SAN099-2419J

The Effect Of Ramp Rate On The C49 To C54 Titanium Disilicide Phase Transformation From Ti And Ti(Ta)

Paul Martin Smith and Glenn Bailey

Sandia National Laboratories, Albuquerque, NM 87185-1084

Yao Zhi Hu and Sing Pin Tay

Steag RTP Systems Inc., 4425 Fortran Dr., San Jose, CA 95134

RECEIVED
OCT 20 1989
OSTI

The C49 to C54 TiSi_2 transformation temperature is shown to be reduced by increasing the ramp rate during rapid thermal processing and this effect is more pronounced for thinner initial Ti and Ti(Ta) films. Experiments were performed on blanket wafers and on wafers that had patterned polycrystalline Si lines with Si_3N_4 sidewall spacers. Changing the ramp rate caused no change in the transformation temperature for 60 nm blanket Ti films. For blanket Ti films of 25 or 40 nm, however, increasing the ramp rate from 7 to 180°C/s decreased the transformation temperature by 15°C . Studies of patterned lines indicate that sheet resistance of narrow lines is reduced by increased ramp rates for both Ti and Ti(Ta) films, especially as the linewidths decrease below $0.4\ \mu\text{m}$. This improvement is particularly pronounced for the thinnest Ti(Ta) films, which exhibited almost no linewidth effect after being annealed with a ramp rate of 75°C/s .

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. Introduction

Self-aligned titanium silicide (Ti-salicide) has been used for many generations of ULSI devices because of its temperature stability and low resistivity.^{1,2} Unfortunately, reliably producing low resistivity TiSi_2 on lines narrower than $\approx 0.3 \mu\text{m}$ is difficult.^{1,3-5} If Ti-salicide is to remain a viable technology for ULSI applications, techniques must be found that overcome this difficulty. Toward that end, we show that the ramp rate used for Ti-salicide processing is an important parameter for controlling this linewidth effect.

Titanium disilicide is a polymorphic material that may exist as the C49 phase or as the thermodynamically favored C54 phase.⁶ During annealing of thin Ti films in contact with Si the first TiSi_2 phase to form is C49, which forms above 500°C , is metastable, and has a high resistivity ($40 - 90 \mu\Omega\text{-cm}$). Upon continued heating to over 700°C the C49 transforms to C54, which is stable and has a low resistivity ($15 - 20 \mu\Omega\text{-cm}$).^{2,4,6,7} The activation energy for this transformation is $\geq 3.7 \text{ eV}$.⁶⁻⁸

Typical Ti-salicide processing^{2,9} consists of depositing a Ti film on a patterned wafer with regions of exposed Si in a field of dielectric material, typically SiO_2 or Si_3N_4 . A rapid thermal process (RTP) is performed at a relatively low temperature, about 700°C , to react the Ti and exposed Si to form C49 TiSi_2 while the remaining Ti is unreacted. This RTP is done in a N_2 ambient, which creates a thin TiN layer over the entire wafer. The low RTP temperature and TiN prevent bridging, or electrical shorting, by reducing lateral Si diffusion.² A wet etch is then used to selectively remove only the TiN and unreacted Ti. A second RTP is performed at a relatively high temperature, about 850°C , to transform the C49 into the desired C54 TiSi_2 phase. Thermal budget issues and TiSi_2 agglomeration^{2,3} limit the temperature of this RTP.

Previous work has shown the C54 TiSi_2 phase selectively nucleates in thin films of C49 TiSi_2 at a grain edge (where three grains meet).¹⁰ Once the linewidth shrinks below the size of an average C49 grain (i.e., bamboo structure) grain edges are rare and nucleation of the C54 phase is significantly reduced.¹ This problem is further aggravated by the fact that typical Ti-salicide thicknesses are also decreasing and the problem is actually caused by the limited volume of TiSi_2 material being transformed. In order to extend Ti-salicide manufacturing to deep submicron applications there have been many studies of the C49 to C54 transformation.³⁻¹⁶ The transformation temperature has been shown to be a function of film thickness,^{6,17} C49 grain size,¹² dopants in the Si,³ and other factors. The transformation temperature is reduced by small quantities of refractory metal, such as Mo, Ta, Nb, or W, introduced at or near the Ti/Si interface.^{5,7,11,13} Earlier work also showed the C49 grain size of blanket Ti films on $\langle 100 \rangle$ Si can be reduced, and the transformation

temperature lowered, by increasing the ramp rate of the first RTP.¹² More recent work showed that higher ramp rates result in lower sheet resistance for deep submicron lines.¹⁴ In this paper we report on varying the as-deposited Ti or Ti(Ta) film thicknesses and ramp rates during RTP of blanket films and patterned lines. The C49 to C54 transformation temperature is reduced by increasing the as-deposited film thickness and by increasing the RTP ramp rate.

II. Experiment

Blanket samples were prepared by sputtering nominally 25, 40, or 60 nm Ti films onto 300 nm of undoped polycrystalline Si (poly-Si). The poly-Si was deposited on a 12.5 nm grown oxide and these substrates were annealed at 600°C for 60 minutes and 900°C for 30 minutes to fully crystallize the poly-Si and reduce film stress prior to Ti deposition. All of the sputter depositions in this study, on both blanket and patterned samples, were performed with no sputter etch. RTP of the blanket samples was carried out at temperatures ranging from 300 to 1000°C with ramp rates of 7, 30, 70, and 180°C/s. The sheet resistance of the as-deposited films and the silicided films were measured by four-point probe. Our definition of the transformation temperature, T_{TR} , follows Lin and Pramanik,¹⁵ and is defined as the temperature where a linear fit to the sheet resistance in the C49 to C54 transformation region intersects a linear fit to the sheet resistance in the C54 region.

Patterned samples of electrically isolated, Ti-silicided lines designed to maximize the linewidth effect were produced on 150 mm Si <100> wafers. The processing started with a 12.5 nm grown thermal oxide followed by 300 nm of deposited poly-Si. The poly-Si was implanted with 8×10^{15} As/cm² at 120 keV, capped with 500 nm of deposited oxide, and annealed at 1100°C in N₂ for 180 minutes to activate the implant and reduce film stress. The oxide was stripped and the poly-Si was patterned to linewidths of 0.27 μ m and greater, as measured by scanning electron microscopy (SEM) after the processing was complete. A 180 nm Si₃N₄ film was deposited on the samples and etched back to form sidewall spacers. The wafers were cleaned in 5:1 H₂SO₄:H₂O₂ for 5 minutes, SC-1 for 10 minutes, SC-2 for 5 minutes, and 30:1 BOE for 1 minute immediately prior to Ti or Ti(Ta) deposition. The nominally 40 nm Ti film was sputter deposited. The nominally 25 and 40 nm Ti(Ta) films were sputtered from a Ti(Ta) target that was produced by evaporating 300 nm of Ta onto the erosion zone of a pure Ti sputter target. The Ta was evaporated onto the Ti target through a patterned shield and the resulting Ti(Ta) target produced approximately 100 nm of sputtered Ti(Ta) material ($\approx$ 4 at. % Ta in Ti) before all the Ta was eroded from the sputter target. Approximately 10 nm of material was deposited from the Ti(Ta) target onto

a dummy wafer to clean the target and then the 25 and 40 nm of Ti(Ta) was deposited onto the patterned wafers. The composition of the Ti(Ta) was determined by Rutherford backscattering spectrometry (RBS) on a similarly produced film. The as-deposited sheet resistance of the films was $\approx 19 \text{ } \Omega/\text{sq.}$ for the 40 nm Ti film, $\approx 25 \text{ } \Omega/\text{sq.}$ for the 40 nm Ti(Ta) film, and $\approx 36 \text{ } \Omega/\text{sq.}$ for the 25 nm Ti(Ta) film. The patterned wafers were diced into samples and annealed in an RTP system at 700°C for 20 seconds with ramp rates of 5, 30, and 75°C/s for the Ti film and 30 and 75°C/s for the Ti(Ta) films. The samples were then etched in SC-1 to remove any TiN and unreacted Ti and the samples were annealed at 850°C for 30 seconds with a ramp rate of 30°C/s .

III. Results and Discussion

A. Blanket Ti Samples

Figure 1 shows sheet resistance versus RTP temperature for the 25, 40, and 60 nm blanket Ti films annealed from 300 to 1000°C with a ramp rate of 70°C/s . There are three distinct transitions for all three thicknesses. The first transition, with increasing temperature, is a resistivity increase that occurs above 300°C and probably corresponds to the formation of a metal rich silicide.¹⁸ The second transition corresponds to the C49 formation and occurs by 620°C in all three cases. The gradual decrease in resistivity between the second and third transitions is probably due to grain coarsening of the C49 phase. The third transition corresponds to the transformation from C49 to C54 and always occurs within a $\approx 30^\circ\text{C}$ temperature window, although the window shifts higher in temperature as the Ti film thickness decreases. Once the third transition is complete, at temperature T_{TR} , the resistivity remains stable until agglomeration begins. Note that the thinnest Ti film has both the highest transformation temperature and the lowest agglomeration temperature. This provides a good illustration of why the Ti-silicide process window is narrowing as device geometries decrease.

Blanket samples with Ti thicknesses of 25, 40, and 60 nm were annealed for 20 seconds at temperatures from 620 to 840°C with ramp rates of 7, 30, and 180°C/s . Figure 2 shows the sheet resistances versus RTP temperatures for the 25 and 60 nm blanket Ti films. It is obvious that the transformation temperature of the 60 nm Ti film is not affected by increasing the ramp rate, while the transformation temperature of the 25 nm Ti film is monotonically reduced by increasing the ramp rate. The transformation temperatures, T_{TR} , for all the blanket films are plotted in Figure 3 as a function of nominal Ti film thicknesses. In all cases, the transformation temperature increased by at least 50°C as the thickness decreased from 60 to 25 nm. Changing the ramp rate did not significantly affect T_{TR} for the 60 nm Ti films. For the 40 and 25 nm Ti films, however, T_{TR} was reduced by 15°C as

the ramp rate was increased from 7 to 180°C. This clearly shows that increasing the ramp rate partially compensates for the increase in T_{TR} that occurs as the film thickness decreases.

B. Patterned Ti and Ti(Ta) Samples

Figure 4 shows sheet resistance as a function of linewidth and ramp rate for the patterned samples with 40 nm Ti. Each data point is an average of two or four measurements and the error bars indicate the maximum and minimum data values. As expected, the sheet resistance increases as the lines narrow, indicating that the transformation is being inhibited by the volume reduction. With a ramp rate of 5°C/s there is already a significant increase by 0.6 μm and the sheet resistance increases by a factor of $\approx 2.4\times$ at the minimum linewidth. As the ramp rate increases the linewidth effect progressively decreases. The sheet resistance increase observed for the sample with the 75°C/s ramp rate was only $\approx 10\%$ at 0.4 μm and only a factor of $\approx 1.8\times$ at the minimum linewidth of 0.27 μm .

For the 40 nm Ti(Ta) film, there was no observed linewidth effect. Because this effect is clearly seen for the 40 nm Ti film, the difference is attributed to the ≈ 4 at.% Ta in the film, which agrees with previously published findings.^{5,13} Figure 5 shows the sheet resistance as a function of linewidth and ramp rate for the patterned samples with 25 nm Ti(Ta) films. As in Figure 4, each data point is an average of two or four measurements and the error bars indicate the maximum and minimum data values. There is an obvious reduction in the linewidth effect due to the increased ramp rate. With a ramp rate of 30°C/s there is an increase in sheet resistance at 0.7 μm that continues to grow with decreasing linewidth until it has increased by a factor of $\approx 2.1\times$ at the minimum linewidth. In sharp contrast, increasing the ramp rate to 75°C/s has essentially eliminated the linewidth effect and there is only a $\approx 10\%$ increase in the sheet resistance even at the minimum linewidth.

IV. Conclusions

This work has shown that the C49 to C54 TiSi_2 transformation temperature is increased by reducing the initial Ti film thickness and reduced by increasing the RTP ramp rate. This effect was observed for Ti and Ti(Ta) films. The transformation temperature increased by at least 50°C for blanket Ti films, from $\approx 720^\circ\text{C}$ to over 770°C , when the film thickness decreased from 60 to 25 nm. The effect of ramp rate on the transformation temperature was strongly affected by the initial film thickness. Varying the ramp rate caused no change in the transformation temperature for the 60 nm blanket Ti films. For blanket films of 25 or 40 nm, however, increasing the ramp rate from 7 to 180°C/s decreased the transformation temperature by 15°C. Studies of patterned lines indicate that sheet

resistance of narrow lines is also reduced by increased ramp rates for both Ti and Ti(Ta) films, especially as the linewidths decrease below 0.4 μm . This improvement is particularly pronounced for the 25 nm Ti(Ta) film, which exhibited virtually no linewidth effect to below 0.3 μm after being annealed with a 75°C/s ramp rate. This result may be of significant technological importance as critical dimensions for semiconductor devices continue to decrease.

The authors would like to thank the personnel at Sandia's Microelectronics Development Laboratory (MDL) for wafer processing. Pat Shea produced SEM micrographs for this work. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

References

- ¹ Q.Z. Hong, J.A. Kittl, and M.S. Rodder, in *Advanced Metallization for ULSI Applications in 1995*, edited by Russell C. Ellwanger and Shi-Qing Wang (Materials Research Society, Pittsburgh, PA, 1996) pp. 431-438.
- ² E.G. Colgan, J.P. Gambino, and Q.Z. Hong, *Mater. Sci. and Engr.* **R16**, 2, 43 (1996).
- ³ E. Ganin, S. Wind, P. Ronsheim, A. Yapsir, K. Barmak, J. Bucchignano, and R. Assenza, in *Materials Research Society Symposium Proceedings Volume 303, Rapid Thermal and Integrated Processing II*, edited by Jeffrey C. Gelpey, J. Kiefer Elliott, Jimmie J. Wortman, and Atul Ajmera (Materials Research Society, Pittsburgh, PA) p. 109 (1993).
- ⁴ L.A. Clevenger, R.A. Roy, C. Cabral, Jr., K.L. Saenger, S. Brauer, G. Morales, K.F. Ludwig, Jr., G. Gifford, J. Bucchignano, J. Jordan-Sweet, P. DeHaven, and G.B. Stephenson, *J. Mater. Res.* **10**, 2355 (1995).
- ⁵ C. Cabral, Jr., L.A. Clevenger, J.M.E. Harper, F.M. d'Heurle, R.A. Roy, C. Lavoie, K.L. Saenger, G.L. Miles, R.W. Mann, and J.S. Nakos, in *Advanced Metallization and Interconnect Systems for ULSI Applications in 1997*, edited by Robin Cheung, Jeffrey Klein, Kazuo Tsubouchi, Masanori Murakami, and Nobuyoshi Kobayashi (Materials Research Society, Warrendale, PA, 1998) p. 557.
- ⁶ Z. Ma and L.H. Allen, *Phys. Rev. B* **49**, 13501 (1994).
- ⁷ R.W. Mann, G.L. Miles, T.A. Knotts, D.W. Rakowski, L.A. Clevenger, J.M.E. Harper, F.M. D'Heurle, and C. Cabral, *Appl. Phys. Lett.* **67**, 3729 (1995).
- ⁸ R.W. Mann, L.A. Clevenger and Q.Z. Hong, *J. Appl. Phys.* **73**, 3566 (1993).
- ⁹ Q. Xu and C. Hu, *IEEE Trans. Electron Devices* **45**, 2002 (1998).
- ¹⁰ Z. Ma, L.H. Allen, and D.D.J. Allman, *Thin Solid Films* **253**, 451 (1994).
- ¹¹ C. Cabral, Jr., L.A. Clevenger, J.M.E. Harper, F.M. d'Heurle, R.A. Roy, K.L. Saenger, G.L. Miles, R.W. Mann, *J. Mater. Res.* **12**, 304 (1997).
- ¹² H.J.W. van Houtum, I.J.M.M. Raaijmakers, and T.J.M. Menting, *J. Appl. Phys.* **61**, 3116 (1987).

- ¹³ C. Cabral, Jr., L.A. Clevenger, J.M.E. Harper, F.M. d'Heurle, R.A. Roy, C. Lavoie, K.L. Saenger, G.L. Miles, R.W. Mann, and J.S. Nakos, *Appl. Phys. Lett.* **71**, 3531, (1997).
- ¹⁴ C.C.D. Tan, L. Lu, A. See, S.Y. Chen, L.H. Chua, K.L.T. Chan and L. Chan, presented at the 1st International Conference on Advanced Materials and Processes for Microelectronics, San Jose, CA, March 15-19, 1999.
- ¹⁵ X.W. Lin and D. Promanik, in *Materials Research Society Symposium Proceedings Volume 429, Rapid Thermal and Integrated Processing V*, edited by J.C. Gelpey, M.C. Ozturk, R.P.S. Thakur, A.T. Fiory, and F. Roozeboom, (Materials Research Society, Pittsburgh, PA) p. 181 (1996).
- ¹⁶ I. De Wolf, D.J. Howard, A. Lauwers, K. Maex, and H.E. Maes, *Appl. Phys. Lett.* **70**, 2262 (1997).
- ¹⁷ H.J.W. van Houtum and I.J.M.M. Raaijmakers, in *Materials Research Society Symposium Proceedings Volume 54, Thin Films - Interfaces and Phenomena*, edited by R.J. Nemanich, P.S. Ho, and S.S. Lau (Materials Research Society, Pittsburgh, PA) p. 37 (1986).
- ¹⁸ S.P. Murarka, *Silicides for VLSI Applications*, (Academic Press, Inc., New York, 1983) Chapter 4.

Figure Captions

Figure 1. Sheet resistance as a function of RTP temperature for 25, 40, and 60 nm Ti films on poly-Si. These samples were processed with a ramp rate of 70°C/s. T_{TR} is the temperature where linear fits to the sheet resistance in the transition region and the C54 region intersect.

Figure 2. Sheet resistance as a function of RTP temperature and ramp rate for 60 nm and 25 nm blanket Ti films on poly-Si. The 70°C/s data has been omitted for clarity. It is obvious that the ramp rate affects T_{TR} of the 25 nm Ti film but not T_{TR} of the 60 nm film.

Figure 3. Transformation temperature, T_{TR} , as a function of nominal, as-deposited, Ti film thickness. Although the transformation temperature always increases with reduced film thickness, increasing the RTP ramp rate minimizes this effect.

Figure 4. Sheet resistance versus patterned linewidth of a 40 nm, as-deposited, Ti film after processing at various ramp rates. The error bars indicate the minimum and maximum values of the measured data. It is obvious that the linewidth effect is monotonically reduced by increasing the ramp rate.

Figure 5. Sheet resistance versus patterned linewidth of a 25 nm, as-deposited, Ti($\approx$ 4 at.% Ta) film after processing at various ramp rates. The error bars indicate the minimum and maximum values of the measured data. The linewidth effect is virtually eliminated by increasing the ramp rate to 75°C/s.

Figure 1. Sheet resistance as a function of RTP temperature for 25, 40, and 60 nm Ti films on Si. These samples were processed with a ramp rate of $70^{\circ}\text{C}/\text{s}$. T_{TR} is the temperature where linear fits to the sheet resistance in the transition region and the C54 region intersect.

Figure 2. Sheet resistance as a function of RTP temperature and ramp rate for 60 nm and 25 nm blanket Ti films on Si. The 70°C/s data has been omitted for clarity. It is obvious that the ramp rate affects T_{TR} of the 25 nm Ti film but not T_{TR} of the 60 nm film.

Figure 3. Transformation temperature, T_{TR} , as a function of nominal, as-deposited, Ti film thickness. Although the transformation temperature always increases with reduced film thickness, increasing the RTP ramp rate minimizes this effect.

Figure 4. Sheet resistance versus patterned linewidth of a 40 nm, as-deposited, Ti film after processing at various ramp rates. The error bars indicate the minimum and maximum values of the measured data. It is obvious that the linewidth effect is monotonically reduced by increasing the ramp rate.

Figure 5. Sheet resistance versus patterned linewidth of a 25 nm, as-deposited, Ti(≈ 4 at.% Ta) film after processing at various ramp rates. The error bars indicate the minimum and maximum values of the measured data. The linewidth effect is virtually eliminated by increasing the ramp rate to 75°C/s.