Reduction of the C54–$TiSi_2$ phase transformation temperature using refractory metal ion implantation

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We report that the ion implantation of a small dose of Mo into a silicon substrate before the deposition of a thin film of Ti lowers the temperature required to form the commercially important low resistivity C54–$TiSi_2$ phase by 100–150 °C. A lesser improvement is obtained with W implantation. In addition, a sharp reduction in the dependence of C54 formation on the geometrical size of the silicided structure is observed. The enhancement in C54 formation observed with the ion implantation of Mo is not explained by ion mixing of the Ti/Si interface or implant-induced damage. Rather, it is attributed to an enhanced nucleation of C54–$TiSi_2$ out of the precursor high resistance C49–$TiSi_2$ phase. © *1995 American Institute of Physics.*

Titanium disilicide has become the predominant silicide in the very large scale integrated (VLSI) microelectronics industry for submicron interconnects to active regions of complementary metal-oxide-semiconductor (CMOS) devices. $TiSi_2$ is a polymorphic material and may exist as a high resistance (60–70 $\mu\Omega$ cm) orthorhombic base-centered C49 phase or as the low resistance (15–20 $\mu\Omega$ cm) orthorhombic face-centered C54 phase.[1,2] When a thin film of titanium on silicon is heated, the high resistance C49 phase forms at temperatures ranging between 550 and 700 °C and then transforms into the low resistance C54 phase at temperatures greater than ~750 °C. The C49 phase forms first because of a lower barrier to nucleation which has been attributed to a lower surface energy of this phase.[3,4] The subsequent transformation of the C49 into the C54 phase is limited by a low driving force (small transformation enthalpy)[5] and a high activation energy (>5.0 eV, depending on dopants and crystallinity of the silicon substrate).[6]

Experimentally, the low driving force and high activation energy for C54 formation results in a very small density of C54 nuclei forming in a C49 matrix during thermal annealing (a typical nucleation density as $<0.05/\mu m^2$). This causes a phenomenon called the "fineline effect" to occur in submicron $TiSi_2$ structures.[7] With the fineline effect, as the linewidth of a structure is decreased into the submicron regime, it becomes increasingly more difficult to use thermal annealing to transform a structure from the high resistance C49 phase into the low resistance C54 phase due to a lack of C54 nuclei. This results in $TiSi_2$ films that are either still in the C49 phase or have a mixture of C49 and C54, and thus have a higher resistance than if they were completely in the C54 phase. This increase in the silicide resistance can decrease the performance of a CMOS circuit by as much as ten percent.[8]

The desire to completely form C54 in a submicron structures has encouraged research in increasing the C54 nucleation density by rapid thermal processing,[9] Sb additions,[10] or preamorphization of the silicon substrate by ion implantation of Xe.[11] These approaches have met with limited acceptance because they have only slightly affected[9] or have not been shown to decrease the dependence of C54 formation on the geometry of the submicron $TiSi_2$ structures.[10,11] This letter describes a new approach in which the temperature of the formation of the low resistance C54 phase is reduced by 100–150 °C in both blanket and submicron $TiSi_2$ films by low dose ion implantation of Mo or W into a silicon substrate before Ti deposition. The advantage of this approach is that in addition to lowering the formation temperature of the C54 phase, the density of C54 nuclei is sufficiently increased to completely convert 0.4 μm $TiSi_2$ features from C49 to C54 during thermal processing, thus eliminating the fineline effect. We postulate that the improved C54 formation characteristics obtained with this technique are due to an enhancement in the nucleation of the C54 phase at the C49 grain boundaries and not to ion implantation damage in the silicon substrate, as in Ref. 11.

In our studies, a refractory metal (W or Mo) was implanted into a silicon (single-crystal or polycrystalline silicon) substrate at 45 keV, using a dose in the range of 1×10^{13}–1×10^{14} ions/cm^2. Tungsten was implanted by using the filament material as the source of the (184 W^+) ion beam and molybdenum was implanted using a molybdenum arc chamber as the source of the (98 Mo^+) ion beam. Samples were prepared using lightly doped *p*-type silicon substrates of (100) orientation and with doped and undoped polycrystalline silicon (polysilicon). Following the metal implant, the samples were annealed in a nitrogen ambient, simulating a junction activation anneal, and a thin layer (25, 35, or 55 nm) of titanium was sputtered on the substrates following a buffered HF.

Figure 1 shows the as-implanted SIMS profile of the Mo for a sample with a dose of 5×10^{13} at/cm^2 implanted at 45 keV. The peak concentration of roughly 3×10^{18} at/cm^3 is located at 35 nm below the silicon surface. Although no stan-

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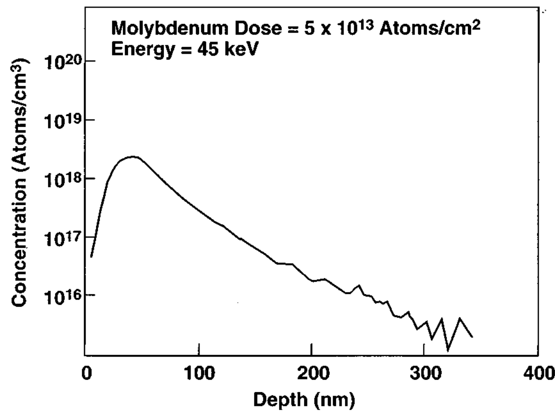


FIG. 1. SIMS depth profile of molybdenum in single-crystal silicon just prior to titanium deposition.

dards were available for tungsten, the general shape of the profile was similar and the surface concentration was estimated to be similar to that of the molybdenum. Very few crystalline defects, no metal or silicide precipitates, and no amorphous regions were found in the (100) single-crystal silicon substrates prior to the titanium sputter process based on TEM cross-section analysis. This indicates that the activation anneal performed before the Ti deposition removed any defect damage caused by the ion implantation. This is an important distinction from the work of Maex *et al.*,[12] or Kuwanu *et al.*,[11] where Ti/Si was intermixed or the silicon substrate was amorphized by Xe ion implantation prior to titanium silicide formation.

The effect of the implanted refractory metal on silicide sheet resistance after a 600 °C, 30 min anneal is shown in Fig. 2 for initial Ti thicknesses of 25, 35, and 55 nm. The titanium silicide samples in Fig. 2 were formed on single-crystal silicon. The samples with the molybdenum implant in the silicon had a resistivity of 16 $\mu\Omega$ cm and were in the low resistance C54 phase versus the samples without a Mo implant, which had a resistivity of >60 $\mu\Omega$ cm and were in the high resistance C49 phase. The samples implanted with tungsten had a resistivity of about 40 $\mu\Omega$ cm, indicating that this sample contained a mixture of both C49 and C54 $TiSi_2$.

To further evaluate the phase-formation characteristics,

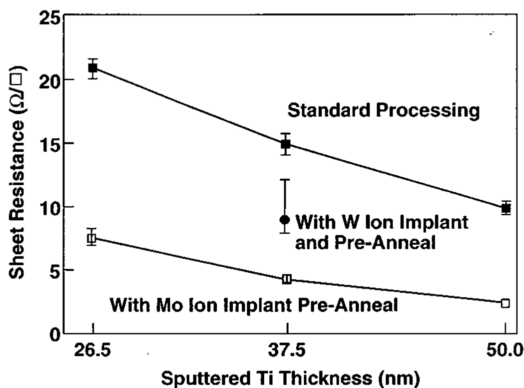
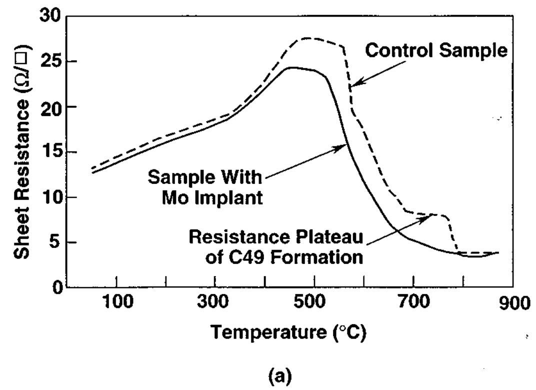


FIG. 2. Sheet resistance after 600 °C formation anneal and selective etch for samples with and without a metal impurity implant.



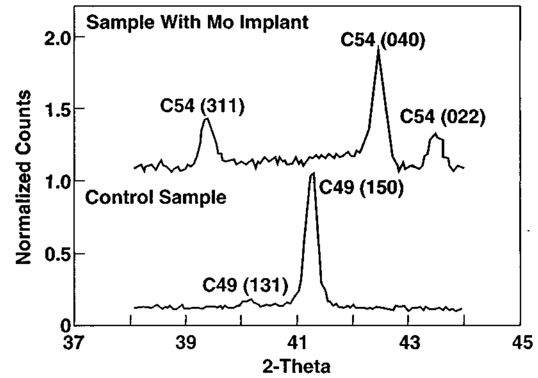


FIG. 3. *In situ* resistance as a function of ramp temperature (a) and the corresponding thin-film x-ray analysis taken on samples cooled from 700 °C (b) for a sample with and without the implanted molybdenum.

samples were specifically prepared for *in situ* resistance measurements by depositing a 300 nm thickness of polysilicon on a layer of thermally grown oxide. The oxide layer was used to electrically isolate the silicide region from the silicon substrate. One of the samples then received a molybdenum implant and a 900 °C, N_2 anneal prior to the titanium deposition, while the control sample was similarly treated except it did not receive a Mo implant. Both samples received a HF dip followed by the deposition of 55 nm of titanium. The resistance of the samples was then measured, *in situ*, during annealing at a heating rate of 15 °C/min. The resulting data is plotted in Fig. 3(a).

From the *in situ* resistance data shown in Fig. 3(a), it is clear that significant differences exist in the phase-formation characteristics for the two different samples. The sample without the Mo implant forms C49 at ~580 °C and remains in this phase until about 780 °C, where it undergoes an abrupt transition to C54.[13] In contrast, the sample with the Mo implant exhibits no distinct resistance plateau, which has previously been shown to be characteristic of C49 formation,[13] between 700 and 800 °C. Rather, this sample transformed directly into the C54 phase at roughly 700 °C. Thin-film x-ray analysis [Fig. 3(b)], taken from Ti/Si samples with and without a Mo implant and annealed at 15 °C/min to 700 °C and quenched, show that the sample with the molybdenum implant had transformed into the low-

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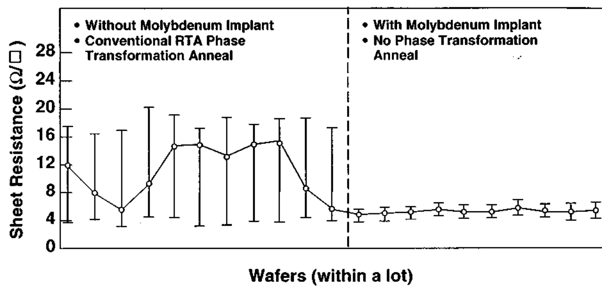

FIG. 4. Sheet resistance data for narrow n^+ doped polysilicon lines comparing efficiency of conversion for the conventional RTA vs the use of metallic impurities with no conversion anneal.

resistance C54 phase at 700 °C, while the control without the Mo implant was still C49–$TiSi_2$.

The enhancement of the C54 formation characteristics for samples with a Mo implant demonstrated for unpatterned silicide films in Figs. 3(a) and 3(b) also occurs in submicron silicide structures. In Fig. 4, the sheet resistance of 0.4 μm $TiSi_2/N^+$ doped polysilicon lines for samples with and without a Mo implant is shown. Both the control sample and the sample with the Mo implant first received a 650 °C, 30 min anneal to form either C49 or C54–$TiSi_2$. In addition, the samples without the Mo implant received an extra 825 °C anneal to help convert them from C49 to C54–$TiSi_2$.The spread in the resistance values for the wafers without the Mo implant indicates that these structures did not fully convert to C54 even after the extra 825 °C anneal. In contrast, the lines which had a Mo implant have fully transformed into the low-resistivity C54 phase even though the only anneal they were exposed to was 650 °C, 30 min. Similar results have also been observed for the C49–C54 transformation on submicron P^+ doped polysilicon lines.

The lowering of the temperature of formation of C54 by 100 to 150 °C that we observed with our technique indicates that Mo implantation greatly enhances the nucleation of C54 in the C49 matrix. This is true even though it is forming at a lower temperature than it would in samples without the Mo implant. This is confirmed by TEM measurements of the C54 grain size which show about a factor of >100 increase in the C54 nucleation density for a Mo implanted sample compared to an unimplanted sample.[14] We believe that the mechanism responsible for the enhanced nucleation of C54 in the Mo implanted samples is an increase in the number of active triple junctions in the C49 where the C54 nucleates. Ma[15] reported that for normal C49–C54 transformations, the nucleation of the C54 phase in C49 occurs at about 10%–15% of the available C49 grain triple points. In our case, we believe that a much higher percentage of C54 nucleation at C49 grain triple points is being obtained. Silicon is the dominant diffusing species during C49 formation.[16] In addition, the thickness of silicon consumed during C49 formation is greater than the Mo implant depth [>44 nm (Si) vs 35 nm (Mo)]. These facts indicate that most of the Mo implanted into the silicon is incorporated into C49 during its formation where we believe it segregates to the C49 grain triple points. This lowers the nucleation barrier for C54 formation by changing surface energies and/or thermodynamic driving forces for formation. Ion mixing or implant generated defects cannot explain our results. In this work, the Mo implant and the high-temperature activation anneal are performed before the Ti deposition. This results in no interface mixing or implant damage being present when the Ti is subsequently deposited and annealed to form C54–$TiSi_2$.

In summary, the temperature required to form the low resistance C54–$TiSi_2$ phase can be reduced by ~100–150 °C through the ion implantation of small quantities of molybdenum into silicon before the deposition of Ti. This lowering of the C49–C54 transformation temperature is coupled with a sharp reduction in the dependence of this transformation on the geometrical size of the silicated structure. The results are attributed to the segregation of Mo–C49 triple points during annealing resulting in a lowering of the nucleation barrier for C54 formation. Similar, though less dramatic results were observed with W implants.

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