$TiSi_2$ and $CoSi_2$ Silicide Formation using N_2^+ Implant

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Abstract— **Silicides have been used in industry since minimum dimensions reached the 1µm node. The goal of this project is to explore Titanium and Cobalt Silicide and incorporate its use into the RIT sub-micron CMOS process. $TiSi_2$ had been the industry standard to decrease this resistivity through the 0.25µm node. The current industry standard is $CoSi_2$, with resistivity independent of its grain size. This allows for the smaller dimensions. However, $CoSi_2$ formation is very sensitive to oxygen contamination. A Ti capping layer may minimize the contamination by reacting with any oxygen. The nitrogen implant prior to metal deposition should suppress agglomeration in the films and improve thermal stability.**
A Transmission Line Model (TLM) structure has been used to extract specific contact resistivity and contact resistance for the silicide. Four point probing will measure the resistivity of the polycide. Results show a reduction in sheet resistance of polysilicon samples after silicidation. RBS and XRD analyses show oxygen contamination.

***Index Terms*— Silicides, Cobalt silicide, Titanium silicide**

As CMOS is scaled to smaller dimensions, the resistivity of polysilicon gates and contacts increase to an unacceptable level. To maintain and improve the speed of transistors, the resistivity of the gates and contacts can be decreased with the use of silicides. The purpose of creating a silicide is to reduce the resistance of polysilicon lines and contacts to silicon. Silicide is the result of the reaction of a metal and silicon. Self-aligned silicide, or salicide can be formed without additional patterning when the metal only reacts with silicon, and not silicon nitride or silicon oxide.

Other metals have been studied for use in silicide processes, such as W, Ta, Mo, and Ti. $TiSi_2$ has been a good solution for gates as small as 0.25µm and was very attractive because of Titanium's ability to reduce oxide layers. However, $TiSi_2$ has many drawbacks such as bridging due to reactions with SiO_2, lower thermal stability, narrow line effects, high silicon consumption, and dopant redistribution.

Cobalt silicide is a potential alternative for the 0.18µm node and below. Bridging is no longer an issue because cobalt will not react with oxide. Thermal stability is increased to 900°C and above. Narrow line effects are eliminated because resistance is no longer related to grain size and dopant interaction and redistribution issues have not been observed.

In previous studies, $CoSi_2$ films have been created with much higher than expected resistance. To reduce this resistance, two techniques will be applied. The first will to use an N_2^+ implant to suppress agglomeration, originally studied to prevent boron penetration into oxide. A second technique will be the minimization of oxygen contamination by including an HF dip before metal deposition and the use of a Ti capping layer. A Titanium cap should make the silicide process less sensitive to a native oxide or oxygen in the ambient of the rapid thermal anneal.

Titanium silicide with a N_2^+ implant will also be studied. Because this implant has been shown to reduce grain size in other silicide films, a reduction in agglomeration is also expected.

Silicide resistivity will be measured using a transfer length method. The TLM structure is a row of rectangular contacts with increasing spacing. This will allow for sheet resistance, contact resistance and specific contact resistivity to be extracted. Silicide resistivity will be measured using four point probing by a resistivity mapper.

II. THEORY

A. Cobalt and Titanium

Table I illustrates a number of properties of Ti and Co. Cobalt is a group VIII transition metal that is brittle, hard and has magnetic properties. Titanium is typically known for its ability to getter materials, and is often used to lower the background pressure of vacuum systems.

TABLE I
MATERIAL PROPERTIES OF COBALT

Property	Titanium	Cobalt	Unit
Atomic Number	22	27	

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Atomic Weight	47.9	58.9	amu
Density	4.5	8.9	gm/cm3
Melting Point	1668	1495	°C
Boiling Point	3287	2870	°C
Thermal Conductivity	0.22	1	W/cm·K
Electrical Resistivity	40	6.24	μΩ·cm
Pauling Electronegativity	1.54	1.88	Paulings

B. Titanium and Cobalt Silicides

Cobalt silicide is produced in two rapid thermal processing (RTP) steps. At approximately 450 °C, a cobalt film will react to the underlying silicon to form CoSi. Unreacted metal is etched away, followed by a second RTP step at 700 °C causes the CoSi to react with Si to create $CoSi_2$. While Co is the main diffuser during most of the $CoSi_2$ formation, Si does diffuse during the CoSi formation[3]. To prevent the possibility of bridging during the CoSi formation, a titanium capping layer will be used. For every angstrom of Co, 3.64 A of silicon is consumed during silicidation.

Titanium silicide is also formed using a two step RTP process. The first step is preformed at approximately 650 °C, creating C-49 phase $TiSi_2$. After the unreacted metal is removed, the second RTP step is preformed at 800 °C to create the lower resistivity C-54 phase. In these reactions, Si is the dominant diffuser[3]. Because Titanium reduces SiO_2, a capping layer is not necessary. For every angstrom of Ti, 2.77 A of silicon is consumed during silicidation.

TABLE II
SILICIDE PROPERTIES

Property	Value	
	$TiSi_2$	$CoSi_2$
Dominant Diffuser	Si	Co
Eutectic Temperature	1330 °C	1195 °C
Resistivity	16 μΩ·cm	18μΩ·cm
Dry Etch Capability	good	poor
Schottky Barrier	0.6 eV	0.64 eV

Cobalt Silicide is preferred over $TiSi_2$ for many reasons, including no strong dopant interaction, reduced bridging effects, plasma etch resistance and no narrow line effects. The few weaknesses include sensitivity to surface conditions prior to cobalt deposition and increased silicon consumption.

C. Nitrogen Implant and Capping Layers

To overcome some of the weaknesses of cobalt silicide formation, a nitrogen implant and a titanium capping layer was used. The purpose of the pre-silicide N_2^+ implant was to prevent agglomeration at high temperatures. The implant causes grain size of the $CoSi_2$ to be smaller, creating a more stable silicide [1]. The Ti capping layer was designed to reduce any SiO_2 present or formed due to O_2 or moisture contamination in the RTP ambient [2]. To further reduce oxygen contamination, an rf back sputter was recommended.

The pre-silicide N_2^+ implant was also included for the $TiSi_2$ samples.

D. TLM

The transfer length method for measuring contact resistance is comprised of a ladder structure with multiple contacts. This structure allows for sheet resistance, contact resistance, and specific contact resistivity to be measured. Fig. 1 illustrates the structure used in this experiment.

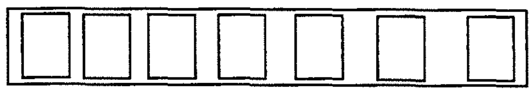


Fig. 1. Transfer length method test structure. The size of the contacts is constant while the distance between contacts is increasing.

For each structure, a plot of total resistance versus distance between contacts is created. The slope of the line leads to sheet resistance, the intercept with the distance axis leads to specific contact resistivity and the intercept with the total resistance axis leads to contact resistance [4].

III. EXPERIMENTAL

Both silicide and polycide was created. To begin, (100) N-type wafers were scribed and RCA cleaned.

A. Polycide Formation

Approximately 500A of pad oxide was grown at 1000 °C in dry O_2 with a soak time of 56 minutes. 3400A of polysilicon was deposited at 610 °C, 300 mT in 100 sccm SiH_4 for 47 minutes. The polysilicon was doped using Emulsitone N-250 N-type spin on glass, baked at 200 °C for 15 minutes, and then driven in using a furnace recipe at 1000 °C in N_2 for 15 minutes. After removal of the spin on glass, sheet resistance of the poly was approximately 40 Ω/sq. Half of the wafer was protected with hard baked photoresist and implanted with $6x10^{-14}$ cm^{-2} N_2^+ at 15 KeV. Wafers were then resist stripped and cleaned. A RTP implant anneal was done at 950 °C for 60 seconds. Immediately after a 50:1 H_2O:HF dip, metal was deposited.

Cobalt was evaporated from shavings of a cobalt sputter target. A molybdenum boat was used with a base pressure of 1.4 $x10^{-5}$ T. The current was approximately 340A at 20V, resulting in a deposition rate of approximately 3A/min. Without breaking

vacuum, titanium was evaporated in a tungsten wire basket with 65A at 5V. The deposition rate of Ti was less than 1 A per minute. The final cobalt thickness was 400A with a 100A titanium cap.

Titanium was sputtered at a base pressure of 3 x10^{-5} T. A presputter was preformed for 10 minutes using 1000W and a sputter pressure of 5.0 mT using Ar. The sputter was preformed at the same parameters for 4 minutes, resulting in a 400A film.

Both silicides require a two step RTP for formation and parameters are as follows:

TABLE III
RAPID THERMAL PROCESSING PARAMETERS

	RTP 1		RTP 2	
Metal	Temp	Time	Temp	Time
Cobalt	550	60	800	60
Titanium	650	60	750/800/850	60

The silicide samples were prepared in a very similar manner. After scribe and clean, wafers were implanted with 4E15 cm^{-2} P-31 at 90 KeV. After a 20 minute anneal in N_2 and 10 minutes in wet O_2 at 1000 °C. The oxide cap was removed in buffered oxide etch. The resulting sheet resistance was approximately 20 Ω/sq with a junction depth of approximately 2.5μm. Low temperature oxide was deposited via CVD at 400 °C in 80 sccm SiH_4 for 53 minutes, resulting in a thickness of approximately 4500A. TLM structures were patterned using the GCA stepper. The LTO was etched using an RIE of 40 sccm CHF_3, 20 sccm SF_6 at 270W in 270 mT for five minutes. A BOE dip followed to remove remaining oxide at the edge of the wafer.

The nitrogen implant used the same parameters as used for the polysilicon samples. After strip, clean and anneal, the wafers were dipped in 50:1 H_2O: HF and immediately sputtered with Ti. The deposition was done at the same time as the polysilicon wafers. Silicidation was preformed using the parameters of table three above.

It was determined that aluminum contacts were necessary for electrical test. Following an HF dip, 1.0μm Al was sputtered from an Al (2% Si) target at a base pressure of 1E-5 T, 1500 W, 5mT sputter pressure with Ar for 20 minutes. After patterning, the aluminum was etched in Al etch at 50 °C for 2 min, 15 seconds.

IV. RESULTS

Measurements were obtained for $CoSi_2$ and $TiSi_2$ polycides and $TiSi_2$ silicide. The data point marked with an asterisk was processed as a base line prior to other $TiSi_2$ samples. There was no difference between N_2^+ implanted samples and non implanted samples.

TABLE IV
POLYCIDE SHEET RESISTANCES

Polycide	RTP1/RTP 2 Temp	Polysilicon ρ_s	Polycide ρ_s
$TiSi_2$	650/750	43.0	23.7
$TiSi_2$	650/800	43.0	22.8
$TiSi_2$	650/850	43.1	26.8
$TiSi_2$*	650/800	42.7	4.1
$CoSi_2$	550/800	42.7	35.3
$CoSi_2$	550/800	43.2	26.6

The only silicide studied was $TiSi_2$. Significantly higher resistances were found between N_2^+ implanted and non-implanted in the higher temperature RTP2 sample. No difference was seen at the 800 °C sample. The 750 °C was not processed.

TABLE V
SILICIDE RESISTANCES AND RESISTIVITES

RTP 2 Temp	Parameter	Value	Unit
800 °C	ρ_s	4.36E-02	Ω /sq
	R_c	68	Ω
	L_T	17	μm
	ρ_c	5.10E-03	Ω·cm2
850 °C no implant	ρ_s	6.90E-02	Ω /sq
	R_c	62	Ω
	L_T	9	μm
	ρ_c	4.53E-03	Ω·cm2
850 °C implanted	ρ_s	7.28E-01	Ω /sq
	R_c	395	Ω
	L_T	22	μm
	ρ_c	2.90E-02	Ω·cm2

ρ_s is the sheet resistance, R_c is the contact resistance, L_T is the transfer length and ρ_c is the specific contact resistivity. The contact spacing vs measured resistance plot did not yield clear linear relationships, leading to ambiguity in the reported results.

V. DISCUSSION

Silicidation did reduce the resistances of the silicon and polysilicon, but did not produce expected results. An optimal $TiSi_2$ should have a sheet resistance of 1.2 Ω/sq and an optimal $CoSi_2$ should have a sheet resistance of 0.5 Ω/sq. The

specific contact resistivity of $TiSi_2$ should be on the order of 10^{-6} Ω·cm^2.

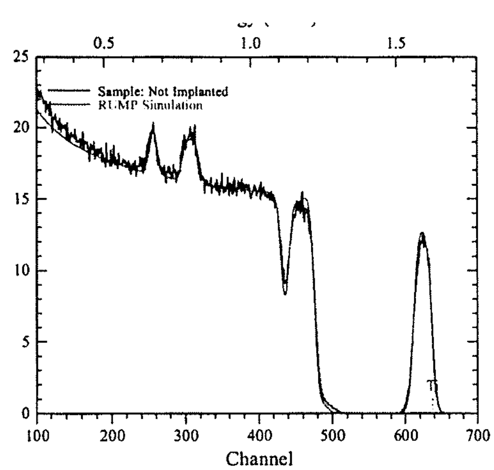
The $TiSi_2$ polysilicon sample that was created separately produced excellent results. Sheet resistance was low, approximately 4 Ω/sq. This initial sample was prepared using the same steps as the others, indicating the recipes and tool settings listed can produce a good silicide.

To find the cause of the unexpectedly high resistances, Rutherford Backscattering and X-Ray diffraction analyses were preformed to study the chemical composition. RBS spectrum shown in Fig. 1 shows no interaction between Ti and Si and shows formation of TiO_2 at the surface. Nitrogen implantation shows no difference in the RBS results. The XRD results confirm these results as no silicide formation is detected and TiO_2 peak is observed (Fig .2). Oxide formation is favored over silicide formation and may have occurred at a few processing problems.

These problems arose at multiple stages in the process. To begin, cobalt could not be sputtered. The original sputter target was approximately 5mm thick. The magnetron of the CVC 601 sputterer did not have the strength to create a plasma. The target was thinned to a 3mm thickness and plasma was still not created. During a second thinning attempt, the target was destroyed. The shavings from thinning were saved, cleaned in acetone and used for evaporation.

During Titanium sputtering, much arcing occurred. This may have resulted in a poor film.

Errors also occurred at rapid thermal processing. During the titanium silicide formation, the N_2 flow was insufficient. Very little gas was flowing, so much oxygen may have been present in the system. During the cobalt silicide formation, the emissivity setting for the tool could not be optimized leading to temperature fluxuations and the possibility that the necessary temperature was never reached.



Fig, 1 RBS spectra (observed and simulated) of unimplanted and annealed sample of Ti on Si.

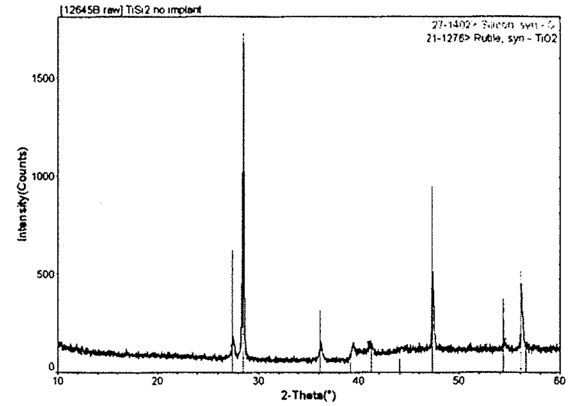


Fig. 2 XRD pattern of implanted and annealed sample of Ti on Si.

VI. Conclusions

Despite fabrication problems, a process has been designed to produce silicides. Care must be taken to avoid oxygen contamination. To produce better results, cobalt should not be evaporated. Titanium should be sputtered with a higher Ar pressure and use a lower base pressure.

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II. References

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