Metallization of W/Co–Ti/Si and simultaneous formation of diffusion barrier and shallow CoSi2 contact in normal flowing nitrogen furnace

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Among the metal silicides, cobalt disilicide (CoSi₂) has the most merits, and it has been the subject of intensive study. The merits of CoSi₂ include low resistivity (15–20 µΩ cm), self-alignment capability, high eutectic temperature (1195°C), low formation temperature, good chemical stability, no formation of cobalt-dopant (arsenic and boron) compound, and capability of epitaxial silicide growth on silicon.

Furthermore, cobalt does not react with silicon oxide below 800°C (Ref. 8) and is inert to nitrogen, in which silicide is formed. However, CoSi₂ still has its drawbacks: cobalt oxide is liable to form when Co on silicon is annealed in a conventional flowing-nitrogen furnace. CoSi₂ reacts with aluminum at low temperatures (~400°C), and the formation of CoSi₂ consumes a large volume of Si substrate (3.64 Å of Si/Å of Co). The two main problems pertinent to some silicides that they consume large amounts of Si substrate and react with Al at low temperatures, can supposedly be solved simultaneously by using a two-metal alloy scheme. The two-metal alloy is usually composed of a noble (or near noble) metal and a refractory metal. Owing to the layered phase separation and the different silicidation temperatures of the two metals, the reaction between silicon and the alloy leads to the formation of a noble-metal silicide on the Si substrate and accumulation of the refractory metal at the top. The amount of silicon consumed can be controlled by varying the composition of the alloy and limiting the reaction temperature so that only a certain amount of noble-metal silicide is formed. On the other hand, the refractory metal can act as a diffusion barrier between the silicide and Al that connects the device outwards. In this scheme, however, all annealings are performed in a vacuum or in a purified He system, neither of which is practical.

In this work, these two problems are solved or mitigated simultaneously using metalization of the W/Co-Ti/Si system. The heat treatments are performed in a normal flowing-nitrogen furnace (N₂). According to the phase diagram of the Ti–W binary alloy, Ti can be dissolved in W at high temperatures. Thus, during annealing at high temperatures, the Ti in the Co-Ti alloy can be segregated into the overlying W film to form W–Ti alloy. The W–Ti alloy is fairly stable with regard to resistance to oxidation at high temperatures. Thus, the situ formed W–Ti is a better passivating film for the underlying Co–Ti to be well silicidized in the Ni₂ ambient. Furthermore, W–Ti is a conventional diffusion barrier between aluminum and silicon (or silicides). A shallow CoSi₂ silicided contact also can be obtained, if all the Ti in the Co–Ti alloy can be segregated into W film. However, excess Ti will cause an intermediate Ti-silicide and/or Ti-oxide to form, if the amount of Ti in the W/Co–Si system exceeds that required to saturate the W film.

In this work, phase transformation of the W(400 Å)/Co₆₃Ti₃₇(360 Å)/Si and Co(400 Å)/Co₆₃Ti₃₇(360 Å)/Si systems, which have different thicknesses of the Co–Ti alloy, is studied by annealing at temperatures ranging from 500 to 900°C, and the optimum conditions for the formation of the W–Ti diffusion barrier and shallow CoSi₂ contact are defined. Selective etching is performed so that the surface morphology and lateral growth of the silicide can be observed by scanning electron micrograph (SEM). And the results supplement those analyses by x-ray diffraction (XRD) and Auger electron spectroscopy (AES) depth profiling. Some samples are then annealed at 950°C
to study further phase transformation of Co- and Ti-silicide. Since CoSi2 can be grown epitaxially on (100) Si by resorting to an intervening Ti layer 17-20 or a Co-Ti alloy, 20 epitaxy of CoSi2 can be anticipated in this W/Co-Ti/Si metallization system. The p' n diodes employing the present scheme to form CoSi2 contact and an in situ W-Ti diffusion barrier are tested by measuring the I-V characteristics after post-Al annealing treatment.

II. EXPERIMENT

The W/Co-Ti bilayer metallization was carried out in a dual electron-beam evaporation system on p-type Si(100) blank and patterned wafers with resistivity of 4-11 Ω cm. Prior to the metal depositions, the wafers were dipped in 20:1 HF for 10 s, rinsed in de-ionized water for 1 min, and then kept in methanol. Co-Ti alloy of 840 and 360 Å in thickness was deposited using two separate e-beam guns to evaporate the Co and Ti simultaneously, at a base pressure of 3.0 x 10⁻⁶ Torr. This was followed by deposition of a 400 Å W film without breaking the vacuum. Rutherford backscattering spectrometry (RBS) was used to determine the composition of the as-deposited Co-Ti alloy. The total thickness of the metal as deposited was measured by Sloan Dektak profilometer after a step-etching with 5:1 HF. The wafers were then annealed in a conventional flowing-nitrogen furnace. After being etched with a solution of NH4OH + H2O2 + 3H2O at ~80 °C, some samples were further annealed at a higher temperature of 950 °C to further study the phase transformation of Co- and Ti-silicides.

XRD spectrum, AES, SEM, transmission electron microscopy (TEM), and sheet resistance measurement were used to characterize the silicide phases and the surface morphology.

III. RESULTS

A. Phase transformation

1. W(400 Å)/Co63Ti37(840 Å)/Si

The composition of the as-deposited Co-Ti alloy was determined by RBS. For annealing below 450 °C, no significant phase transformation is observed. When the annealing temperature is raised to 500-600 °C, phase transformation can be observed; the AES depth profiles for the samples annealed at 500 °C for 10 h [Fig. 1(a)] indicate that all the Co in the Co-Ti alloy has been segregated and transformed into Co-silicide in contact with the Si substrate. At the same time, a portion of the Ti is segregated into the overlying W layer and the remaining portion remains as a separate Ti layer between the Co-silicide and W-Ti layer. Instead of being silicidized, the intervening Ti layer is oxidized. The Ti in the W layer is uniformly distributed at 500 °C; at 550 °C, some of the Ti is preferably segregated on the surface and oxidized. The Co-silicides were identified by the XRD spectrum as CoSi and CoSi2 phases.

The XRD spectrum reveals that CoSi survives even after annealing at 650 °C for 30 min [Fig. 2(a)]. The peaks of W are also evident; this indicates that Ti is dissolved in the W layer without forming a compound. At 700 °C, the AES depth profiles in Fig. 3(a) show that in addition to the Co-silicide in contact with the Si substrate, Ti-silicide begins to form and mixes with the outer part of Co-silicide, while the thickness of the intervening Ti-oxide is reduced. Titanium in the W layer is also preferentially accumulated at the interface.


FIG. 1. AES depth profiles for W(400 Å)/Co63Ti37(840 Å)/Si annealed at (a) 500 °C for 600 min and (b) 550 °C for 120 min.

FIG. 2. XRD spectra of W(400 Å)/Co63Ti37(840 Å)/Si annealed for 30 min at (a) 650 °C and (b) 900 °C.
on the surface and oxidized, as in Fig. 1(b), for samples annealed at 550 °C. The peaks of CoSi 2 in the XRD spectrum disappear at this temperature. Although at 650 °C the AES depth profile is similar to that at 700 °C, with an intermediate zone made up mostly of Co, Ti, and Si, as shown in Fig. 3(a), the zone is in fact made up of Co-silicide embedded in Ti metal and can be easily etched away, as demonstrated in Sec. III B. On the other hand, no evident peaks belonging to Ti or Ti-silicide can be identified on the XRD spectrum. At 750 °C, the phase transformation remains similar to that at 700 °C, except that less Ti-oxide remains between the mixed Co- and Ti-silicide layers and the W-Ti layer. At 800 °C, no intervening Ti-oxide layer remains; it has all been replaced by Ti-silicide, as illustrated in Fig. 3(b). Nearly all of the overlying W-Ti alloy is oxidized. At 900 °C, W is entirely transformed into WSi 2 , which is separately located on the Ti-silicide and CoSi 2 layers, as demonstrated by the AES depth profile and XRD pattern shown in Figs. 3(c) and 2(b), respectively. There is no evidence showing mixing of Ti in the W-silicide layer. The Ti-silicide is identified to be TiSi 2 and Ti 3 Si 4 . The contact CoSi 2 and the Ti-silicide layers still cannot separate clearly at this temperature; there is a layer evidently consisting of mixed Co- and Ti-silicide interventing between the CoSi 2 and Ti-silicide. Overall phase transformation of the W(400 Å)/Co 63 Ti 37 (840 Å)/Si at various temperatures is summarized in Table I. At temperatures between 650 and 950 °C, the intensity of the (400) reflection of the CoSi 2 phase increases with increasing annealing temperature, as can be seen by comparing Fig. 2(a) with Fig. 2(b). This indicates that CoSi 2 has a strong preferred orientation toward (400) at high temperatures. In fact, epitaxy of CoSi 2 occurs in this system. The TEM image and diffraction pictures show that CoSi 2 has become epitaxial on the (100)Si substrate in some areas. Although the surface is covered by W- and Ti-silicides, interface dislocations between CoSi 2 and Si substrate are still visible in the image picture of Fig. 4(a). The diffraction spots belonging to CoSi 2 are indicated in Fig. 4(b).

Table I. Summary of phase transformation of the W(400 Å)/Co 63 Ti 37 (840 Å)/Si system at 500–900 °C in normal flowing nitrogen ambient.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phase transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>W-Ti/Ti-oxide/Co-silicide/Si</td>
</tr>
<tr>
<td>550–600</td>
<td>Ti-oxide/W-Ti/Ti-oxide/Co-silicide/Si</td>
</tr>
<tr>
<td>560</td>
<td>Ti-oxide/W-Ti/Ti-oxide/Co-silicide/Ti-co-silicide/Si</td>
</tr>
<tr>
<td>700–750</td>
<td>Ti-oxide/W- and Ti-oxide/m.s./CoSi 2/Si</td>
</tr>
<tr>
<td>800</td>
<td>Ti-oxide/W- and Ti-oxide/m.s./CoSi 2/Si</td>
</tr>
<tr>
<td>900</td>
<td>WSi 2/TiSi 2/m.s./CoSi 2/Si</td>
</tr>
</tbody>
</table>

The AES depth profiles for W(400 Å)/Co 63 Ti 37 (840 Å)/Si annealed for 30 min at (a) 700 °C, (b) 800 °C, and (c) 900 °C are shown in Fig. 3. The AES depth profile in Fig. 3(a) shows that at 700 °C, a large portion of the W-Ti layer is oxidized only on the shallow surface at this temperature. At 830 °C, the Ti in the Ti-accumulation region is partially silicidized and a large portion of the W-Ti layer is oxidized from the surface [Fig. 5(b)]. The Ti-silicide is confirmed to be TiSi 2 by the XRD spectrum shown in Fig. 5(c). At 900 °C, all the W and Ti are transformed into silicides similar to the thicker W(400 Å)/Co 63 Ti 37 (840 Å)/Si system at 500–900 °C is summarized in Table II. In this system, not only the (400) and the strongest (220) peaks of the CoSi 2 phase, but also those of (111) together with others, are detected when the phase is formed. That the grain orientation is different from that of the thicker alloy.

system of W(400 Å)/Co₆₃Ti₃₇(840 Å)/Si may be attributed to the fact that ~14 Å of cobalt was inadvertently deposited before codeposition of the Co–Ti alloy. The Co-silicide has a low tendency of epitaxial growth in this system because of the thin intervening Co film.

Sheet resistance after 30 min isochronal annealing is depicted in Fig. 6. It can be seen that the resistance decreases all the way starting from 500°C and reaches a stable low value at ~620°C. This implies that the CoSi phase disappears at 620°C, which is consistent with the XRD results, which indicate that the signal of the CoSi phase disappears from the XRD spectrum at 620°C.

**B. Selective etching**

The purpose of performing selective etching using NH₄OH + H₂O₂ + 3H₂O at 80°C is to investigate the silicide lateral growth by SEM and to supplement the infor-

TABLE II. Summary of phase transformation of the W(400 Å)/Co₆₃Ti₃₇(360 Å)/Si system at 500-900°C in normal flowing-nitrogen ambient.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Phase transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>500-620</td>
<td>W-Ti/Co-silicide/Si</td>
</tr>
<tr>
<td>620-760</td>
<td>W-Ti/CoSi₂/Si</td>
</tr>
<tr>
<td>830</td>
<td>W- and Ti-oxide/W-Ti/CoSi₂/Si</td>
</tr>
<tr>
<td>900</td>
<td>WSi₅/TiSi₂/m.s./CoSi₂/Si</td>
</tr>
</tbody>
</table>

*a.m.s. stands for mixed silicides of Co and Ti.*

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mation from the AES depth profile concerning whether a layer of mixed Ti- and Co-silicides or of Co-silicide embedded in Ti is formed after annealing. The etching solution removes the Ti and the embedded Co-silicide but not the mixed silicide layer of Co and Ti.

For the system of W(400 Å)/Co₆₃Ti₃₇(840 Å)/Si, the AES depth profile in Fig. 7(a) shows that Co-silicide together with the Ti-oxide layer remains after etching following the 550 °C anneal; materials over the intermediate Ti-oxide layer have been removed [cf. Fig. 1(b)]. When the annealing temperature is raised to between 700 and 800 °C, a mixed silicide layer composed of Ti and Co silicides on the surface as well as the contact Co-silicide is left after etching, as shown in Fig. 7(b) [cf. 3(a)]. In contrast, only contact Co-silicide is left after etching following the annealing at 650 °C; this implies that the apparently mixed silicide of Co and Ti is in fact a layer of Co-silicide embedded in Ti. It should also be noted that the intervening Ti-oxide formed above 650 °C disappears after etching.

Figures 8(a) and 8(b) show SEM micrographs of the W(400 Å)/Co₆₃Ti₃₇(840 Å)/Si system annealed at 550 and 750 °C, respectively, for 30 min. No silicide lateral growth is observed. The discontinuous and protrudent bright spots over the silicon contact area in Fig. 8(a) are presumably Ti-oxide left over after etching, because the AES depth profile in Fig. 7(a) reveals that Ti-oxide on the Co-silicide remains after etching. However, for the samples annealed between 650 and 800 °C, both the SEM micrographs and the AES depth profiles, for example, Fig. 8(b) and Fig. 7(b), respectively, show that no evident Ti-oxide layer remains on the surface after etching; this is presumably due to the thinner Ti-oxide, or else the Ti-oxide formed at these temperatures is not stable and thus can beetched away. Figure 8(b) also reveals that the etching leaves residues on the silicon oxide for the 750 °C annealed sample but not on that for the 550 °C annealed sample [Fig. 8(a)]. The residues on the silicon oxide might be Ti-oxide. The AES depth profile for W(400 Å)/Co₆₃Ti₃₇(840 Å) on silicon oxide annealed at 750 °C for 30 min is shown in Fig. 9; much of the titanium is segregated to the surface and becomes oxidized, and the Co-Ti alloy inside is oxidized as well.

For the W(400 Å)/Co₆₃Ti₃₇(360 Å)/Si system, since no Ti-silicide is formed during annealing, even at a temperature of 760 °C, and since the W-Ti can be etched away, AES depth profiles show that only Co-silicide is left after etching. Although at 830 °C some Ti-silicide is formed embedded in the inner part of the W layer, it still can be removed by etching, as revealed by the AES depth profile in Fig. 10. There is no obvious change in sheet resistance after selectively etching away the overlying W-Ti layer, as the annealing is performed above 620 °C, where all the Co is transformed into CoSi₂; this implies that sheet resistance of the W-Ti/CoSi₂ contact is mainly determined by the contact CoSi₂. Figure 8(c) shows the SEM micrograph for the W(400 Å)/Co₆₃Ti₃₇(360 Å)/Si sample annealed at 760 °C for 30 min followed by etching; no residue remains on the silicon oxide, but the oxide surface is slightly corrugated. However, if the annealing temperature is lowered to 620 °C, the surface of the silicon oxide is very smooth [Fig. 8(d)]. No silicide lateral growth occurs in this system. The AES depth profile for W(400 Å)/Co₆₃Ti₃₇(360 Å) on silicon oxide after annealing at 760 °C for 30 min is shown in Fig. 11. Basically, the W-Ti layer is only oxidized on the shallow surface; no Ti-oxide is observed on the silicon oxide after selective etching. Some tungsten from the overlying W layer diffuses into the Co-Ti alloy.

Fig. 8. Plan-view SEM micrographs for W(400 Å)/Co$_{63}$Ti$_{37}$ (840 Å)/Si finished with etching after annealing at (a) 550 °C for 120 min and (b) 750 °C for 30 min; plan-view SEM micrographs for W(400 Å)/Co$_{63}$Ti$_{37}$ (360 Å)/Si finished with etching after annealing at (c) 760 °C for 30 min and (d) 620 °C for 30 min.

Fig. 9. AES depth profiles for W(400 Å)/Co$_{63}$Ti$_{37}$ (840 Å) on silicon oxide annealed at 750 °C for 30 min.

Fig. 10. AES depth profile for W(400 Å)/Co$_{63}$Ti$_{37}$ (360 Å)/Si after annealing at 830 °C for 30 min and etching.

Furthermore, the Co-Ti-W alloy formed on the silicon oxide also contains a fairly high concentration of oxygen. The tungsten and oxygen in the Co-Ti alloy will hinder its silicidation; thus, silicide lateral growth is prevented. Some of the oxygen gettered in the alloy may come from the underlying silicon oxide, and thus the oxide surface is corrugated.

C. Second annealing

For the system of W(400 Å)/Co_{63}Ti_{37}(840 Å)/Si, where Ti-silicide is formed mixing in the outer part of the contact Co-silicide after annealing at 700–800 °C, further annealing at a higher temperature will make the contact CoSi_2 and Ti-silicide separate more clearly. The AES depth profile in Fig. 7(c) shows that a separate layer of Ti-silicide evolves on the surface after the system has undergone the first annealing at 750 °C, followed by selective etching, and a second annealing at 950 °C for 30 min; before the second annealing all the Ti-silicide resides in the Co-silicide [see Fig. 7(b)]. However, there is still a mixed-silicide zone between the Ti-silicide and the contact CoSi_2. TiSi_2 can be identified on the XRD spectrum. Epitaxy of CoSi_2 in the metallization of the W(400 Å)/Co_{63}Ti_{37}(840 Å)/Si system can easily be observed after two-step annealing at 650 and 950 °C, where only CoSi_2 is grown. The interface dislocations are clearly visible in the TEM image micrograph shown in Fig. 12(a). The diffraction pattern shown in Fig. 12(b) is obtained from the zone axis (100).
substrate pole of the area imaged in Fig. 12(a); the spots from both (100) and (110) CoSi$_2$ crystal grains resemble those reported by Yalisove et al.$^{21}$

For the system of W(400 Å)/Co$_{63}$Ti$_{37}$(360 Å)/Si, the sheet resistance does not change after the second annealing at 950 °C if the first annealing is performed above 620 °C and the overlying W–Ti is removed by selective etching; this implies that all the Co has been transformed into CoSi$_2$ during the first anneal and there is no further phase transformation during the second, higher temperature anneal.

IV. DISCUSSION

A. Practical optimum process for simultaneous formation of W–Ti diffusion barrier and shallow CoSi$_2$ contact

For the thinner alloy system of W(400 Å)/Co$_{63}$Ti$_{37}$(360 Å)/Si, neither a Ti-oxide nor a Ti-silicide layer is formed by annealing at temperatures even as high as 760 °C, because all of the Ti is alloyed with the W layer, which is only oxidized on the shallow surface. On the other hand, all the Co-silicide has been transformed into CoSi$_2$, phase at 620 °C, as confirmed by the AES depth profiles, XRD analysis, and sheet resistance measurement. Thus, the W–Ti diffusion barrier and shallow CoSi$_2$ silicided contact can be formed simultaneously in just one annealing step. Furthermore, W–Ti is more efficient than W as a diffusion barrier to aluminum because a very stable and insoluble TiO$_2$ can be formed on the W–Ti surface to impede Al corrosion.$^{22}$ The other effect of Ti in W is that it precipitates at the grain boundary of the tungsten and thus blocks the fast-diffusion path for aluminum and silicon. In all, the overlying W film in this system plays a triple role: it serves as (i) a medium to form a stable passivating film (W–Ti) for the silicidation of the underlying metal in a normal flowing nitrogen furnace; (ii) a medium to accommodate the nonsilicided species (Ti) in the alloy so that a shallow silicided contact can be formed; and (iii) a medium to form a diffusion barrier. The titanium in this system acts as a "stabilizer" for the diffusion barrier and passivating film.

If the thin-film densities of cobalt and titanium are 8.7 and 4.5 g cm$^{-3}$, respectively, so that their respective atomic masses are 58.93 and 47.90, there will be an equivalent amount of 173 Å of titanium and 187 Å of cobalt in the Co–Ti alloy for the W(400 Å)/Co$_{63}$Ti$_{37}$(360 Å)/Si system. Since all the Co is transformed into CoSi$_2$ and 3.64 Å of Si is consumed per angstrom of Co metal, only 680 Å of Si substrate is consumed after the silicidation anneal. Thus, ~630 Å less silicon is consumed compared with the case of pure Co, where the same thickness of 360 Å Co reacts to form CoSi$_2$. The thickness of CoSi$_2$ derived from the present Co–Ti alloy system is 658 Å, since 3.52 Å of Co$_{63}$Ti$_{37}$ is formed per angstrom of cobalt. The composition of W–Ti alloy is 90.9% W to 9.1% Ti by weight, given that all the 173 Å of Ti is alloyed with the 400 Å of W and the thin-film densities for Ti and W are 4.5 and 19.3 g cm$^{-3}$, respectively. This composition is nearly equal to that of the conventional diffusion barrier of Ti:W (10:90 wt %) reported by Ghathe et al.$^{18}$

The present metallization system of W(400 Å)/Co$_{63}$Ti$_{37}$(360 Å) was deposited on a p+n junction with a junction depth of 0.26 μm to simultaneously form the in situ W–Ti barrier layer and CoSi$_2$ contact using the silicidation scheme developed in this study. The I–V characteristics, as illustrated in Fig. 13, indicate that the Al (7500 Å)/W–Ti/CoSi$_2$($p^+ n$) diode is able to sustain a postaluminum annealing at 550 °C for 20 min; the reverse leakage current at $-5$ V is 2–3 nA/cm$^2$ and the forward ideal factor is 1.04.

For the thicker alloy system of W(400 Å)/Co$_{63}$Ti$_{37}$(840 Å)/Si, bilayer TiSi$_2$/CoSi$_2$ silicided contact can be formed with the first annealing at 700–800 °C, followed by selective etching and a second annealing at 950 °C; if residues of Ti-oxide on the silicon oxide is not problematic or can be removed by other means. TiSi$_2$ can also act as a diffusion barrier to CoSi$_2$, because it reacts with aluminum at temperatures higher than 500 °C.$^{23}$ Furthermore, the two-step annealing is self-aligned for silicide formation.

B. Epitaxy of CoSi$_2$ on Si

Titanium in the Co–Ti alloy system may act to reduce the native oxide, leading to a fresh and clean silicon surface on which epitaxy of CoSi$_2$ is more feasible.$^{19,20}$ On the other hand, because there is less Co at the interface with the Si substrate for the Co–Ti alloy than there is in the case of pure cobalt silicidation, fewer grains of Co-silicide in preferred orientation with a favorable free energy are likely to nucleate. The fewer available nuclei are helpful to preferred orientation (or epitaxy) for silicide. In the system of W(400 Å)/Co$_{63}$Ti$_{37}$(840 Å)/Si, epitaxy of CoSi$_2$ can be successfully grown. However, in the W(400 Å)/Co$_{63}$Ti$_{37}$(360 Å) system, where an inadvertently deposited thin Co layer of 14 Å intervened between the Co–Ti alloy and Si substrate, epitaxy of CoSi$_2$ did not occur, because no Ti was available to reduce the residual oxide and limit the nucleation during the early silicidation stage of Co. The silicide growth rate is also lower because there is less Co available from the alloy. Thus, the transformation rate of Co-silicide is lower for the W/Co–Ti/Si system than it is for the Co/Si system; the CoSi$_2$ phase still exists after 650 °C annealing for 30 min, or after 500 or 550 °C annealing for a prolonged time in the W(400 Å)/Co$_{63}$Ti$_{37}$(840 Å)/Si system.

C. Phase array of WSi$_2$/TiSi$_2$ (or another Ti-silicide)/CoSi$_2$/Si

The phase array of WSi$_2$, TiSi$_2$ (or another Ti-silicide), and CoSi$_2$ on the Si substrate at 900 °C, where the thermo-dynamic equilibrium dominates, can be roughly explained based on the interface energy between Si and silicide.$^{24}$ When silicide is formed, there is a volume change associated with the volume difference between the reacting species (metal and Si) and the silicide. This constitutes the dominant component of stress between the silicidate and the
Si substrate at the temperature of silicidation formation. Among the three silicides, CoSi₂ has the least volume change and should be in contact with Si. Although no data are available concerning the interface energy between CoSi₂ and TiSi₂ or that between CoSi₂ and WSi₂, it can be inferred from the closer volume change of TiSi₂ and CoSi₂ that TiSi₂ must adjoin CoSi₂ and that WSi₂ must be located outward. WSi₂ can be well formed in the system of W/Ti/Si deposited by the technique of e-beam evaporation can be attributed to the reduction of interface silicon oxide by Ti or breakdown of interface silicon oxide by Co; at the same temperature of 900°C, no W-silicide is formed for W directly deposited on the Si substrate by e-beam evaporation under the same deposition conditions.

V. CONCLUSIONS

(1) Simultaneous formation of a W–Ti diffusion layer and shallow CoSi₂ silicided contact is feasible. This is demonstrated by annealing the W(400 Å)/Co₅₇Ti₄₃(360 Å)/Si system at temperatures ranging from 620 to 760°C in a normal flowing-nitrogen furnace. Silicide lateral growth does not occur in this silicidation scheme. The p⁺n diode with a junction depth of 0.26 μm metallized with this silicidation scheme result in Al/W/Ti/CoSi₂/p⁺n diodes, which are able to withstand a post-AI annealing treatment at 550°C for 20 min without any degradation in performance.

(2) Self-aligned bilayer TiSi₂/CoSi₂/Si silicided contact can be formed using a thicker Co₅₇Ti₄₃ alloy of 840 Å with the first annealing performed at 700–800°C and a second annealing at a higher temperature after selective etching.

(3) For the system composed of cobalt, titanium, and tungsten deposited on the Si substrate, WSi₂/TiSi₂/CoSi₂/Si can be formed at high temperatures, such as 900°C.

(4) Localized epitaxy of CoSi₂ on (100)Si is feasible by annealing the appropriate W/Co–Ti/Si system in a normal flowing-nitrogen furnace.

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