

Study of C49-TiSi₂ and C54-TiSi₂ formation on doped polycrystalline silicon using *in situ* resistance measurements during annealing

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In situ resistance versus temperature or time for reactions between 32 and 57.5 nm of titanium and undoped or doped polycrystalline silicon (boron, arsenic, or phosphorus, 7.9×10^{19} – $3.0 \times 10^{20}/\text{cm}^3$) has been measured and no clear correlation was found between the activation energy for the formation of the industrially important low-resistance C54-TiSi₂ phase and its formation temperature. It is also demonstrated that with certain moderate doping levels typical of complementary metal-oxide-semiconductor manufacturing, boron or phosphorus-doped polycrystalline silicon can delay the formation of C54-TiSi₂ more than arsenic-doped polycrystalline silicon. Finally, by using *in situ* resistance measurements, it is demonstrated that the “two-step” thermal annealing process similar to a salicide process requires less thermal annealing time at high temperatures to form C54-TiSi₂ than a single “one-step” thermal anneal at the same temperature. © 1994 American Institute of Physics.

I. INTRODUCTION

Thin-film silicides have generated interest in the semiconductor industry over the last 15 years due to their applications in very large-scale-integration (VLSI) and ultralarge-scale integration (ULSI) complementary metal-oxide-semiconductor (CMOS) circuits.¹ This is because silicides allow for the formation of source, gate, and drain contacts which can significantly reduce the resistance of CMOS gate conductors and/or the source/drain series resistance compared to nonsilicided structures.^{2,3} The lower resistance that silicide contacts provides translates into improved CMOS device performance in terms of switching speed or source/drain drive current.^{3–6}

TiSi₂ has become the most widely used silicide for CMOS source, gate, and drain contacts because of its low resistivity, good thermal stability, and ability to be used in a self-aligned (salicide) process.^{7,8} TiSi₂ is a polymorphic material which forms the high-resistivity (60–70 $\mu\Omega$ cm) C49 base-centered orthorhombic structure from a reaction between titanium and silicon at temperatures between 550 and 650 °C and then transforms into the low-resistivity (15–20 $\mu\Omega$ cm) C54 face-centered orthorhombic structure at annealing temperatures over 650 °C. Since the high resistivity of C49-TiSi₂ is unsuitable for high-performance CMOS device contacts and local interconnections the complete conversion of this phase into the low-resistivity C54-TiSi₂ phase by thermal annealing is critically important.

The C49-TiSi₂ to C54-TiSi₂ transformation has been studied by various authors. Beyers and Sinclair⁹ and d'Heurle *et al.*¹⁰ were the first to identify the polymorphic nature of TiSi₂. The activation energies for C49-TiSi₂ forma-

tion and the C49-TiSi₂ to C54-TiSi₂ transformation have been reported to vary from 1.5 to 2.8 eV and 3.5 to 7.0 eV, respectively,^{2,3,11–19} depending on the particular processing conditions used. Lasky *et al.*,⁷ Agnello and Fink,²⁰ and Ganin *et al.*²¹ have shown that the smaller the silicide features are, the more difficult it becomes to completely transform C49-TiSi₂ into C54-TiSi₂. In general, highly doped *n*-type silicon (especially arsenic doped) is thought to have the highest activation energies for C54-TiSi₂ formation and thus to be the hardest to transform from C49-TiSi₂ to C54-TiSi₂ in patterned or blanket films.^{7,22,23}

In this work we apply the technique of measuring the electrical resistance of titanium/electronically doped polycrystalline silicon bilayer thin films *in situ* during isothermal and temperature-ramped annealing to form both C49- and C54-TiSi₂. This technique has allowed for the detailed monitoring of the effects of annealing cycles, electronic dopants, and titanium film thicknesses on reaction temperatures, reaction times, and activation energies for C49-TiSi₂ and C54-TiSi₂ formation. In particular, we show that for titanium/doped polycrystalline silicon structures, there is no correlation between activation energies for C54-TiSi₂ formation and the temperature and/or annealing times required for its formation. Contrary to earlier reports,^{7,22,23} we also demonstrate that under certain circumstances the amount of thermal processing required for the formation of C54-TiSi₂ on phosphorus- or boron-doped polycrystalline silicon can exceed that required for arsenic-doped polycrystalline silicon. Finally, we demonstrate that a low-temperature preanneal (600 °C, 45 min) to form C49-TiSi₂ followed by a higher-temperature anneal (675 or 725 °C) to convert the C49-TiSi₂ into C54-TiSi₂ requires less annealing time at the higher tem-

perature to form the C54-TiSi₂ phase than a single annealing step at the higher temperature. These results demonstrate the utility of using *in situ* resistance measurements during annealing to study C49-TiSi₂ and C54-TiSi₂ formation.

II. EXPERIMENT

Samples were prepared by first depositing 250–500 nm of polycrystalline silicon by low-pressure chemical-vapor deposition (LPCVD) onto thermally grown silicon oxide. Boron, arsenic, or phosphorus was then implanted into the polycrystalline silicon at energies ranging from 10 to 50 keV. The samples were then coated with 50 nm of SiO₂ grown by LPCVD and then annealed at 900 °C for 60 min to redistribute and activate the dopants. The oxide was then chemically stripped and dopant profiles were measured by secondary-ion-mass spectroscopy (SIMS) analysis. In all cases the dopants were uniformly distributed throughout the polycrystalline silicon layer and the concentrations ranged from 7.9×10^{19} to $3 \times 10^{20}/\text{cm}^3$. The wafers were then dipped in dilute HF to remove any remaining native SiO₂ and loaded into either a MRC 643 magnetron or Varian M2000 sputter deposition system. For samples loaded in the MRC system, 32 nm of titanium was deposited at an Ar sputtering pressure of 10 mT, while for samples loaded into the Varian system, 57.5 nm of titanium was deposited at an Ar sputtering pressure of 4 mT.

The resistance of the titanium/polycrystalline silicon thin film was measured *in situ* during annealing as a function of either temperature at a constant heating rate, or time at a constant annealing temperature.¹⁶ For the constant heating rate experiments, the heating rates were varied from 0.5 to 20 °C/min from 25 to 900 °C, while for isothermal annealing experiments, samples were annealing at either 675, 725, or 735 °C. A small subset of the samples that were used for isothermal experiments was preannealed at 600 °C for 45 min in order to preform C49-TiSi₂. All samples were annealed in He that was first purified at 850 °C in a titanium getter to eliminate any contamination in the annealing gas. The resistance measurement was done *in situ* using a square four-point-probe technique on blanket samples and the data collection was computer controlled. After annealing, x-ray-diffraction measurements were performed for phase identification.

III. RESULTS

The *in situ* resistance versus temperature data for titanium thin films on doped and undoped polycrystalline silicon substrates shows several features which are characteristic of silicide formation. Figure 1 is a plot of resistance and the temperature derivative of resistance versus temperature for 57.5 nm of titanium on top of arsenic-doped polycrystalline silicon. The concentration of the arsenic was $2.7 \times 10^{20}/\text{cm}^3$ and heating rate was 6 °C/min. There are two sharp decreases in the resistance of the film from 550 to 650 °C and from 700 to 725 °C. These decreases in the resistance of the film correspond to three sharp minima in the derivative curve, a double minimum “peak” for the 550–650 °C temperature range and a single minimum “peak” for the 700–

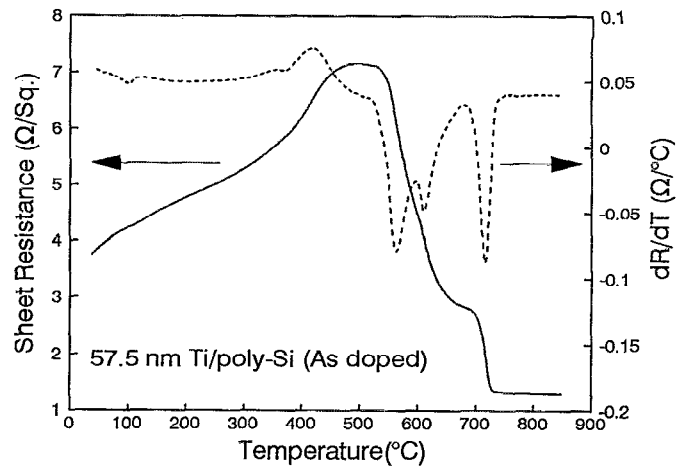


FIG. 1. *In situ* resistance vs temperature and the temperature derivative of resistance vs temperature for 57.5 nm of titanium on top of 300 nm of polycrystalline silicon taken at a heating rate of 6 °C/min. The polycrystalline silicon was doped with arsenic at a concentration of $2.7 \times 10^{20}/\text{cm}^3$.

725 °C temperature. The derivative of the resistance versus temperature curves for the constant scan rate experiments was found to be a reliable method for comparing the reaction sequence of one sample against another and was used extensively in this work.

The structural origins of the peaks in the derivative curve of Fig. 1 were analyzed with x-ray diffraction. As shown in Fig. 2, samples were heated to various points in the transformation process and then quenched and analyzed using x-ray diffraction. The resulting x-ray-diffraction data are shown in Fig. 3. Figure 3(a) shows that the as-deposited titanium has a hcp structure with two preferred orientations, (002) and (101). This result was found to be the same for all the films deposited in the Varian M2000 system, regardless of the doping levels of the polycrystalline underneath the

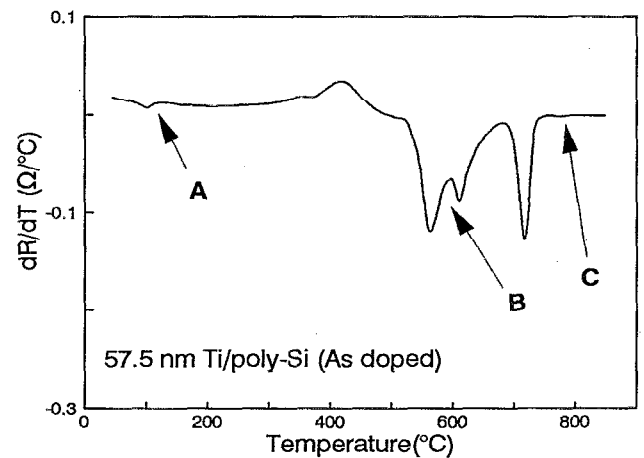


FIG. 2. Temperature derivative of the *in situ* resistance vs temperature for 57.5 nm of titanium on top of 300 nm of polycrystalline silicon taken at a heating rate of 6 °C/min. The polycrystalline silicon was doped with arsenic at a concentration of $2.7 \times 10^{20}/\text{cm}^3$. The labels A, B, C refer to temperatures to which separate samples were heated for x-ray-diffraction analysis.

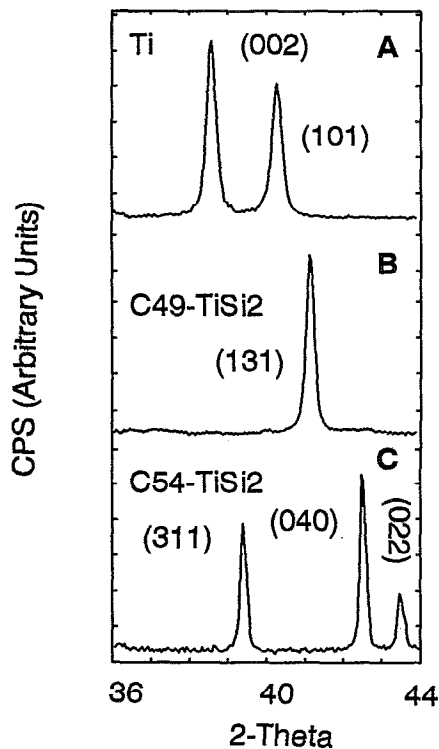


FIG. 3. X-ray-diffraction spectrum for samples A, B, and C of Fig. 2.

titanium. For the titanium films deposited in the MRC system (32 nm), the as-deposited titanium orientation was exclusively (002). Figure 3(b) shows the x-ray-diffraction spectrum for a sample heated to a temperature between the first and second minima in the derivative curve of Fig. 2. These data indicate that by this temperature, the titanium and polycrystalline silicon have reacted to form C49-TiSi₂, allowing for the identification of the first minimum in the derivative curve (and the first big resistance drop in Fig. 1) as being due to C49-TiSi₂ formation. The x-ray-diffraction spectrum (not shown) for samples heated to a temperature between the second and third minima in Fig. 2 indicates that the film is still C49-TiSi₂, indicating that the second minimum is not due to a silicide transformation. There was some experimental evidence that the presence of the second minimum was correlated with the appearance and disappearance of the (060) orientation of C49-TiSi₂. Figure 3(c) shows the x-ray-diffraction spectrum for a sample heated to a temperature just higher than the third minimum in the derivative curve of Fig. 2. These data show that annealing to this temperature causes the C49-TiSi₂ to transform into the low-resistivity C54-TiSi₂ phase and allows the third minimum in the derivative curve (and the second big resistance drop in Fig. 1 at 700 °C) to be identified as being due to the transformation of C49-TiSi₂ into C54-TiSi₂.

As shown in Fig. 4, the derivative minimum for both the C49-TiSi₂ and C54-TiSi₂ formation shift to higher temperature with increasing heating rate. This effect has been reported before for C49 and C54-TiSi₂ formation from a reaction between titanium and undoped polycrystalline silicon and it can be related to the activation energy of TiSi₂ forma-

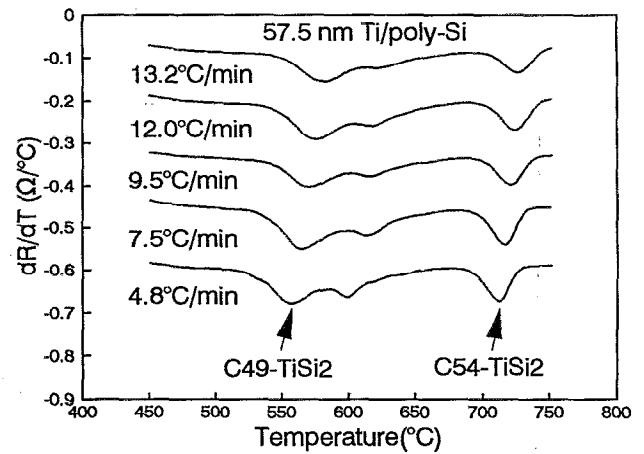


FIG. 4. Temperature derivative of the *in situ* resistance vs temperature for 57.5 nm of titanium on top of 300 nm of polycrystalline silicon for heating rates from 4.8 to 13.2 °C/min. The polycrystalline silicon was doped with arsenic at a concentration of $2.7 \times 10^{20}/\text{cm}^3$.

tion by a method called the Kissinger analysis,^{16,19,24} i.e.,

$$\ln(R/T_p^2) = C - (Q/kT_p), \quad (1)$$

where R is the heating rate, k is Boltzmann's constant, Q is the activation energy, C is a constant, and T_p is the characteristic temperature for either C49 or C54-TiSi₂ TiSi₂ formation at the heating rate R . For this work we assume that this characteristic temperature is the temperature at which the derivative minimum for C49-TiSi₂ or C54-TiSi₂ formation is at its lowest value.

Figure 5 is a plot of Eq. (1) for the derivative data shown in Fig. 4 for the formation of C49 and C54-TiSi₂ formed from a reaction between 57.5 nm of titanium and arsenic-doped polycrystalline silicon. From this figure, the activation energies for C49 and C54-TiSi₂ formation were determined to be 2.8 ± 0.3 and 5.6 ± 0.2 eV, respectively. A similar set of kinetic analysis was done for the formation of C49 and C54-TiSi₂ from a reaction between 57.5 nm of titanium and boron-doped phosphorus-doped, and undoped polycrystalline silicon. The resultant activation energies for C49-TiSi₂ and C54-TiSi₂ formation are summarized in Table I. For this set

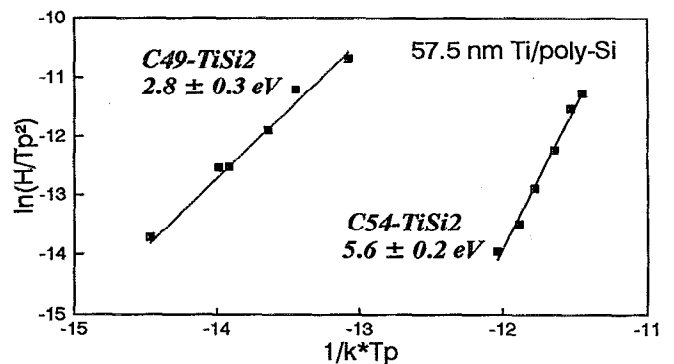


FIG. 5. Kissinger plots for C49-TiSi₂ and C54-TiSi₂ formation calculated from the data of Fig. 4.

TABLE I. A comparison of the activation energy energies for C49-TiSi₂ and C54-TiSi₂ formation from the reaction between 57.5 nm of titanium and polycrystalline silicon. The standard deviation for all the activation energies was between 0.2 and 0.3 eV.

| Dopant type and amount in polycrystalline silicon | Activation energy for C49-TiSi ₂ formation (eV) | Activation energy for C54-TiSi ₂ formation (eV) |
|---|--|--|
| Arsenic: $2.7 \times 10^{20}/\text{cm}^3$ | 2.5 | 5.6 |
| Boron: $2.7 \times 10^{20}/\text{cm}^3$ | 2.8 | 6.5 |
| Phosphorus: $3.0 \times 10^{20}/\text{cm}^3$ | 2.4 | 5.0 |
| Undoped | 2.6 | 6.0 |

of samples the boron- and arsenic-doped polycrystalline silicon had the lowest and highest activation energies for C49-TiSi₂ formation (2.4 and 2.8 eV, respectively) while the phosphorus- and boron-doped polycrystalline silicon has the lowest and highest activation energies for C54-TiSi₂ formation (5.0 and 6.5 eV, respectively). The standard deviation for all the activation energies ranged from 0.2 to 0.3 eV.

The temperature for both C49-TiSi₂ and C54-TiSi₂ formation varies with the type of electronic dopant present in the polycrystalline silicon that is consumed during silicide formation. Figure 6 plots the temperature derivative of the *in situ* resistance versus temperature at a heating rate of 12 °C/min for the undoped, and phosphorus-, boron-, and arsenic-doped samples used in Table I. The phosphorus doping level was $3.0 \times 10^{20}/\text{cm}^3$ while the boron and arsenic levels were both $2.7 \times 10^{20}/\text{cm}^3$. From the minima in the derivative curves in this figure the samples with the lowest to highest C54-TiSi₂ formation temperatures (ranging from 700 to 730 °C) are undoped, and boron-, arsenic-, and phosphorus-doped polycrystalline silicon as summarized in Table II. This order for increasing formation temperatures is different than the order for increasing activation energies for C54-TiSi₂ formation shown in Table I. In that case, the substrates with the

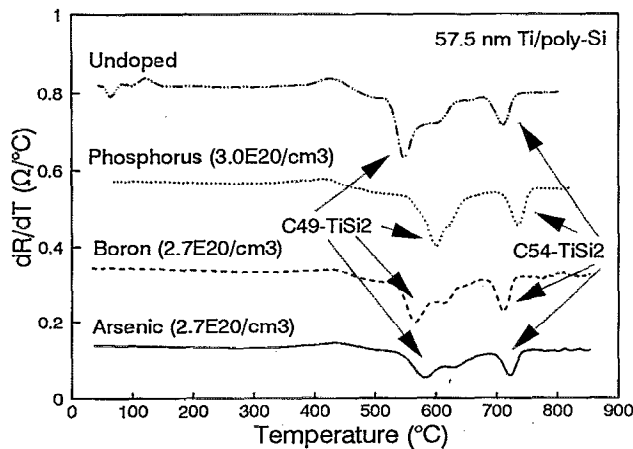


FIG. 6. Temperature derivative of the *in situ* resistance vs temperature for 57.5 nm of titanium on top of 300 nm of polycrystalline silicon at a heating rate of 12 °C/min. The polycrystalline silicon was either undoped or doped with $2.7 \times 10^{20}/\text{cm}^3$ boron, $2.7 \times 10^{20}/\text{cm}^3$ arsenic or $3.0 \times 10^{20}/\text{cm}^3$ phosphorus.

TABLE II. Summary of the C49-TiSi₂ and C54-TiSi₂ formation temperatures vs doping type and concentration in polycrystalline silicon for initial titanium film thicknesses of 57.5 and 32 nm.

| C49-TiSi ₂ and C54-TiSi ₂ formation temperatures | Titanium=57.5 nm | Titanium=32 nm |
|--|---|--|
| | Lowest | Dopant type and concentration in polycrystalline silicon |
| to | undoped | undoped |
| | boron doped ($2.7 \times 10^{20}/\text{cm}^3$) | phosphorus doped ($7.9 \times 10^{19}/\text{cm}^3$) |
| | arsenic doped ($2.7 \times 10^{20}/\text{cm}^3$) | arsenic doped ($9.1 \times 10^{19}/\text{cm}^3$) |
| Highest | phosphorus doped ($3.0 \times 10^{20}/\text{cm}^3$) | boron doped ($2.3 \times 10^{20}/\text{cm}^3$) |

lowest to highest activation energy for C54-TiSi₂ formation (5.0–6.5 eV) are phosphorus- and arsenic-doped, undoped, and boron-doped polycrystalline silicon.

There is a one-to-one correlation between the C54-TiSi₂ formation temperature as determined from the temperature derivative of the *in situ* resistance versus temperature data as shown in Fig. 6 and the amount of time required at a set isothermal annealing temperature to transform a titanium/polycrystalline silicon thin film into C54-TiSi₂. Figure 7 is a plot of the isothermal resistance at 675 °C for the titanium/undoped, and boron-, arsenic-, and phosphorus-doped polycrystalline substrates of Fig. 6. From this figure, all the samples reach a resistance of about 4 Ω/□, characteristic of the conversion of the titanium/polycrystalline silicon bilayer film into C49-TiSi₂/polycrystalline silicon, within a few minutes of the start of the isothermal annealing. In contrast, the amount of time required to convert the C49-TiSi₂ into C54-TiSi₂ (i.e., the time to reach the resistance value of C54-TiSi₂, about 1.2 Ω/□ for these films) varies widely with the doping of the polycrystalline silicon from about 25 min for the undoped polycrystalline silicon structure to over 200 min for the phosphorus-doped polycrystalline sample. In this

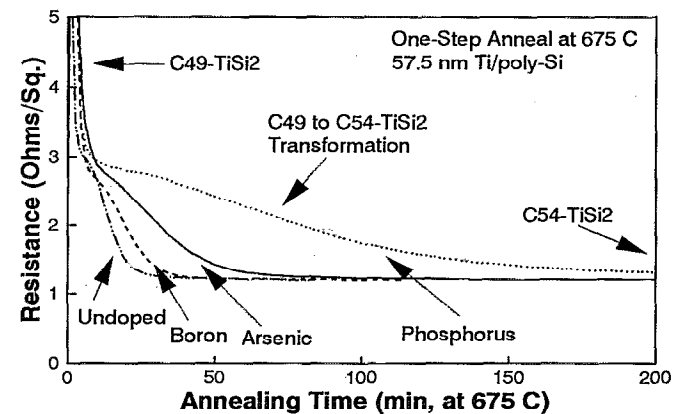


FIG. 7. *In situ* resistance vs time at 675 °C for 57.5 nm of titanium on top of 300 nm of polycrystalline silicon. The polycrystalline silicon was either undoped or doped with $2.7 \times 10^{20}/\text{cm}^3$ boron, $2.7 \times 10^{20}/\text{cm}^3$ arsenic or $3.0 \times 10^{20}/\text{cm}^3$ phosphorus.

TABLE III. The amount of annealing time (min) at 675 °C required for 57.5 nm of titanium on polycrystalline silicon to react to form C54-TiSi₂ and reach a sheet resistance of 2 Ω/□ for a one-step vs two-step annealing process. The resistance of 2 Ω/□ is characteristic of a 57.5 nm titanium/polycrystalline silicon thin film that is mostly converted into C54-TiSi₂. The one-step anneal was a single anneal at 675 °C while the two-step anneal was an anneal at 600 °C for 45 min followed by a single anneal at 675 °C.

| Dopant type and amount in polycrystalline silicon | One-step anneal time at 675 °C (min) | Two-step anneal time at 675 °C (min) |
|---|--------------------------------------|--------------------------------------|
| Arsenic: $2.7 \times 10^{20}/\text{cm}^3$ | 31.0 | 26.5 |
| Boron: $2.7 \times 10^{20}/\text{cm}^3$ | 19.5 | 16.1 |
| Phosphorus: $3.0 \times 10^{20}/\text{cm}^3$ | 79.6 | 56.7 |
| Undoped | 14.2 | 11.9 |

case the samples with the lowest to highest times required for complete conversion of the titanium/polycrystalline bilayer thin film into C54-TiSi₂ are undoped, and boron-, arsenic-, and phosphorus-doped polycrystalline silicon which is the same order as increasing C54-TiSi₂ formation temperatures determined from the derivative curves of Fig. 6.

Using a "two-step" annealing process requires less annealing time at the highest annealing temperature to convert the titanium/polycrystalline silicon thin film into C54-TiSi₂ than a single "one-step" annealing process at that same temperature. Table III presents plots the annealing time at 675 °C for both the one- and two-step annealing process required to convert the as-deposited doped and undoped samples of Fig. 6 into a resistance of 2 Ω/□, which is characteristic of a film that is mostly C54-TiSi₂. This table demonstrates that regardless of the dopant type and concentration in the polycrystalline silicon, 3–24 min less annealing time at 675 °C is required for C54-TiSi₂ formation when formed with a two-step as compared to the one-step process. The thermal annealing of the two-step samples varied from the one-step samples in that they received a 600 °C, 45 min pre-anneal before the 675 °C C54-TiSi₂ transformation anneal. This anneal was done to preconvert these samples into C49-TiSi₂ (as confirmed by x-ray-diffraction analysis) before the 675 °C anneal.

When the titanium film thickness is decreased to 32 nm, the formation temperatures for both C49 and C54-TiSi₂ are increased. Figure 8 is a plot of the temperature derivative of resistance versus temperature at a heating rate of 12 °C/min for 57.5 nm titanium/polycrystalline silicon and 32 nm titanium/polycrystalline silicon where the polycrystalline silicon was doped with either $2.7 \times 10^{20}/\text{cm}^3$ (57.5 nm titanium sample) or $2.3 \times 10^{20}/\text{cm}^3$ (32 nm titanium sample) boron. From this figure, the temperature of the derivative minimum associated with both the C49-TiSi₂ and C54-TiSi₂ formation increase by 40 °C for C49-TiSi₂ and 70 °C for C54-TiSi₂ when the titanium thickness is decreased from 57.5 to 32 nm.

In addition to the 32 nm titanium samples having higher C49- and C54-TiSi₂ formation temperatures compared to the 57.5 nm titanium samples, the ordering of samples with the lowest to highest C54-TiSi₂ formation temperature is different. Figure 9 plots the temperature derivative of the *in situ*

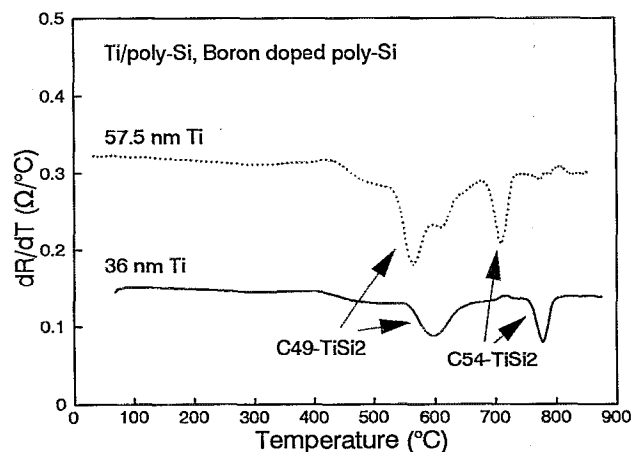


FIG. 8. Temperature derivative of the *in situ* resistance vs temperature for either 32 or 57.5 nm of titanium on top of polycrystalline silicon at a heating rate of 12 °C/min. The polycrystalline silicon was or doped with either $2.7 \times 10^{20}/\text{cm}^3$ (32 nm titanium) or $2.3 \times 10^{20}/\text{cm}^3$ (57.5 nm titanium) of boron.

resistance versus temperature at a heating rate of 12 °C/min for 32 nm of titanium on top of polycrystalline where the polycrystalline silicon is undoped or doped with $7.9 \times 10^{19}/\text{cm}^3$ phosphorus, $2.3 \times 10^{20}/\text{cm}^3$ boron, or $9.1 \times 10^{19}/\text{cm}^3$ arsenic. In this case, the ranking of the C54-TiSi₂ formation temperatures, lowest to highest (from 750 to 790 °C), is undoped, and phosphorus-, arsenic-, and boron-doped polycrystalline silicon. These results are summarized in Table II and are different than the 57.5 nm titanium films shown in Fig. 4. In that case the ordering for C54-TiSi₂ formation temperature from lowest to highest was undoped, and boron-, arsenic-, and phosphorus-doped polycrystalline substrates. It should be noted, however, that even though the ordering among the dopants for the C54-TiSi₂ formation temperature was different for the samples with 32 or 57.5 nm titanium, the same general trends for isothermal

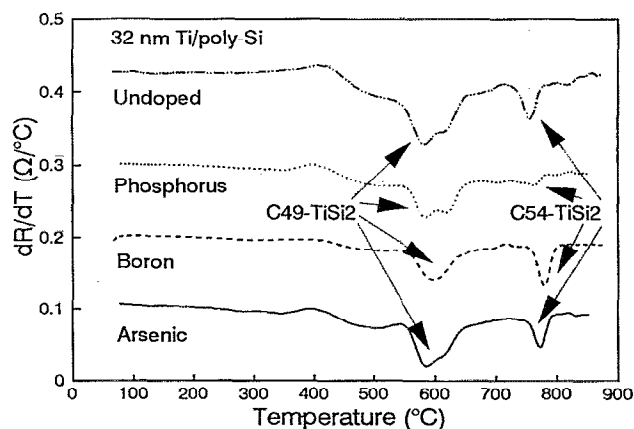


FIG. 9. Temperature derivative of the *in situ* resistance vs temperature for 32 nm of titanium on top of 300 nm of polycrystalline silicon at a heating rate of 12 °C/min. The polycrystalline silicon was either undoped or doped with $2.3 \times 10^{20}/\text{cm}^3$ boron, $9.1 \times 10^{19}/\text{cm}^3$ arsenic or $7.9 \times 10^{19}/\text{cm}^3$ phosphorus.

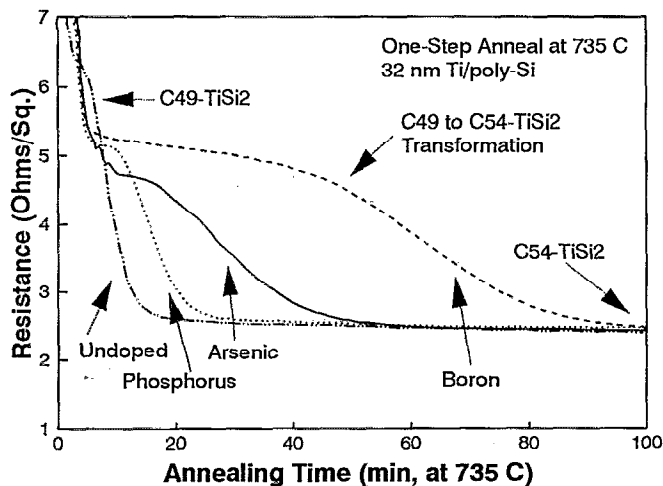


FIG. 10. *In situ* resistance vs time at 675 °C for 32 nm of titanium on top of 300 nm of polycrystalline. The polycrystalline silicon was either undoped or doped with $2.3 \times 10^{20}/\text{cm}^3$ boron, $9.1 \times 10^{19}/\text{cm}^3$ arsenic, or $7.9 \times 10^{19}/\text{cm}^3$ phosphorus.

annealing times required to form C54-TiSi₂ were observed for all samples (see Figs. 9 and 10)—samples with higher C54-TiSi₂ formation temperatures as determined by the temperature derivative of resistance versus temperature data measured under constant heating rate conditions required longer isothermal annealing times to transform into C54-TiSi₂ from the original titanium/polycrystalline silicon thin films. In addition, Table IV shows that the 32 and 57.5 nm titanium samples were also similar in that samples annealed with a two-step annealing process (600 °C, 45 min + 725 °C) required less annealing time at 725 °C to form C54-TiSi₂ than the samples annealed with a one-step annealing process at 725 °C.

IV. DISCUSSION

To date, there is only a limited amount of published results on the correlation between the measured activation energy for C54-TiSi₂ formation and the temperature of thermal annealing required to form the C54-TiSi₂ phase.^{14–16} Matsubara and co-workers¹⁴ showed that both the annealing temperature required to form C54-TiSi₂ from a reaction between

TABLE IV. The amount of annealing time (min) at 725 °C required for 32 nm of titanium on polycrystalline silicon to react to form C54-TiSi₂ and reach a sheet resistance of 3.6 Ω/□ for a one-step vs two-step annealing process. The resistance of 3.6 Ω/□ is characteristic of a 32 nm titanium/polycrystalline silicon bilayer film that is mostly converted into C54-TiSi₂. The one-step anneal was a single anneal at 725 °C while the two-step anneal was an anneal at 600 °C for 45 min followed by a single anneal at 725 °C.

| Dopant type and amount in polycrystalline silicon | One-step anneal time at 725 °C (min) | Two-step anneal time at 725 °C (min) |
|---|--------------------------------------|--------------------------------------|
| Arsenic: $9.1 \times 10^{19}/\text{cm}^3$ | 66.5 | 53.5 |
| Boron: $2.3 \times 10^{20}/\text{cm}^3$ | 209.4 | 135.9 |
| Phosphorus: $7.9 \times 10^{19}/\text{cm}^3$ | 31.0 | 28.4 |
| Undoped | 24.1 | 20.4 |

titanium and arsenic-doped <100> silicon, and the measured activation energy for C54-TiSi₂ formation increase with increasing concentrations of arsenic. On the other hand, Li *et al.*¹⁵ have shown that antimony doping of codeposited TiSi₂ increases the activation energy for C54-TiSi₂ formation and decreases its formation temperature. For C54-TiSi₂ formation from a reaction between titanium and polycrystalline silicon in which the silicon is either undoped or doped with phosphorus, boron, or arsenic, the results of Figs. 4 and 5 and Tables I and II indicate that there is no correlation between increasing activation energy for C54-TiSi₂ formation and the annealing temperature and/or time required to form it.

The work of Matsubara and co-workers,¹⁴ Li *et al.*,¹⁵ and the results presented in this article indicate that in general it is probably not useful to use the activation energies for C54-TiSi₂ formation as a gauge of the amount of thermal annealing required to form this phase. This is because there is not always a straightforward relationship between the activation energy for C54-TiSi₂ formation and its formation temperature when it is formed under different conditions. The activation energy for C54-TiSi₂ formation from the work of Matsubara and co-workers,¹⁴ Li *et al.*,¹⁵ and the results presented in this article was determined by first calculating the fraction of C54-TiSi₂ formed during a set of annealing experiments, where it was assumed that the amount of C54-TiSi₂ formed was directly proportional to an experimentally measurable property (x-ray-diffraction peak area, or resistance in the above examples). Using the Avrami analysis,²⁵ this fraction transformed is exponentially proportional to the activation energy for C54-TiSi₂ formation, nucleation site densities, nucleation rates, growth rates, atomic jump frequencies, nuclei geometry, and the C54-TiSi₂ formation temperature. In turn these parameters are all dependent on various material properties such as the titanium deposition technique and the grain structures of the titanium, polycrystalline silicon, and C49-TiSi₂.^{26–32} For example, Cabral *et al.*³¹ and Hara *et al.*^{26,27} have recently shown that the formation temperature for C54-TiSi₂ is dependent on the Ar pressure during the sputter deposition of the initial titanium film, a fact they attributed to the dependence of the C54-TiSi₂ formation on the texture and microstructure of the as-deposited titanium film (which varies with deposition pressure³²). In addition, van Houtum and co-workers³⁰ and Mann and co-workers²⁸ have shown that the C54-TiSi₂ nucleation kinetics are dependent on the precursor C49-TiSi₂ grain structure, with a higher C54-TiSi₂ formation temperatures correlated with a larger C49-TiSi₂ grain size. Thus, with all these dependencies, it is difficult to make a general correlation between the activation energy for C54-TiSi₂ formation and a characteristic formation temperature. This would be expected to be especially true for the samples used in this article where the different electronic dopants in the polycrystalline silicon would be expected to affect each of the relevant kinetic parameters differently. It is interesting to note that for the work of Matsubara and co-workers,¹⁴ and Li *et al.*¹⁵ there is a correlation, although opposite in the two cases, between the activation energies for C54-TiSi₂ formation and its formation temperature and the amount of either

arsenic or antimony in the silicide films. This suggests that in the limited cases where the titanium or amorphous TiSi_2 precursor thin films are deposited in exactly the same way and where a single type of dopant is used, the various kinetic parameters are simple enough that there is a correlation between the activation energy for C54-TiSi_2 formation and its formation temperature.

It is an important result that a larger amount of thermal annealing was required to form C54-TiSi_2 from a reaction between titanium and silicon when the polycrystalline silicon was either heavily doped with phosphorus (Figs. 7 and 8) or boron (Fig. 10). In contrast with other published reports,^{22,23} our results indicate that C54-TiSi_2 formation is not always the most difficult on arsenic-doped silicon substrates. While there is one published report of C54-TiSi_2 having a higher growth rate on arsenic-, as compared to phosphorus-doped, substrates,³³ most of the published literature has shown arsenic-doped substrates to have the greatest effect on retarding the C54-TiSi_2 formation rate compared to other dopants.^{7,22,23} There are several possible explanations for the different results found in the present set of experiments. First, in previous work of Beyers and co-workers²² and Park *et al.*²³ showing arsenic retarding the formation of C54-TiSi_2 more than phosphorus, they used similar amounts of phosphorus or arsenic at concentration levels above $5 \times 10^{20}/\text{cm}^3$.³ In this article lower doping levels are used (between 7.9×10^{19} and $3 \times 10^{20}/\text{cm}^3$) and the concentrations of arsenic, phosphorus, and boron are different for each of the two metal thicknesses. At high doses, previous published work indicates that arsenic dopants in the silicon substrate do retard C54-TiSi_2 formation more than phosphorus or boron dopants due to TiAs precipitate formation and/or arsenic pileup at the titanium/silicon interface.^{22,23,34} The results presented in this article indicate that this observation is not universally applicable to all possible dopant implant conditions. At arsenic concentrations less than $5 \times 10^{20}/\text{cm}^3$ one would expect a smaller amount of TiAs formation or dopant pileup at the titanium/silicon interface which would retard the formation of C54-TiSi_2 less than if the arsenic concentration was higher. Thus, when comparing the arsenic-doped samples to more highly doped boron- or phosphorus-doped samples, the amount of dissolved phosphorus or boron in C49-TiSi_2 could be high enough to have a greater delaying effect on C54-TiSi_2 transformation kinetics. This hypothesis would explain the data shown in Figs. 6 and 7 and 9 and 10 where the samples with the longest required annealing time to form C54-TiSi_2 have the highest doping levels (Figs. 6 and 7, phosphorus: $3.0 \times 10^{20}/\text{cm}^3$, Figs. 9 and 10, boron: $2.3 \times 10^{20}/\text{cm}^3$). Another important difference between this work and previous work that could contribute to the different results is that in previous work, *ex situ* measurements after annealing such as transmission electron microscopy or four-point resistance measurements were used to study silicide formation. With *ex situ* measurements it is hard to detect subtle differences in C54-TiSi_2 formation rates on differently doped silicon substrates due to difficulty in choosing a set of heating conditions that will highlight the desired effects. With the *in situ* resistance measurements used in this study, the entire transformation process from a titanium/silicon bi-

layer thin film to C54-TiSi_2 is recorded during the annealing cycle and subtle differences between different samples are more obvious.

The fact that a shorter annealing time at the C54-TiSi_2 formation temperature is possible using a two-step anneal process (a first anneal at 600°C to preform C49-TiSi_2 and then a second formation anneal at either 675 or 725°C to transform the C49-TiSi_2 into C54-TiSi_2) as compared to just a one-step (anneal at 675 or 725°C) can be explained by one of two mechanisms. First, during the first step of the two-step anneal, the titanium/silicon bilayer film is converted into C49-TiSi_2 . Thus, when the film is annealed for the second part of the two-step anneal, it can immediately start converting from C49-TiSi_2 into C54-TiSi_2 . In comparison, when the titanium/silicon film is transformed into C54-TiSi_2 by using a single one-step anneal, C49-TiSi_2 must form first and then start to transform into C54-TiSi_2 . This reaction step takes a finite amount of time and, compared to a two-step process, increases the total amount of annealing time at the highest annealing temperature to completely transform the sample into C54-TiSi_2 . Another possibility is that some small nuclei of C54-TiSi_2 form during the first anneal of the two-step process. These nuclei would have to be small since x-ray-diffraction analysis of all the samples taken at this stage detected only C49-TiSi_2 ; but if they did exist, they would immediately start to grow during the second part of the two-step anneal and the sample would require a shorter amount of annealing time at this temperature to transform into C54-TiSi_2 compared to a sample that did not have the pre-existing nuclei. Other possible explanations for the differences in two-step and one-step transformation anneals dealing with dopant effects and C49-TiSi_2 grain-size distributions do not explain our results. If dopant effects were a controlling factor, one would expect a larger amount of annealing at the highest temperature for the two-step anneal compared to the one-step anneal due to the fact that the additional low-temperature anneal would increase the concentration of dopants in the precursor C49-TiSi_2 . Similarly, if the C49-TiSi_2 grain size were important, one would also expect a larger required amount of annealing at the highest temperature for the two-step anneal compared to the one-step anneal due to the additional low-temperature anneal which should give a larger C49-TiSi_2 grain size and longer C54-TiSi_2 formation times³⁰ for the two-step annealing process. It must also be noted that the results presented in this work were for samples annealed in purified He, not nitrogen as is typically done in the semiconductor industry. This eliminated any effects of titanium nitride formation on the C54-TiSi_2 formation kinetics. Also, the samples were not chemically etched after the first anneal of the two-step process. This allowed for the thickness of the C49-TiSi_2 formed during the first anneal of the two-step process to be the same for all the different doped polycrystalline silicon substrates and eliminated thickness variations in the C49-TiSi_2 as a factor influencing the C49- to C54-TiSi_2 transform kinetics.

Finally, it should be mentioned that the fact that higher temperatures for C54-TiSi_2 formation determined from *in situ* resistance measurement at constant heating rates correlate with a larger amount of time required during an *in situ*

isothermal resistance measurement to form C54-TiSi₂. This has practical implications in the development of titanium silicide thin films for electronic applications. In practice, it is quicker to perform and analyze the results of an *in situ* resistance measurement under a constant heating rate condition as opposed to an isothermal heating condition which in turn is much quicker than using *ex situ* resistance measurements to obtain the same information.³⁴ Thus, the development time required to create a titanium silicide process for a CMOS circuit can be significantly optimized by using *in situ* resistance measurements under constant heating rate conditions.

V. CONCLUSION

We have shown that *in situ* resistance versus temperature and/or time measurements can be used to study the formation of C54-TiSi₂ from a reaction between titanium films (32 or 57.5 nm) and undoped or doped polycrystalline silicon thin films. Activation energies for the formation of C54-TiSi₂ from a reaction between 57.5 nm of titanium and undoped, and boron-, phosphorus, and arsenic-doped polycrystalline silicon (2.7×10^{20} – $3.0 \times 10^{20}/\text{cm}^3$) were measured to be from 5.0 to 6.5 eV. These activation energies did not correlate with the formation temperature for the C54-TiSi₂ phase. In particular, the sample with the highest formation temperature (phosphorus-doped polycrystalline silicon, $3.0 \times 10^{20}/\text{cm}^3$), did not have the highest activation energy for formation (5.0 eV). Our results also show that under certain conditions typical of CMOS manufacturing, boron- or phosphorus-doped polycrystalline silicon will delay the formation of C54-TiSi₂ more than arsenic-doped polycrystalline. Finally, for all samples examined in this work, a two-step isothermal annealing process (600 °C, 45 min plus 675 or 725 °C) similar to a silicide process required less annealing time at high temperature to form C54-TiSi₂ than a single one-step anneal at the same temperature.

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