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Characteristics of $TiSi_2$ contact to BF_2-doped single-silicon

J. S. CHOI, S. H. PAEK, Y. S. HWANG, S. H. CHOI
Department of Material Engineering, Hanyang University, Seoul, Korea, 133-791
D. W. KIM, H. K. MOON, J. K. CHUNG, W. S. PAEK, T. U. SIM, J. G. LEE
SAMSUNG Electronics Semiconductor R & D, Kyunggi Province, Korea, 441-742

The reaction mechanism of titanium silicide was investigated for varying amounts, of BF_2 dopant on a Si-substrate. Titanium thin films were prepared by direct current sputtering on non-doped and BF_2-implanted silicon wafers. The heat treatment temperatures, by rapid thermal annealing (RTA), were varied in the range 600–800 °C for 20 s. C49 $TiSi_2$ forms at 700 °C and almost all of its phase is transformed into C54 $TiSi_2$ with a very low resistivity value (16 μΩ cm) at 800 °C. When the amount of impurities is increased, the sheet resistance of Ti-silicides also increased while its thickness decreased. The main cause of the thickness reduction of Ti-silicide is the growth of enhanced native oxide. Dopants are chiefly redistributed in the interface between the Ti-silicide and the Si-substrate. It is believed that the formation of titanium boride increases the contact resistance during the Ti-silicide formation for samples annealed at 750 °C and 800 °C.

1. Introduction
The development of 64M DRAM or beyond requires low-resistivity interconnect materials. Many studies on silicides ($TiSi_2$, $MoSi_2$, $TaSi_2$) have investigated their resistivity and stability at high temperatures [1]. Among these materials, research interest has focused on Ti-Silicides since they have the lowest resistivity. Ti-silicide material can be applied to a device as a polycide interconnect line. Because of the requirement of shallow junctions, sufficient thermal energy cannot be provided to activate the implanted impurities. As a result, the contact resistance will increase [2]. It is expected that using Ti-silicides as contact materials prevents an increase in the contact resistance. However, highly concentrated impurities will be redistributed during annealing processes. This redistribution of impurities within a device can affect the $TiSi_2$ growth mechanisms and cause device degradation [3, 4]. In this study, the movement of added impurities is traced and the mechanism of Ti-silicides formation is investigated, to see the application of Ti-silicide as a contact metal. The contact resistance is measured to examine the stability of the $TiSi_2$ process.

2. Experimental procedure
Fig. 1 presents a flow chart of the experimental processes. A 25 nm blocking oxide is grown before BF_2-ion implantation with 90 keV. To activate the added impurities, samples implanted with BF_2 ions were annealed at 900 °C under ambient N_2 for 30 min.

After the removal of the blocking oxide, the sheet resistance was measured and the native-oxide thickness was evaluated using an ellipsometer and transmission electron microscopy (TEM). To examine the effect of the native oxide, two kinds of samples were prepared. One sample had the native oxide eliminated by a 100:1 HF dipping process for 120 s and the other samples did not have the dipping process. Also, non-implanted samples were prepared to verify the influence of BF_2 impurities in the silicide formation. Titanium 50 nm thick was deposited by direct current (d. c.) magnetron sputtering. In the Ti-silicide reaction, a RTA heat cycle ranging from 600 °C to 800 °C under ambient Ar was applied for 20 s.

The sheet resistance of these samples were measured using a 4-point probe after the residue of Ti from the reaction was removed by dipping in an NH_4OH:H_2O_2:DI water = 1:2:5 etchant. To evaluate the thickness of silicide formed, square patterns were made by photo/etch steps and then their thicknesses were measured by an α-step. The distribution of added impurities was also examined by SIMS, and the contact resistance measured in Kelvin resistor patterns. The etch contact size of these patterns was 0.7^2, 0.9^2, and 1.1^2 μm^2.

3. Results and discussion
3.1. Formation
Table I presents the values of sheet resistance, thickness and resistivity as a function of RTA temperature for samples formed on bare wafers. At 600 °C the sheet-resistance value of 282 Ω/□ indicates Ti-silicide hardly forms. The resistivity of 15 μΩ cm suggests that

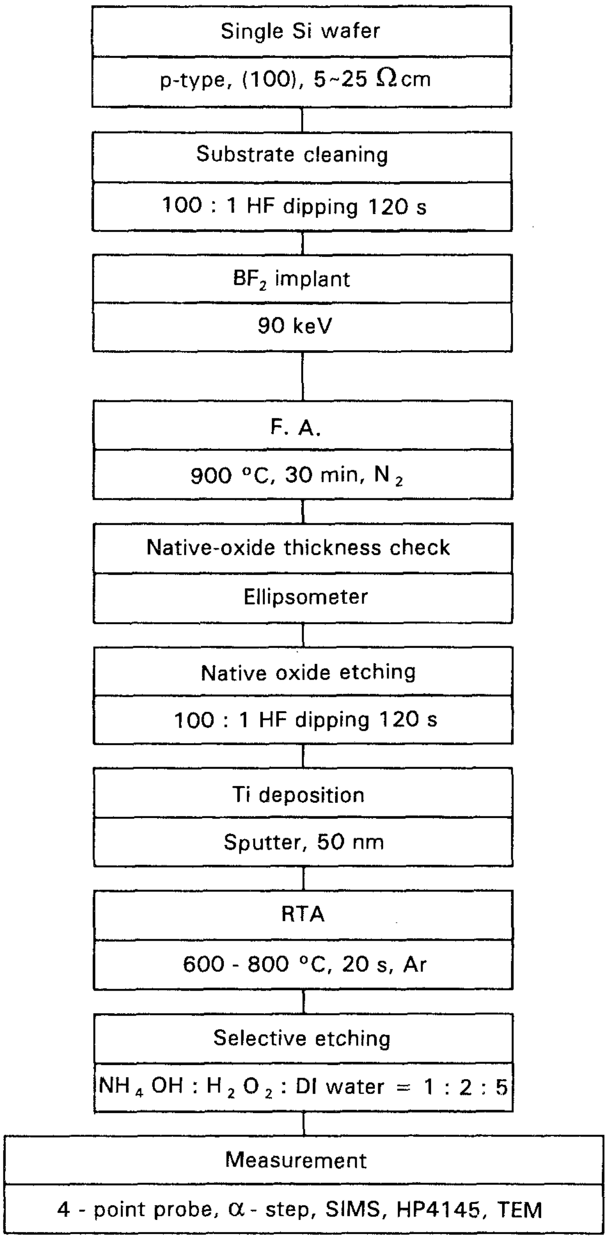


Figure 1 Flow chart of the experimental processes.

TABLE I Sheet resistance, thickness, and resistivity of Ti-silicides as a function of annealing temperature

	Temperature (°C)		
	600	700	800
Separation			
Resistance (Ω/□)	282	12	1.5
Thickness (nm)	20	60	102
Resistivity (μΩ cm)	572	74	15

most of the C49 $TiSi_2$ is changed to the very stable C54 $TiSi_2$ at 800 °C [5–7].

To examine the influence of BF_2 impurities during the formation of Ti-silicide two samples were prepared, one with BF_2 implantation at a dose of 5×10^{15} cm^{-2} and the other without BF_2 implantation. Fig. 2 shows the Ti-silicide thickness at various RTA temperatures. The BF_2 dose of 5×10^{15} cm^{-2} can suppress Ti-silicide formation. The samples treated by RTA at 700 °C show more obvious effects than the samples treated at 800 °C. Fig. 3 shows the thickness of Ti-silicide and sheet resistance values for various doses of added impurities at 700 °C.

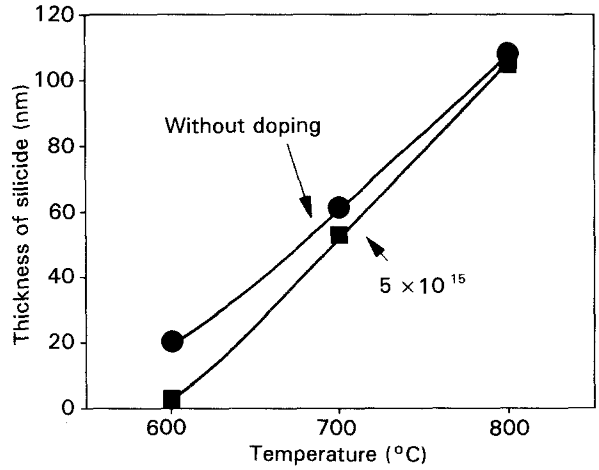


Figure 2 The difference of the silicide thickness as a function of annealing temperature, between the P^- substrate and the substrate implanted with 5×10^{15} cm^{-2} of BF_2.

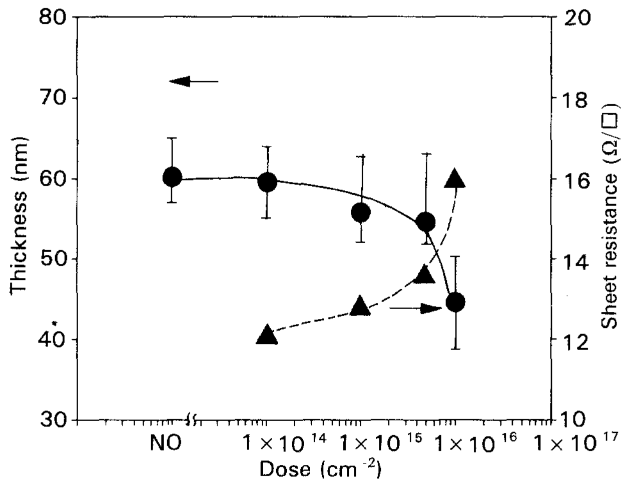


Figure 3 Sheet resistance and thickness of Ti-silicides as a function of BF_2 dosage after annealing at 700 °C for 20 s.

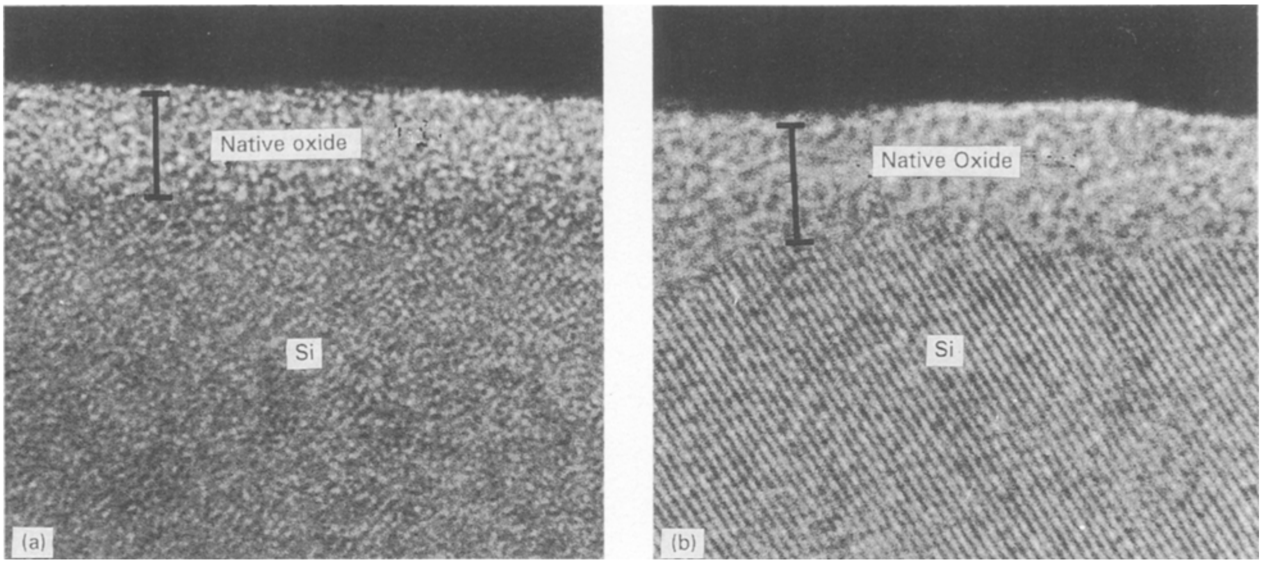
When increasing amounts of impurities are added, the thickness of Ti-silicide decreases while its sheet resistance increases. Up to a dose of 5×10^{15} cm^{-2} little change is seen, but significant change is noticed at a dose of 1×10^{16} cm^{-2}.

3.2. The effect of native oxide

The change in the thickness of the native oxide was closely observed as the amount of implanted impurities varied. Table II shows the thickness of native oxide as a function of the amount of implanted impurities. When the dose of implanted impurities is 1×15^{15} cm^{-2}, the thickness of grown native oxide maintains its value at 1.6 nm. But, at a dose of 5×10^{15} cm^{-2}, the native-oxide thickness reaches 1.8 nm while the thickness of native oxide quickly increases to 4.1 nm at a dose of 1×10^{16} cm^{-2}. These results show that the oxidation enhancement phenomenon can

TABLE II The measured thickness of native oxide and Ti-silicide varying with BF_2^+ the dosage of BF_2^+ implanted

		Thickness (nm ± 10%)				
		Amount of BF_2 (cm^{-2})				
		–	1×10^{14}	1×10^{15}	5×10^{15}	1×10^{16}
before	Native oxide	1.5	1.5	1.6	1.8	4.1
etching	Ti-silicide			53.4	51.6	42.3
after	Native oxide	0.7	1.1	1.2	1.3	3.4
etching	Ti-silicide			55.5	54.2	45.7



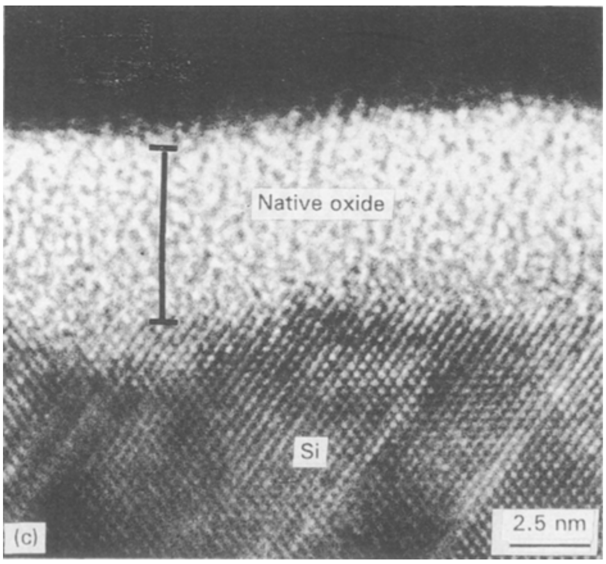


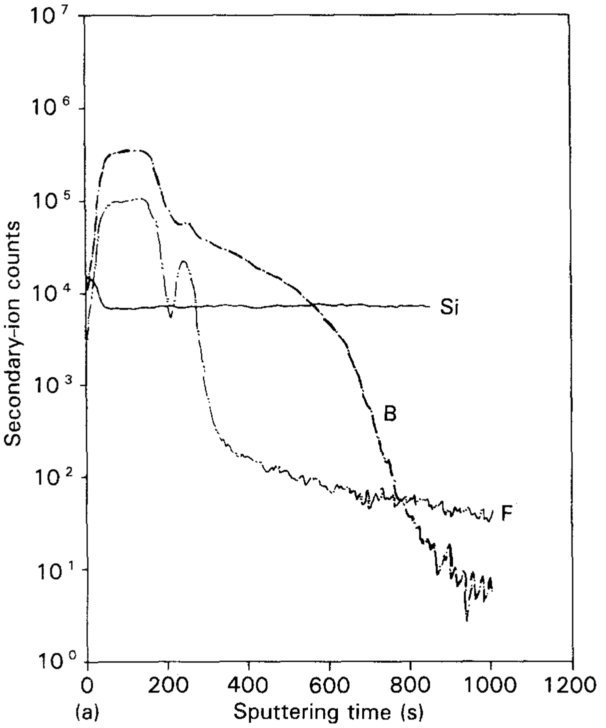
Figure 4 Cross-sectional TEM pictures of the native oxides formed on P^+–Si substrates: (a) without BF_2 implantation, (b) with 5×10^{15} cm^{-2} of BF_2, and (c) with 1×10^{16} cm^{-2} of BF_2.

even occur in native oxide. This is supported by previous reports which deal with the oxidation enhancement phenomenon at a very high boron concentration level [8]. TEM analysis was used to verify this phenomenon. Fig. 4 shows the thickness of native oxide according to the amount of BF_2 implantation. In Fig. 4 there is little difference between the specimen without implantation and the specimen with 5×10^{15} cm^{-2} of BF_2. But in Fig. 4c, with 1×10^{16} cm^{-2} of BF_2, the native oxide is greatly thickened. The TEM results show the same tendency as the ellipsometer measurement in Table II.

However, in Table II the thickness of silicides slightly decreases up to a dose of 5×10^{15} cm^{-2}. When the dose of BF_2 reaches 1×10^{16} cm^{-2}, the thickness reduction even reaches 10 nm. This trend of thickness reduction in silicides is very similar to the thickness increase of native oxide as the boron dose increases. In order to analyse the effect of native oxide on Ti-silicides formation more precisely, two kinds of samples were prepared. Native oxide was eliminated in one type of sample by a 100:1 HF dipping process for 120 s and the other type of sample did not undergo the dipping process. For these two cases the thickness of Ti-silicides were measured and the results are presented in Table II as a function of the amounts of impurity twenty points were taken for every sample to measure the thickness and show the mean values. The Ti-silicide layer of samples where the native oxide was removed is thicker than the samples without the dipping process, for the same amount of implants. This result shows that oxidation enhancement is the dominant factor preventing Si from further diffusion.

3.3 The behaviour of dopant and contact resistance

The influence of BF_2 was examined to trace the movement of impurities toward the region of



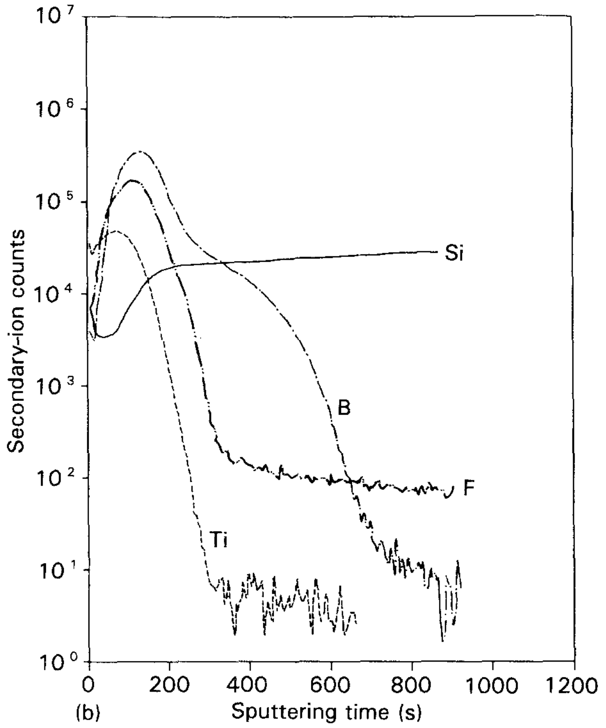
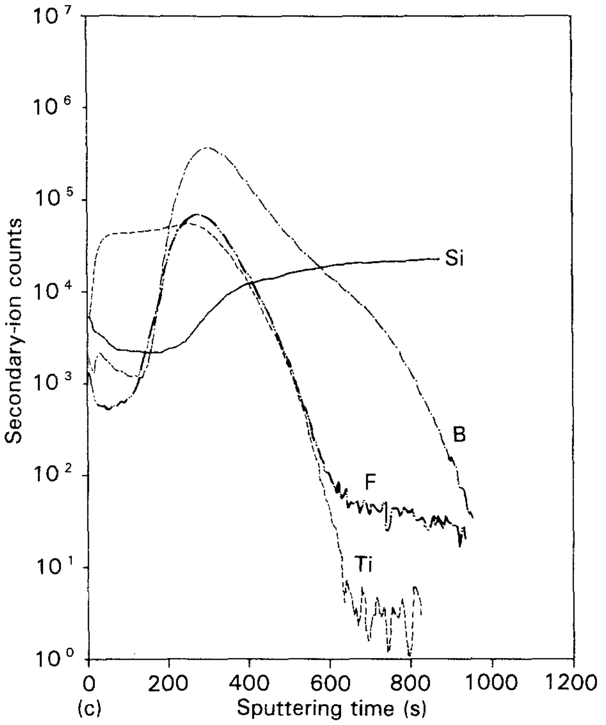


Figure 5 SIMS impurity distributions of the sample implanted by 5×10^{15} cm^{-2} of BF_2 and heat treated under the following conditions: (a) as-deposited, (b) annealed at 700 °C, and (c) annealed at 800 °C.



Ti-silicides and to find its redistribution activities. A secondary-ion mass spectroscopy (SIMS) depth-distribution profile of BF_2 implantation at a dose of 5×10^{15} cm^{-2} are shown as a function of RTA temperature in Fig. 5. At a temperature of 600 °C, where Ti-silicide formation has not yet begun, boron stays in a single-crystal region. However, at temperatures of 700 °C and 800 °C, where Ti-silicide formation begins to occur, boron piles up in a boundary between silicon and silicides. When the dopants showed such a behaviour, the interface reaction mechanism between BF_2-doped silicon and $TiSi_2$ and the effects of dopant redistribution on device properties were studied.

Fig. 6 shows contact resistance as a function of RTA temperature and contact size. The contact resistance decreases as contact size increases under the same RTA temperature. However, the contact resistances, within the same size, all increase when the RTA temperature is increased from 700 °C to 800 °C.

It can be thought that this increase in the contact resistance is caused by the redistribution of dopant. Other studies have reported that dopants severely diffuse out of silicon during the silicidation and that they have a low concentration at the silicon surface [9, 10]. Generally, the low surface concentration increases the contact resistance [11]. But, in this study, the increase of contact resistance seems to have a different cause. The SIMS data in this study show that borons accumulate at the interface between Ti-silicide and silicon. The accumulation is due to the low solid solubility of boron in $TiSi_2$ [12]. In Fig. 5c the amount of boron is greater than the solid solubilities ($< 10^{18}$ cm^{-3}) [13] in the Ti-silicide layer near the interface. It is possible that the excess borons react with titanium and form titanium boride, because titanium boride is stable at the range of the annealing temperature [13, 14]. Therefore it is believed that the formation of titanium boride is the main cause of the increase of the contact resistance.

Fig. 7 shows the contact resistance of the sample of Ti-silicide annealed at 700 °C and 800 °C and the conventional TiN/Ti barrier as contact material. The contact resistance of the sample annealed at 800 °C is higher than that of TiN/Ti. For the sample annealed at 700 °C, the contact resistance is lower than that of TiN/Ti. It is believed that this is because the amount of borons is not sufficient to form titanium boride at

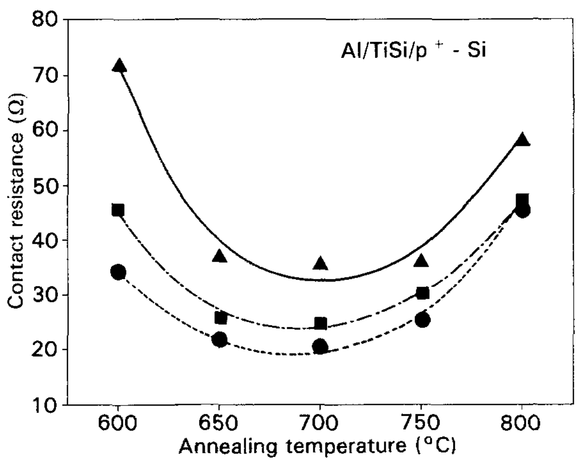


Figure 6 The measured contact resistance as a function of temperature with various contact sizes: (– – –) 1.1 × 1.1 μm², (— - —) 0.9 × 0.9 μm², (——) 0.7 × 0.7 μm².

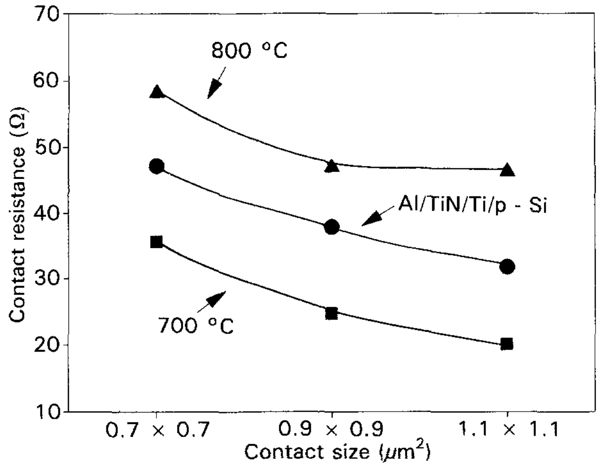


Figure 7 Contact resistance with contact size for TiN/Ti/Si and Ti-silicide formed at 700 °C and 800 °C

700 °C. This seems to show that the Ti-silicide annealed at 700 °C is applicable as a contact material. (However, temperature cycles associated with Borosilicate glass (BPSG) formation can be sufficient to promote titanium boride formation. Conclusively, the application of a Ti-silicide contact on BF_2-doped single-silicon may cause problems in the reliabilities of devices.

4. Conclusion

The resistivity results show that C49 $TiSi_2$ is formed at 700 °C and that it is all converted to C54 $TiSi_2$ at 800 °C. With increasing BF_2 implantation on a Si substrate, Ti-silicide formation is increasingly suppressed. In particular, it was severely suppressed at a dose of 1×10^{16} cm^{-2}. When the amount of BF_2 impurities increases the thickness of native oxide increases, but the thickness of Ti-silicides decreases. The sudden increase in native-oxide thickness at a BF_2 dose of 1×10^{16} cm^{-2} is closely correlated to the sharp decrease in Ti-silicide thickness under the same condition. The main factor which prevents the formation of Ti-silicides is considered to be the enhancement of native oxide with increasing amounts of dopants. The distribution of added impurities show that the BF_2 impurities piled up at an interface between silicides and silicon during Ti-silicide formation. The contact resistance increases when the annealing temperature increases from 700 °C to 800 °C at the same contact size. This increase is due to the formation of titanium boride at the interface of Ti-silicide and silicon.

References

1. T. YACHI, *IEEE Electron Device Lett.* **5** (7) 1984 217.
2. S. M. SZE, "VLSI technology" (McGraw-Hill, New York, 1988).
3. M. WITTMER, C. Y. TING, and K. N. TV, *J. Appl. Phys.* **54** (1983) 699.
4. J. AMANO and P. MERCHANT, *Appl. Phys. Lett.* **44** (1984) 744.
5. R. BEYERS and R. SINCLAIR, *J. Appl. Phys.* **57** (1985) 5240.
6. H. J. W. VAH HOUTUM, I. J. M. M. RAAIJMAKERS and T. J. M. MENTING, *J. Appl. Phys.* **61** (1987) 3116.
7. T. C. CHOU, C. Y. WONG, and K. N. TU, *J. Appl. Phys.* **62** (1987) 2275.
8. J. S. CHOI, S. S. PARK, Y. G. LEE, and J. A. YOO, *SST Semiconductor Tech. J. (Korea)* **2** (1987) 295.
9. C. M. OSBURN, Q. F. WANG and M. KELLAM, *Appl. Surf. Sci.* **53** (1991) 291.
10. T. YOSHIDU, M. FUKUMOTO and T. OHOZONE, *J. Electrochem. Soc.* **135** (1988) 481.
11. Y. H. KU, S. K. LEE and D. L. KWONG, *Appl. Phys. Lett.* **54** (1989) 1684.
12. JUN AMAHO, P. MERCHANT, T. R. LASS and J. N. MILLER, *J. Appl. Phys.* **59**(8) (1986) 2689.
13. P. GAS, V. DELINE, F. M. D. HEURLE, A. MICHEL and G. SCITTA, *J. Appl. Phys.* **60**(5) (1986) 1634.
14. F. LA VIA, V. PRIRITERA and E. RIMINI, *Appl. Surf. Sci.* **53** (1991) 377.

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