Low temperature formation of C54–TiSi$_2$ using titanium alloys

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We demonstrate that the temperature at which the C49 TiSi$_2$ phase transforms to the C54 TiSi$_2$ phase can be lowered more than 100 °C by alloying Ti with small amounts of Mo, Ta, or Nb. Titanium alloy blanket films, containing from 1 to 20 at. % Mo, Ta, or Nb were deposited onto undoped polycrystalline Si substrates. The temperature at which the C49–C54 transformation occurs during annealing at constant ramp rate was determined by *in situ* sheet resistance and x-ray diffraction measurements. Tantalum and niobium additions reduce the transformation temperature without causing a large increase in resistivity of the resulting C54 TiSi$_2$ phase, while Mo additions lead to a large increase in resistivity. Titanium tantalum alloys were also used to form C54 TiSi$_2$ on isolated regions of arsenic doped Si(100) and polycrystalline Si having linewidths ranging from 0.13 to 0.56 μm. The C54 phase transformation temperature was lowered by over 100 °C for both the blanket and fine line samples. As the concentration of Mo, Ta, or Nb in the Ti alloys increase, or as the linewidth decreases, an additional diffraction peak appears in *in situ* x-ray diffraction which is consistent with increasing amounts of the higher resistivity C40 silicide phase. © *1997 American Institute of Physics.* [S0003-6951(97)02550-3]

Titanium disilicide is the most widely used self-aligned silicide because of its low resistivity, minimal contact resistance, and high thermal stability. On heating Ti deposited on Si, the first disilicide phase to form is the high-resistivity C49 phase. Additional heating is needed to form the low-resistivity C54 phase.[1,2] This phase transition becomes increasingly difficult in submicron features, because of the low density of nucleation sites.[3] Heating of C49 TiSi$_2$ above 900 °C leads to morphological instabilities such as inversion[4,5] and agglomeration[5] rather than phase transformation. Recently, Mouroux *et al.*[6] and Cabral *et al.*[7] have shown that a thin layer (<3 nm) of Mo or W at the Ti/Si interface reduces the C54 transformation temperature. In this work, titanium alloys of Mo, Ta, or Nb are shown to be effective in lowering the C49–C54 transformation temperature by more than 100 °C both in blanket films and in patterned submicron lines.

Silicide formation was studied for blanket Ti(1–10 at. % Mo, Ta, or Nb) films, 29 to 35 nm in thickness, deposited on 150 nm of poly-Si. The samples were annealed in N$_2$ at a ramp rate of 3 °C/s up to 900 °C while x-ray diffraction and sheet resistance were simultaneously monitored, using the IBM/MIT beamline X20C.[8] The diffraction profiles were measured with a position-sensitive detector composed of a linear array of photodiodes. A second set of blanket films, 30–50 nm in thickness of composition Ti(1–20 at. % Mo, Ta, or Nb) was annealed at a ramp rate of 0.25 °C/s to 900 °C in He after which room temperature resistivity measurements were made.

Submicron lines were formed using x-ray lithography together with standard Si processing techniques. Both Si(100) and poly-Si isolated lines were doped with As using an implant dose of 3×10^{15} ion/cm^2. 31 nm Ti(5.5 at. % Ta) was deposited on Si(100) lines ranging in width from 0.20 to 0.56 μm and 34 nm Ti(5.2 at. % Ta) was deposited on poly-Si lines ranging in width from 0.13 to 0.35 μm. The C49 silicide fine lines were formed using a self-aligned process, comprising a first anneal followed by a selective etch. They were annealed at a ramp rate of 3 °C/s up to 1025 °C in N$_2$ in order to determine the C54 transformation temperatures using *in situ* x-ray diffraction.

In situ sheet resistance analysis of Ti(Ta) films reveals that the C54 transformation temperature is lowered by 125 °C compared to nonalloyed TiSi$_2$. Sheet resistance as a function of temperature is plotted in Fig. 1 for the reaction of Ti, Ti(3.3 at. % Ta) and Ti(5.9 at. % Ta) with poly-Si. First consider the reaction of Ti with poly-Si represented by the solid curve. In the temperature range between 400 °C and
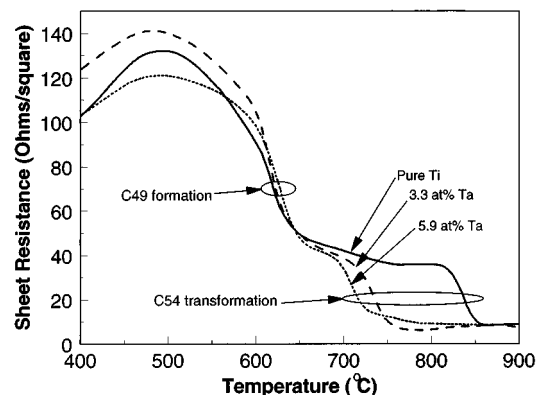

FIG. 1. *In situ* sheet resistance as a function of temperature comparing the formation of blanket TiSi$_2$ starting from 29 nm Ti, 32 nm Ti(3.3 at. % Ta), and 35 nm Ti(5.9 at. % Ta) on polycrystalline silicon. The films were annealed at a ramp rate of 3 °C/s up to 900 °C in N$_2$.
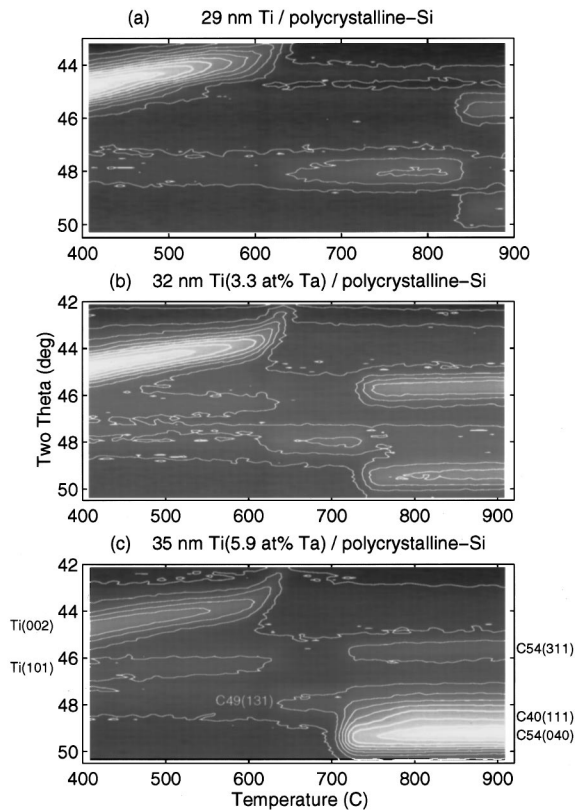
FIG. 2. *In situ* x-ray diffraction analysis as a function of temperature comparing the formation of blanket TiSi$_2$ starting from (a) 29 nm Ti, (b) 32 nm Ti(3.3 at. % Ta), and (c) 35 nm Ti(5.9 at. % Ta) on polycrystalline silicon. The films were annealed at a ramp rate of 3 °C/s up to 900 °C in N$_2$ while a 2θ x-ray diffraction range from 42.0° to 50.5° was monitored. Higher intensity is represented by lighter shading.

FIG. 3. Resistivity as a function of atomic percent Mo, Ta, and Nb additive for blanket TiSi$_2$ films, after a 0.25 °C/s from room temperature to 900 °C anneal treatment in He. The resistivity ranges for the C49 TiSi$_2$ phase (60–70 $\mu\Omega$ cm) and the C54 TiSi$_2$ phase (14–20 $\mu\Omega$ cm) are depicted by the horizontal dashed lines.

500 °C an increase in sheet resistance indicates Si diffusion into Ti. At approximately 500 °C the sheet resistance drops until a plateau region is reached at about 650 °C, indicating the region over which the C49 phase is stable. At about 840 °C the final drop in sheet resistance signifies the C49–C54 transformation. Comparing the solid curve with the two dashed curves it is evident that for increasing percentages of Ta there is a large decrease in the C49–C54 transformation temperature.

These same films that were simultaneously analyzed with *in situ* x-ray diffraction are shown in Fig. 2. All three plots show x-ray diffraction intensity over a diffraction angle (2θ) covering approximately 8° as a function of temperature from 400 °C to 900 °C. Figure 2 shows the formation of TiSi$_2$ on poly-Si from pure Ti [Fig. 2(a)], Ti 3.3 at. % Ta [Fig. 2(b)] and Ti 5.9 at. % Ta [Fig. 2(c)]. The 2θ range was chosen such that it encompassed the following peaks: Ti(002)(44.7°), Ti(101)(46.5°), TiSi$_2$ C49(131)(47.8°), TiSi$_2$ C54(311)(45.8°) and TiSi$_2$ C54(040)(49.5°). First consider the case of Ti on poly-Si in Fig. 2(a). The Ti(002) peak is present up to a temperature of 625 °C, after which the C49 phase forms indicated by the presence of the C49(131) peak between 625 °C and 840 °C. At 840 °C the C49–C54 transformation takes place. Comparing the pure Ti case [Fig. 2(a)] with that of Ti 3.3 at. % Ta [Fig. 2(b)] and 5.9 at. % Ta [Fig. 2(c)] it is observed that as the concentration of Ta is increased the range of temperature over which the C49(131)
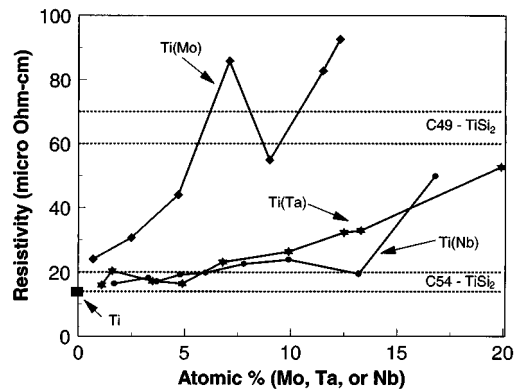
peak exists decreases and the C49–C54 transformation temperature decreases. Also note that a peak has developed at a 2θ value of 48.5° and can be seen as a shoulder off the C54(040) peak in Fig. 2(c). This shoulder peak matches closely with the (111) orientation of the C40 (Ti,Ta)Si$_2$ silicide.[9]

A comparison of C54 TiSi$_2$ formed from Ti alloys reveals that the lowest resistivities and transformation temperatures are obtained for films with less than 10 at. % Ta or Nb. Figure 3 shows room temperature resistivities for Ti(Mo), Ti(Ta), and Ti(Nb) silicides in the composition range from 1 to 20 at. % deposited on poly-Si and annealed at a ramp rate of 0.25 °C/s to 900 °C in He. When more than 2 at. % Mo is added to Ti the resistivity of the annealed samples increases above 30 $\mu\Omega$ cm. However, the annealed resistivity values remain below 30 $\mu\Omega$ cm for Ta and Nb additions up to 10 at. %. The C54 transformation temperature determined by *in situ* x-ray analysis, as a function of atomic percent Ta or Nb added to Ti, is presented in Fig. 4. As the concentration of Ta or Nb in the Ti is increased, up to 10 at. % the temperature at which the C49–C54 transformation takes place drops from 835 °C to 685 °C. The monotonic decrease in the transformation temperature is accompanied by an increasing amount of the C40 phase mixed with the C54 phase.
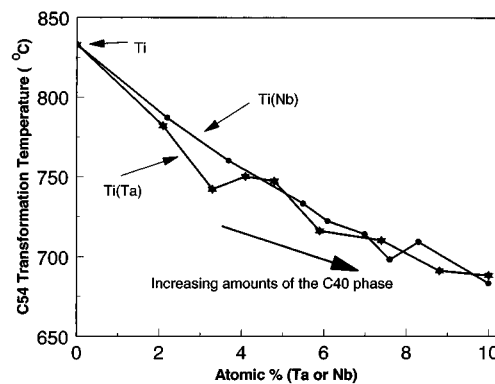

FIG. 4. C54 TiSi$_2$ phase transformation temperature as a function of atomic percent Ta and Nb additive for blanket TiSi$_2$ films. The films were annealed at a ramp rate of 3 °C/s up to 900 °C in N$_2$ while *in situ* x-ray diffraction was performed.
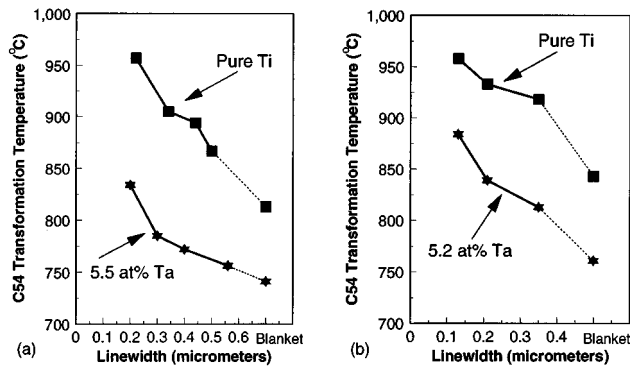
FIG. 5. C54 TiSi$_2$ phase transformation temperature as a function of linewidth for submicron (a) Si(100) isolated features metallized with 31 nm of Ti or Ti(5.5 at. % Ta), and (b) polycrystalline Si isolated features metallized with 31 nm Ti or 34 nm Ti(5.2 at. % Ta). The lines were annealed at a ramp rate of 3 °C/s up to 1025 °C in N$_2$ while *in situ* x-ray diffraction was performed.

On isolated submicron Si(100) and poly-Si Ti(Ta) alloy structures the temperature at which the C49–C54 phase transformation takes place is reduced below 900 °C. Figure 5 shows two plots of C54 transformation temperature as a function of linewidth for Si(100) structures [Fig. 5(a)] and poly-Si structures [Fig. 5(b)]. For the Ti metallized lines the transformation temperature increases substantially as linewidth decreases demonstrating the so called "linewidth effect." [3] Using Ti(5.5 at. % Ta) the transformation temperature on Si(100) also increases as the linewidth decreases, but remains lower than values for pure Ti. This improvement allows for C54 formation below the onset of thermal degradation above 900 °C. Similar effects are observed on poly-Si isolated structures [Fig. 5(b)]. It is also observed from the x-ray diffraction analysis (not shown) that increasing amounts of C40 phase occur as the linewidth is decreased.

The addition of less than 10 at. % Ta or Nb to Ti causes predominantly C54 TiSi$_2$ formation with resistivities below 30 $\mu\Omega$ cm and transformation temperatures as low as 685 °C. Linde's rule [10] can be used to explain the low resistivity silicide formation for Ta and Nb additions compared to the high resistivity formation for Mo additions. The low temperature C54 formation is possibly caused by an increase in the number of C49 triple junctions leading to increased nucleation density or caused by crystallographic templates provided by the C40 silicide phase.

The lower transformation temperatures (<900 °C) in submicron lines indicate enhanced C54 nucleation. It is generally true that alloying elements decrease grain size, here the smaller C49 grains may result from pinning of the grain boundaries by the additive or by a silicide of the additive. Nucleation of the C54 phase is reported by Ma *et al.*[11] to take place at 10%–15% of the C49 grain boundary triple junctions. Since the grains of the Ti alloy C49 phase may be smaller and grain growth reduced, this material may contain a higher density of triple junctions thus prompting lower transformation temperatures and improved conversion in submicron lines. Figure 2(c) reveals that the C49–C54 transformation occurs at 715 °C but substantial grain growth of the C54 phase does not occur until 760 °C, as shown by an increase in the C54(040) peak intensity. Therefore, x-ray dif-

fraction analysis indicates the C54 grains that form from the alloy C49 phase are smaller than those formed from pure Ti suggesting greater nucleation. Miles *et al.*[12] also demonstrated that smaller C54 grains resultd when implanted Mo near the Ti/Si interface is used to enhance C54 formation.

Another possible mechanism leading to greater C54 nucleation is the presence of crystallographic templates provided by the additive binary disilicides. MoSi$_2$ (low temperature), TaSi$_2$, and NbSi$_2$ all have the C40 "CrSi$_2$" prototype structure in which the hexagonal planes stack in an ABC-ABC order, closely related to the C54 structure in which identical hexagonal planes stack in an ABCD-ABCD order. The differences in interatomic spacings between C54 TiSi$_2$ and C40 TaSi$_2$ are small therefore solid solutions of TiSi$_2$–TaSi$_2$ have nearly identical spacing.[13] Mouroux *et al.*[6] have reported that when using a Mo layer between Ti and Si to enhance the C54 formation, x-ray diffraction reveals a peak from (Ti$_{0.4}$Mo$_{0.6}$)Si$_2$ or (Ti$_{0.8}$Mo$_{0.2}$)Si$_2$, both of which have the C40 structure. In our work, Fig. 2(c) shows a shoulder peak that has developed at about 715 °C at an angle of 48.5°. This peak is a close match for the (Ti,Ta)Si$_2$(111) peak recorded by Dahan *et al.*[9] The (Ti,Ta)Si$_2$ phase is isomorphous with C40 TaSi$_2$. This suggests that the C40(Ti,Ta)Si$_2$ phase may provide a crystallographic template for the nucleation of the C54 TiSi$_2$.

In conclusion, the formation temperature of the C54 TiSi$_2$ phase is reduced by more than 100 °C with the addition of small quantities of Mo, Ta, or Nb to Ti, both in blanket films and in patterned structures. The enhanced formation in fine structures indicates that the alloy addition may provide increased nucleation and/or a crystallographic template for the phase transformation.

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