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Influence of Rapid Thermal Ramp Rate on Phase Transformation of Titanium Silicides

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ULSI technology requires low resistance, stable silicides formed on small geometry lines. Titanium disilicide ($TiSi_2$), which is the most widely used silicide for ULSI applications, exists in two crystallographic phases: the high resistance, metastable C49 phase and the low resistance, stable C54 phase. The major issue with $TiSi_2$ is the increasing thermal budget required to transform the C49 phase into the low resistance C54 phase as linewiths decrease below 0.25 µm. Annealing above 900°C to obtain this transformation often results in thermal degradation, so it is desirable to reduce the transformation temperature. The transformation temperature has been shown to be a function of many factors including microstructure, grain size, and impurities. In this paper we report an investigation of rapid thermal silicidation of titanium films (250, 400, and 600 Å) on single crystalline silicon at temperatures from 300 to 1000°C. The ramp rates for these experiments are 5, 30, 70, and 200°C/s. The transformation temperature decreases as the ramp rate increases and as the initial film thickness increases. Scanning electron microscopy (SEM) is used to analyze the resultant film microstructure. The ramp rate influence on Ti silicidation is also investigated on polycrystalline Si lines with widths ranging from 0.27 to 3.0 µm.

Introduction

The coming generation of submicron MOS ULSI circuits is expected to require more advanced self-aligned silicide (SALICIDE) technology. Because of the stability of their contacts with silicon and because of their self-passivating property in an oxygen-rich environment, silicides have been preferred over pure metals (1). To date, $TiSi_2$ SALICIDATION has been the process of choice in the semiconductor industry due to its temperature stability and low resistivity. Unfortunately, submicron lines of $TiSi_2$ made from very thin initial Ti films are predominantly the high resistivity C49 phase (2). The troublesome but necessary transformation of the high resistivity C49 phase into the low resistivity C54 phase, an intrinsic material limitation, complicates further scaling of the $TiSi_2$ process. Recently, efforts have been made to overcome these problems. Silicidation was enhanced by pre-amorphization, using ion-implantation with ions of B, Sb, Ge, or others on narrow gate and source/drain regions (3-6). By introducing small quantities of a refractory metal, such as molybdenum, tantalulm, niobium, or tungsten at or near the titanium/silicon interface, the temperature required to form the C54 phase

$TiSi_2$ can be reduced by as much as 100°C (7). Furthermore, the resulting C54-$TiSi_2$ film exhibits small grain size and improved thermal stability.

Nickel mono-silicide (NiSi) has certain advantages over $TiSi_2$ and has been considered as a potential candidate for next generation SALICIDE applications. However, NiSi is limited since it transforms to the higher resistivity $NiSi_2$ phase and agglomerates above 700°C (8). $CoSi_2$ has also been studied extensively (9,10), especially because of the ease of formation on submicron lines without the phase transformation problem. $CoSi_2$ has a resistivity of 16-18 $\mu\Omega$-cm, which is comparable to $TiSi_2$. In production, cobalt technology is also easily implemented on deep submicron lines; has better stability in the presence of dopants; less stress; better plasma etch resistance; lower contact resistance, and a larger process window. As device dimensions are reduced, some advantages are even more pronounced (11). Therefore $CoSi_2$ is a serious candidate to replace $TiSi_2$ for future technologies. However, the fact that $CoSi_2$ consumes more Si than either $TiSi_2$ or NiSi is a significant shortcoming.

In order to extend Ti SALICIDE manufacturing to deep submicron applications there have been detailed studies of the C49 to C54 transformation. The transformation temperature has been shown to be a function of many factors including the silicon microstructure (12), film thickness (13,14,15), C49 grain size (15,16), and impurities present in the film (17). Earlier work has shown (15,16) that the grain size in C49 $TiSi_2$ specimens can be controlled by varying the heating ramp rate (dT/dt). The largest grain sizes were obtained after annealing in a furnace with a ramp rate of 0.4°C/s. Smaller grained $TiSi_2$ films were made by rapid thermal processing (RTP) with ramp rates up to 220°C/s. More recent work (18) also showed that higher ramp rates result in lower sheet resistance for deep submicron polysilicon lines. In this paper we report on RTP of thin titanium films (250, 400, and 600 Å) on single crystalline silicon substrates at temperatures from 300 to 1000°C. The ramp rates for these experiments are 1, 30, 70, and 200°C/s. In order to study the phase transformation, scanning electron microscopy (SEM) is used to characterize the resulting microstructure. The ramp rate influence on Ti SALICIDATION was also investigated on patterned polycrystalline Si lines with widths ranging from 0.27 to 3.0 μm.

Experiment

An RTP system was used to perform the anneals in a nitrogen ambient. One reason for the success of RTP for Ti SALICIDATION is its excellent ambient and temperature control (19) as this process is extremely sensitive to trace amounts of O_2 and H_2O. With our RTP system it is easy to reach O_2 concentrations below 1 ppm and to control wafer temperatures down to 300°C. Samples were prepared by sputtering Ti (250, 400, or 600 Å) on single crystal silicon substrates. RTP of these samples was carried out at temperatures from 300 to 1000°C. The target ramp rates used were 5, 30, 70, and 200 °C/s. The sheet resistance of the as-deposited films and the silicided films were measured with a four point probe. In order to study the ramp rate effects on the resulting film morphology, SEM was used to characterize the thin silicide microstructure.

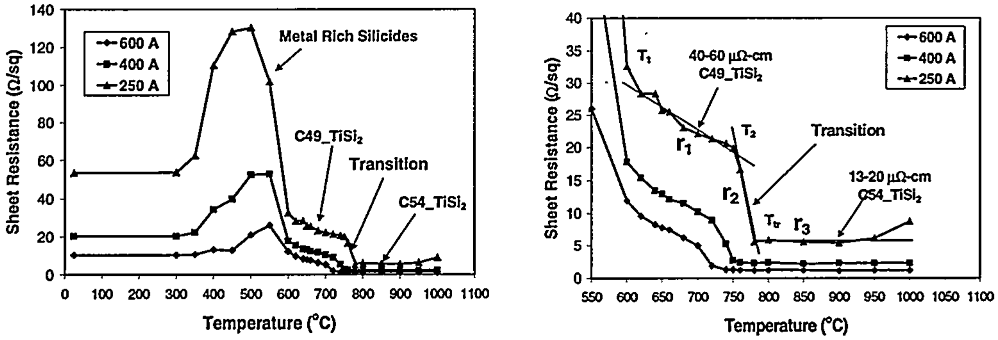
Patterned samples of electrically isolated, thin salicided lines with Si_3N_4 spacers were produced on 150 mm Si wafers. The samples were produced by first growing a 125 Å thermal oxide, then depositing 3000 Å of poly-Si. This poly-Si layer was implanted with

8×10^{15} As/cm^2 at 120 keV, capped with 5000 Å of TEOS oxide, and annealed at 1100 °C in N_2 for 180 minutes. The oxide was stripped and the poly-Si lines were patterned to varying linewidths of 0.27 μm and greater, as measured by SEM. An 1800 Å Si_3N_4 film was then deposited on the samples and etched back to form Si_3N_4 sidewall spacers. The 250 Å or 400 Å Ti films were deposited after cleaning the samples in 5:1 H_2SO_4:H_2O_2 for 5 minutes, SC-1 for 10 minutes, SC-2 for 5 minutes, and 30:1 BOE for 1 minute. The as-deposited sheet resistances of the Ti films were measured to be approximately 36 Ω/sq. for the 250 Å film and 19 Ω /sq. for the 400 Å film. The patterned samples were annealed in the RTP system at 700°C for 20 seconds with three ramp rates of 5, 30, and 200°C/s (RTA1). After RTA1 the patterned samples were etched in SC-1 to remove any TiN and unreacted Ti. Finally, the samples were annealed at 850°C for 30 seconds with a ramp rate of 30°C/s (RTA2).

Results and Discussion

1. Titanium Silicidation for Various Ti Film Thicknesses

Figure 1(a) shows sheet resistances vs. RTP temperature for 250, 400, and 600 Å Ti films on single crystal silicon <100> substrates. For all three Ti thicknesses, the plots of sheet resistance versus anneal temperature reveal three distinct transitions. The first transition is a drastic resistivity increase that occurs above 300 C and corresponds to the formation of metal rich silicides (a mixture of TiSi and Ti_5Si_3). Referring to Figure 1(b) the second transition, which corresponds to the formation of the C49 $TiSi_2$ phase, begins to occur above 600°C and is completed by 620°C in all three cases. The third transition, which corresponds to the transformation from C49 to C54 $TiSi_2$, occurs at increasing temperature, T_2, as the initial film thickness decreases. Once this third transition is complete the resistivity remains stable until agglomeration begins. It is interesting to note that the lower temperature extreme, the C49 to C54 transformation temperature, is highest for the 250 Å film and the upper temperature extreme, where agglomeration begins, is lowest for the 250 Å film.



(a) (b)

Fig.1 (a) Sheet resistance as a function of RTA temperature for 250, 400, and 600 Å Ti films on Si; (b) Enlarged section of Fig.1(a)

The $TiSi_2$ film is in the high resistivity C49 phase between the second and third transitions. The resistivity of the C49 $TiSi_2$ decreases with increasing temperature, which is probably caused by grain coarsening. The slope of this change, denoted by r_1 in Figure

1(b) and Table 1 is known as the sensitivity of RTA1, the first salicide RTP process. It increases with decreasing film thickness. The slope of the third transition, where the low resistivity C54 $TiSi_2$ phase (13-20 μΩ-cm) is formed, is denoted by r_2 in Figure 1(b) and Table 1. The beginning of this last transition, T_2, is defined as the temperature at which the linear fit in the C49 region and the linear fit in the transition region intersect. It is interesting to note that the slope in this third transition region, or the rate of C54 formation, increases as the film thickness decreases. Table 1 also indicates that there is no resistivity change ($r_3 = 0$) after the third transition occurs (until agglomeration begins). This implies that the transformation to the C54 phase produces stable material and that annealing to higher temperatures serves no purpose. T_{tr} is defined as the temperature at which the linear fits to the C49 to C54 transition region and the linear fit to the C54 resistivity intersect. As shown in Table 1, the transition temperature, T_{tr}, rises considerably with decreasing film thickness.

Table 1: Ti Silicidation Characteristics for Various Thicknesses

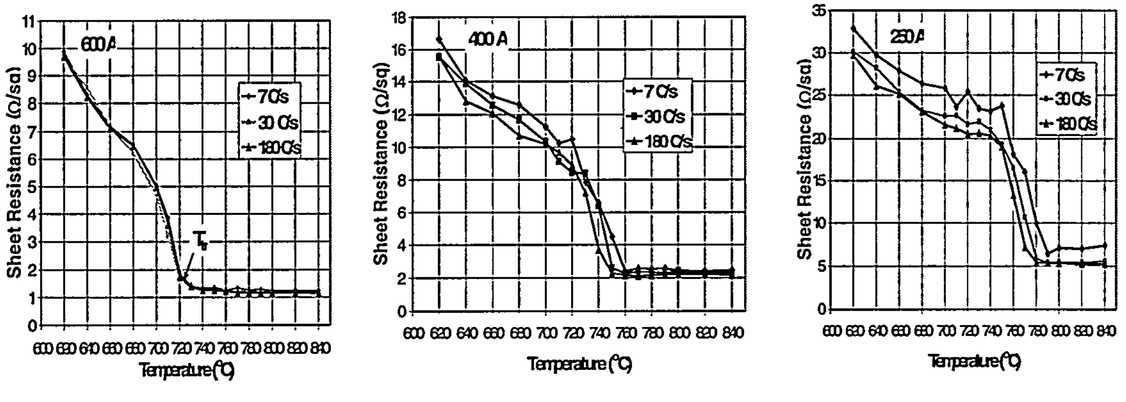
Ti Film Thickness (Å)	RTA1 (T_1-T_2) (°C)	r_1 (RTA1) Ω/sq/°C	r_2 (TRAN.) Ω/sq/°C	r_3 (RTA2) Ω/sq/°C	T_{tr} (C-54) (°C)
600	620-700	0.056	0.143	0	724
400	620-720	0.061	0.217	0	753
250	620-740	0.072	0.512	0	780

2. Ramp Rate Effect on C49 to C54 Phase Transformation

$TiSi_2$ is a polymorphic material and may exist as an orthorhombic base-centered (C49) phase with 12 atoms per unit cell, or as the thermodynamically favored orthorhombic face-centered (C54) phase with 24 atoms per unit cell (20). When a Ti coated Si wafer is heated at temperatures above 500°C, the higher-resistivity (40 – 60 μΩ-cm) metastable C49 phase forms first. Once the C49 phase has formed, a sufficient amount of additional energy must be supplied to overcome the nucleation barrier and enable the phase transformation to the lower resistivity (13 – 20 μΩ-cm) C54 phase. The activation energy required to convert a thin film of C49-$TiSi_2$ on c-Si (100) to C54-$TiSi_2$ is ≥5.6 eV (21). Previous investigations have indicated that the driving force for the C49 to C54 transition is determined by the geometrical component of the free energy (surfaces, grain size), stoichiometry, and impurities (15). It was known from the previous publications (16,22) that the phase transformation temperature decreases with the RTA1 ramp rate. This is due to the smaller grain size of the C49 phase formed with higher RTA1 ramp rate.

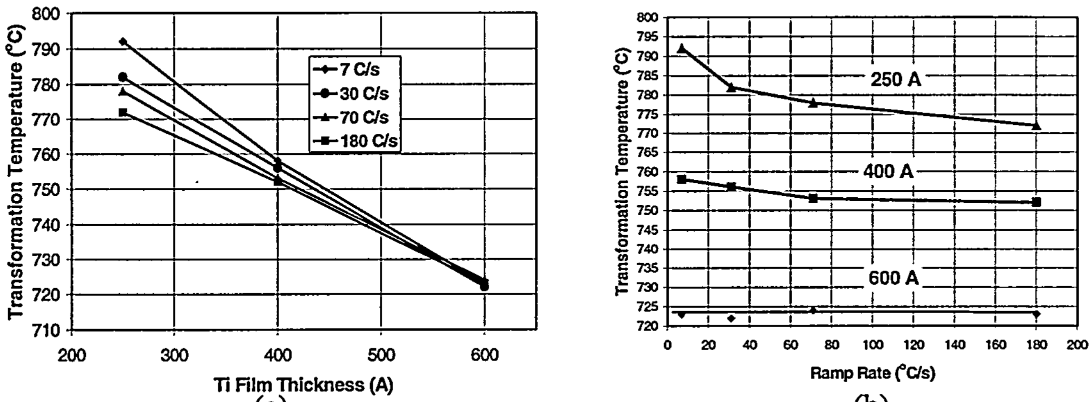
Measurements of the temperature at which the C49 to C54 transformation occurs depend on the analysis method (16,23-25). The transformation temperature can be determined from sheet resistance measurements, X-ray diffraction (XRD) analysis, and other techniques. It has been shown (16) that the transformation temperatures derived from XRD and sheet resistance measurements are the same to within experimental error (±5°C). In this paper we define the transformation temperature, T_{tr}, as the minimum temperature at which the C54-$TiSi_2$ film has reached its lowest resistivity, as shown in Figure 1(b).

In order to study the effect of ramp rate on transformation temperature, samples with different Ti thicknesses were annealed for 20 seconds with ramp rates from about 5°C/s to about 200°C/s. The annealing temperatures ranged from 620 to 840°C. The RTP results are shown in Figure 2(a) for 600 Å Ti films, Figure 2(b) for 400 Å Ti films, and Figure 2(c) for 250 Å Ti films



(a) (b) (c)

Figure 2. Ramp rate effect on the transformation temperature for various Ti thicknesses. (a). 600 A; (b) 400 A; and (c) 250 A.



(a) (b)

Figure 3. Transformation temperature as a function of Ti film thickness (a) and as a function of RTA ramp rate (b).

It was found that both thickness and ramp rate affect the transformation temperature. Thicker Ti films cause the transformation to occur at lower temperatures. The ramp rate effects are different for different Ti film thickness. For the 600 Å Ti films, ramp rates from 7 to 180°C/s do not affect the transformation temperature. However, for the 250 Å Ti film increasing the ramp rate significantly reduces the transformation temperature. The transformation temperature as a function of Ti film thickness and as a function of

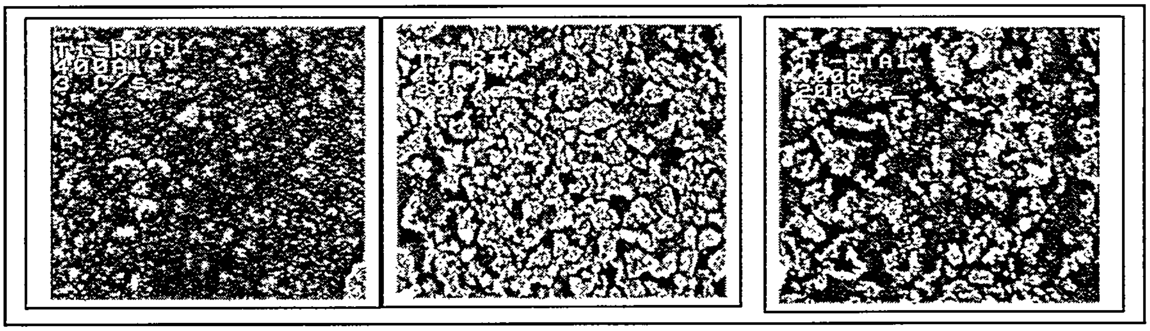
RTP ramp rate is shown in Figures 3(a) and 3(b), respectively. The transformation temperature increases by more than 50°C as the thickness decreases from 600 Å to 250 Å in all cases. On the other hand, the transformation temperature of the 250 Å Ti film decreases by 20°C as the ramp rate increases from 7°C /s to 180°C /s. A summary of transformation temperature dependence on both ramp rate and thickness is shown in Table 2.

Table 2. Transformation Temperatures for Various Thicknesses and Ramp Rates

Ramp Rate °C/s	T_{tr}(°C) 600 Å Ti Film	T_{tr}(°C) 400 Å Ti Film	T_{tr}(°C) 250 Å Ti Film
180	723	752	772
70	724	753	779
30	722	756	782
7	723	758	792

3. SEM Analysis of Ramp Rate Effects

The transformation temperature, T_{tr}, is dependent on the microstructure of the C49 $TiSi_2$ film (15, 16, 22). It has been shown that by varying the ramp rate it is possible to control the grain size in the C49 $TiSi_2$ film (15,16). The largest C49 grain sizes are produced with the lowest ramp rates, while smaller grains are produced by higher ramp rates. In order to study the microstructure of the C49 $TiSi_2$ films, 400 Å Ti films were annealed at 700°C for 20 seconds with ramp rates of 3, 30, and 200°C/s. After annealing, the samples were etched in an SC-1 solution (NH_4OH:H_2O_2:H_2O at 1:1:5) at 75°C for 120 seconds, and the resulting surface was decorated with a 1% HF solution. The samples were then inspected by SEM and the resulting micrographs are shown in Figures 4(a), 4(b), and 4(c). It is clear that the higher ramp rates create smaller grains, which is in agreement with the previous work (16).



(a) (b) (c)

Fig.4 SEM micrographs of 400 Å Ti film on Si after RTA1 at different ramp rates: (a) 3 °C /s; (b) 30 °C /s ; (c) 200 °C /s

4. Ramp Rate Effect on Patterned Samples with Narrow Linewidths

Figure 5 shows the sheet resistance as a function of linewidth and ramp rate for the patterned samples with 400 Å Ti films. As previously shown, the transformation is inhibited by reduced volume (i.e. thinner lines) and reduced ramp rates. The linewidth effect is much more pronounced for the samples ramped at 5°C/s and a significant resistivity increase is already seen for lines of 0.6 µm. It is interesting to note that the sheet resistance for ramp rates of 30 and 200°C/s remains low (<4.2 Ω/sq) for patterned lines as narrow as 0.4 µm. The effect of the very high ramp rate only becomes apparent at very narrow line widths, for example, the 0.27 µm patterned lines. This decrease in resistivity with increasing ramp rate may be of significant technological importance as the critical dimensions for semiconductor devices continue to decrease.

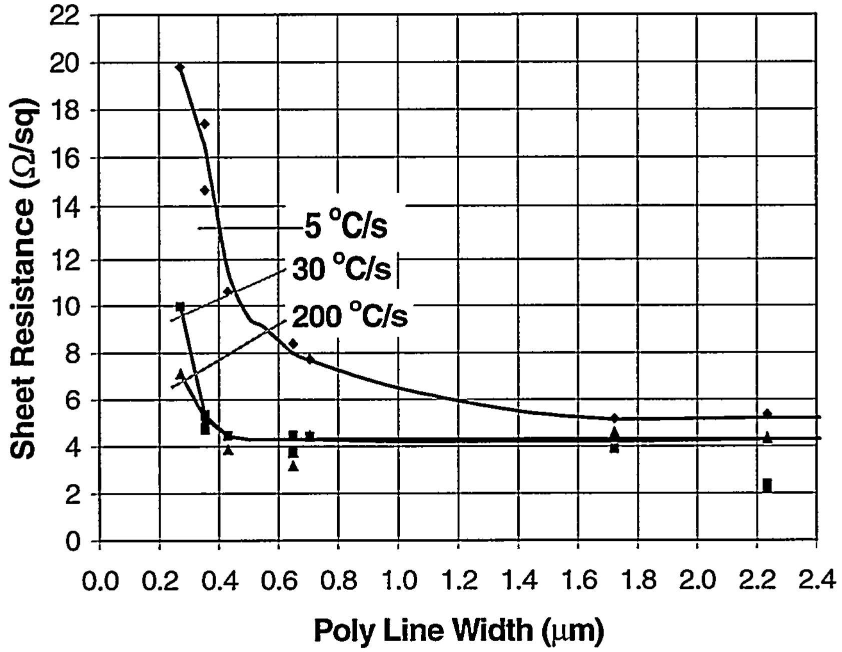


Figure5. Ramp rate effect on sheet resistance of poly lines with different line widths.

Conclusions

It has been found that the C49 $TiSi_2$ to C54 $TiSi_2$ transformation temperature is dependent on both the initial Ti thickness and temperature ramp rate. The transformation temperatures increase by more than 50°C when the thickness decreases from 600 Å to 250 Å. The effect of the ramp rate on the transformation temperature is stronger for thinner films. For the 250 Å Ti films the transformation temperature decreased about 20°C when the ramp rate was increased from 7 to 180°C/s. SEM analysis showed that the ramp rate controls the C49 grain size, with higher ramp rates producing a smaller grain structure. This is of critical importance because the C49 grain structure significantly affects the C49 $TiSi_2$ to C54 $TiSi_2$ transformation. The studies of thin patterned lines indicate that the sheet resistance produced by ramp rates of 200°C/s is significantly lower than the sheet resistance produced by ramp rates of 5°C/s. This ramp rate effect becomes most pronounced for lines with widths below 0.4 µm.

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