate totally during the SALICIDE process. Furthermore, Ge may enhance dopant activation and reduce the contact resistance. It is speculated that this new technology of reducing C₄₀ grain size to 40–70 nm can be applied to the CMOS device with gate length down to 0.1 μm based on the nucleation density model [13] which indicates that low sheet resistance can be obtained when C₄₀ grain size is smaller than the line width.

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