

The C49 to C54-TiSi₂ transformation in self-aligned silicide applications

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We show that when processing conditions closely mimic those used in the conventional self-aligned silicide process, the effective activation energy for the polymorphic phase transformation of orthorhombic base-centered (oC12) C49-TiSi₂ to the low-resistivity orthorhombic face-centered (oF24) C54-TiSi₂ phase is over 1 eV higher than previously reported literature values where a 1-step heat cycle was used. For C49-TiSi₂ films formed at temperatures of 600 and 625 °C on (100) single crystal silicon substrates, the activation energy was determined to be 5.6 ± 0.3 and 5.7 ± 0.13 eV, respectively, for the transformation of this phase into C54-TiSi₂ in the temperature range of 625–700 °C. The higher activation energy obtained with the simulation of the self-aligned silicide processing conditions suggests that the conventional processing may need to be modified for future semiconductor applications.

To compensate for the increased parasitic resistance accompanying the feature size reduction in the semiconductor industry, the self-aligned silicide (Salicide) technology was developed. Titanium silicide has become the most widely used silicide in very large scale integration (VLSI) technology for Salicide applications because of its low resistivity, ability to be self-aligned, and relatively good thermal stability. Despite the advantages of TiSi₂ over other possible silicide choices and its importance to the semiconductor industry, there are certain important characteristics of this material that are not well known. Because TiSi₂ is a polymorphic material and forms the high-resistivity (60–90 $\mu\Omega$ cm) metastable C49 phase first before undergoing a transformation to the lower resistivity (12–20 $\mu\Omega$ cm) C54 phase, the kinetics of this transformation are of essential practical importance.^{1,2} In a previous investigation by Thompson *et al.*, it was determined that the activation energy for this transformation on SiO₂ was 4.45 eV.³ In a recent study, we discussed the phase transformation kinetics as studied by *in situ* resistance measurements for one step continuous annealing on polysilicon where it was concluded that the bulk of the film always proceeds through the C49 phase before being fully converted to C54 and the activation energy for the transformation was determined to be 3.8 eV.⁴ In this investigation, the C49 to C54 transformation kinetics are studied on (100) silicon substrates following the most commonly used self-aligned silicide processing methods that involve both a formation anneal and a phase transformation anneal step.

Over the past 10–15 years, a generally accepted set of processing conditions have evolved that include: (1) pre-clean, (2) titanium deposition, (3) <700 °C silicide formation, (4) selective etch, and (5) ≥ 700 °C phase transformation anneal. The initial formation temperature is kept below 700 °C in order to minimize over-spacer bridging

while the second transformation anneal is generally performed at temperatures of 50–200 °C above the formation temperature to insure full transformation for best control of sheet resistance. More recently, rapid thermal annealing at temperatures > 850 °C has shown the most promise for the transformation anneal step.⁵

Samples were prepared by *e*-beam evaporation of titanium on precleaned (100) silicon wafer substrates that were 125 mm in diameter. The evaporation pressure was maintained at 1×10^{-7} Torr and the thickness was 57.5 nm. The C49-TiSi₂ was formed either at 600 °C for 45 min or 625 °C for 20 min, both in a nitrogen ambient. A conventional selective etch was done in a Huang A solution at 65 °C followed by a low temperature silicon nitride deposition of 20 nm in order to minimize any further ambient interactions. The isothermal transformation of the C49 to C54 TiSi₂ was done at 625, 650, 675, and 700 °C for each of the two C49-TiSi₂ formation conditions.

The film thicknesses and stoichiometry were analyzed by Rutherford backscattering spectroscopy (RBS) using 1.5 MeV, ⁶He⁺ beam with a backscattering angle of 160°. Sheet resistance measurements were made using a conventional four-point-probe method and optical microscopy was used to characterize the microstructure.

The RBS data obtained immediately after the formation and selective etch steps indicated that the films were both stoichiometric TiSi₂, however the samples formed at 600 °C were roughly 25%–30% thinner than those formed at 625 °C. The sheet resistance measured after the selective etch was 11.9 and 9.5 Ω/\square corresponding to the 600 °C formation and 625 °C formation, respectively. The resistivity of the C49-TiSi₂ was $\sim 65 \mu\Omega$ cm and was independent of the formation temperature.

The sheet resistance was measured as a function of

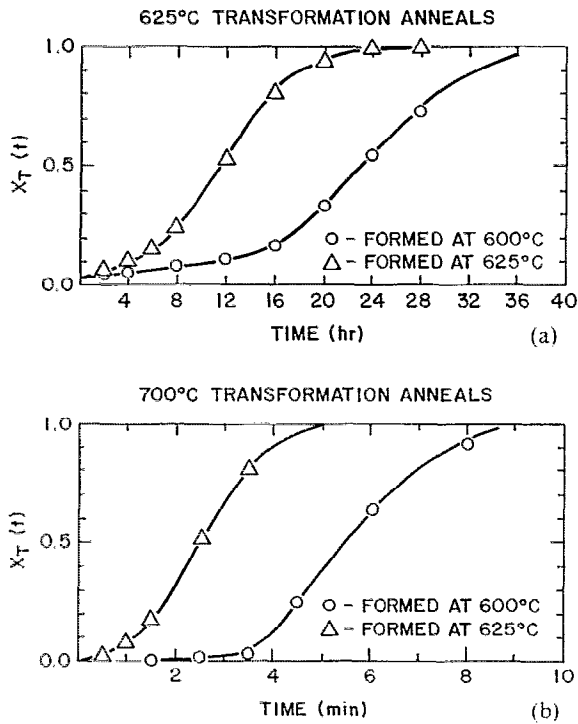


FIG. 1. Fraction of the film transformed to C54-TiSi₂ vs time at 625 °C (a) and at 700 °C (b).

time at temperature and converted to fraction of C54-TiSi₂ transformed by the relationship

$$X_T = [\rho_0 - \rho(t)] / (\rho_0 - \rho_f), \quad (1)$$

where X_T is the fraction of the film transformed to C54-TiSi₂ and ρ_0 , $\rho(t)$ and ρ_f are the sheet resistance values of C49, the measured time dependent resistivity and the resistivity of the C54 phase, respectively. The resistivity of the C54-TiSi₂ was $\sim 15 \mu\Omega \text{ cm}$ for the samples in this study.

Figures 1(a) and 1(b) show the data plotted for two of the transformation temperatures studied. An induction period is more pronounced for the samples formed at 600 °C than those formed at 625 °C across the entire range of transformation temperatures. Optical micrographs taken at various stages of the nucleation and growth process are shown in Figs. 2(a) and 2(b) representing the initial stages of the C54-phase grain growth. The C54-TiSi₂ grains are observed to grow radially once the stable nuclei have formed. As the films reached the final stages of the transformation, the grain diameter to film thickness ratio could frequently be found in excess of 100:1 for the conditions studied.

The activation energy E_a was determined by plotting the $\ln t(X_T=1/2)$ vs $1/kT$ for the temperature range of 625–700 °C according to the Arrhenius relation

$$\tau(X_T=1/2) = \tau_0 \exp(E_a/kT). \quad (2)$$

This is shown in Fig. 3 for the samples formed at both 600 and 625 °C. This method yielded an activation energy for nucleation and growth of the C54 phase of $5.6 \pm 0.3 \text{ eV}$ and $5.7 \pm 0.13 \text{ eV}$ for the films formed at 600 and 625 °C, re-

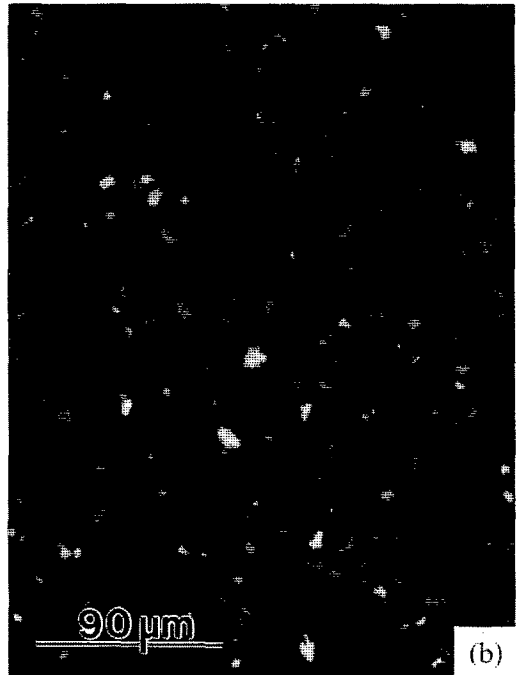
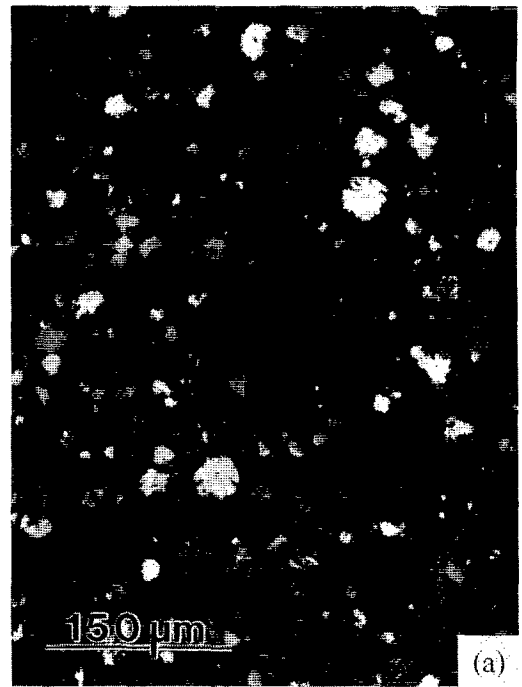


FIG. 2. Optical micrographs showing the radial growth of the C54 phase TiSi₂ crystals. Microstructure after 20 h at 625 °C, formed at 600 °C (a) and after 8 h at 625 °C, formed at 625 °C (b).

spectively. Because the activation energy does not refer to one specific mechanism but incorporates both nucleation and growth, one may prefer the term “effective” activation energy. This effective activation energy would be expected to vary with temperature since the nucleation driving force is a function of temperature. However, since the temperature range over which our activation energy measurements were taken is small, we assume that the nucleation contribution to the effective activation energy and the total acti-

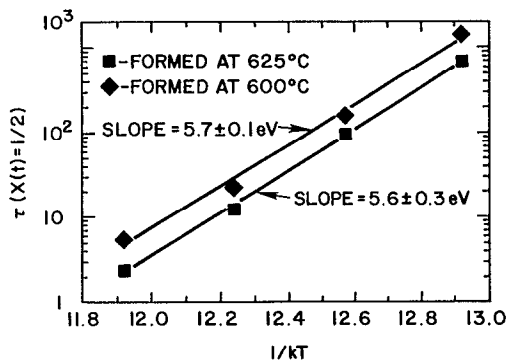


FIG. 3. Arrhenius plots of the time required to transform 1/2 of the film to C54-TiSi₂ for samples formed at 600 and 625 °C. Activation energies for the transformation were 5.6 ± 0.3 eV for the samples formed at 600 °C and 5.7 ± 0.13 eV for the samples formed at 625 °C.

vation energy is constant. For the sake of consistency with prior literature we will refer to the effective activation energy simply as the activation energy.

The larger activation energies for the C49-TiSi₂ to C54-TiSi₂ transformation formed by the two step annealing cycle compared to previous reported values of 3.8 to 4.5 eV for this reaction formed during a single annealing cycle,^{3,4} indicate that the nucleation and/or growth mechanisms are different for the two different processing techniques. One possible explanation for this is that the activation energy for the C54-TiSi₂ formation is due to heterogenous nucleation and growth and this value depends on the interfaces and grain structure of the C49-TiSi₂ from which it forms.⁶ It has been shown that the C49 to C54 transformation temperature is dependent upon both substrate and C49 grain size.^{3,6} The interfaces and grain structure of the C49-TiSi₂ are possibly different for the two step annealing process reported in this communication and the previously reported one step annealing processes.⁶ In the present

study using the two step annealing cycle, the important interfaces are C49-TiSi₂/(100) silicon, C49-TiSi₂/Si₃N₄, and C49-TiSi₂/C49-TiSi₂ grain boundaries. For the one-step annealing process previously reported, the interfaces were C49-TiSi₂/inert gas or vacuum and C49-TiSi₂/polycrystalline-Si or SiO₂, and the C49-TiSi₂ grain size should be smaller compared to the two cycle annealing due to the lack of C49-TiSi₂ thermal annealing before the formation of C54-TiSi₂.⁶

From the results of this work it is suggested that for future Salicide applications, the conventional two-step, (formation and transformation) annealing process may not continue to be feasible. For the specific case where the first step formation was performed at temperatures < 625 °C, and no prenucleation of the C54-TiSi₂ phase occurs, the activation energy for the transformation step is quite high, i.e., > 5.5 eV. Some solutions to this problem have been previously discussed and may involve higher temperature RTA 1-step formation/transformation processing⁷ or other methods of altering the nucleation rate.⁸

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