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Preparation and characterization of ultra-thin cobalt silicide for VLSI applications

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Abstract. Ultra-thin cobalt silicide ($CoSi_2$) was formed from 10 nm cobalt film by solid phase reaction of Co and Si by use of rapid thermal annealing (RTA). The Ge^+ ion implantation through Co film caused the interface mixing of the cobalt film with the silicon substrate and resulted in a homogeneous silicide layer. XRD was used to identify the silicide phases that were present in the film. The metallurgical analysis was performed by RBS. XRD and RBS investigations showed that final RTA temperature should not exceed 800°C for thin (< 50 nm) $CoSi_2$ formation.

Keywords. $CoSi_2$; RTA; XRD; RBS.

1. Introduction

Metal silicides are extensively used in very large scale integrated circuit device processing as interconnects, Schottky barriers, ohmic contacts and low resistivity gates (Murarka 1983). Both decrease in device dimensions and a drive for very high speed have increased the demand for improved interconnects with low resistance/capacitance (RC) coupling. Thin films of refractory metal silicides have been the subject of much interest in recent years owing to their widespread use as contact materials in VLSI. The ability of etching procedures for selectively removing unreacted metal over the oxide without etching the silicide film formed on silicon surfaces allows for the self alignment placement of contacts. Thus a self aligned silicide (SALICIDE) process has been proposed in VLSI and VHSIC circuit technologies to reduce the RC time constant contributed by the source, drain and gate areas (Murarka 1983; Revegz *et al* 1983). For VLSI use, the silicides must possess a wide combination of properties among which the most important is its resistivity. Among the refractory metal silicides, $TiSi_2$ and $CoSi_2$ with resistivities in the range of 15–20 μ ohm cm are the best conductors (Nicolet and Lau 1983; Park *et al* 1984).

Although titanium silicide ($TiSi_2$) has been drawing more attention in recent years as an integrated circuit metallization, cobalt silicide with its excellent properties is used in modern VLSI processes. The formation of $TiSi_2$ by thermal silicidation is very sensitive to the oxygen or other impurities (carbon or nitrogen) present in the annealing gas ambient (Taur *et al* 1987). The restriction on the annealing gas ambient is less critical for Co than for Ti. $CoSi_2$ has many other desirable properties. Cobalt is unreactive to titanium. Therefore, the use of Co should make the deposition of clean films easier and should reduce the risk of reaction with oxide films. Thus the SALICIDE process using the $CoSi_2$ is more simple.

The final thickness of the $TiSi_2$ layer will depend on the deposited Ti film thickness, the reaction temperature and the reaction time. This is contrary to the Co-silicidation reaction, where the resulting silicide thickness is exactly defined by the deposited Co film

thickness. $CoSi_2$ produces fairly low stress when film is formed on Si and it shows good resistances to most plasma processes (Tabasaki *et al* 1987). Because of these advantages, $CoSi_2$ seems to be an attractive alternative to $TiSi_2$.

As device geometries are scaled down to smaller dimensions, conventional furnace annealing for silicide formation are now being replaced by rapid thermal annealing (RTA). This method avoids oxidation problem originated in furnace annealing. It is also shown that RTA yields smooth high conductivity $CoSi_2$ films free of problems associated with furnace annealing (Yachi 1984; Tabasaky *et al* 1987).

The ion-beam mixing can break up the native oxide at the metal/Si interface and achieve interface mixing that enhances metal-Si reaction rate and results in smooth silicide/silicon interface. Ion-beam mixing with low doses does not produce detectable silicide layers but it is known that above a critical dose the properties of the silicide formed by subsequent annealing are drastically improved. Only mixing at doses greater than equal to a critical dose results in an abrupt silicide–silicon interface, in a smooth surface morphology and in low specific resistivity values (Hamdi and Nicolet 1984; Ku *et al* 1990; Kasko *et al* 1992).

In most of the recent sub-micron VLSI, shallow junctions (100–200 nm) are present under the cobalt region. The encroachment of the contact silicide into the depletion region of the junction can cause excessive leakage currents. Now a days devices are made on thin ($\sim$ 100 nm) silicon film of a silicon-on-insulator (SOI) substrate. In such devices, contact silicide thickness must be very thin in order to have proper device characteristics. Successful contacts in such thin films can be formed by using thinner than typical (100–200 nm thick) silicides. Thus the formation of ultra-thin silicide film draws a special attention in VLSI process.

The formation of ultra-thin (< 50 nm) silicides requires an optimal control of silicidation process and potential to scale down the process. Thinner $CoSi_2$ films showed severe agglomeration and consequently, an increase in room temperature sheet resistance upon moderate annealing (Phillips *et al* 1990). One cost effective method of ultra-thin silicide formation, compatible with the self-aligned technology, would be low energy ion-beam mixing of Ge into thin (10–12 nm) cobalt film followed by two-step moderate RTA. Formation and evaluation of ultra-thin ion-beam mixed $CoSi_2$ films (< 50 nm) produced by sputter deposition of Co on Si has been discussed in this paper. The structural and electrical properties of the $CoSi_2$ films are presented in § 3.

2. Preparation of ultra-thin $CoSi_2$ films

Thin films of 10–12 nm Co were deposited by sputtering on N-type ⟨100⟩ Si substrate. All the wafers were chemically cleaned and dipped in 1% HF to remove the native oxide layer immediately before loading in the sputtering chamber. The vacuum before sputtering was better than 2×10^{-6} torr, the pressure during sputtering with argon was 7×10^{-4} torr. The thickness of the cobalt films were measured from the step heights of the surface profile obtained from Solan DEKTAK II. The thickness of the cobalt film varied from 9·9 to 12 nm. Thermal silicidation of cobalt conventionally involves the conversion of the complete Co film to the CoSi phase through an intermediate Co_2Si phase during a first thermal treatment and a second conversion to the final silicide phase, $CoSi_2$, during a subsequent thermal treatment.

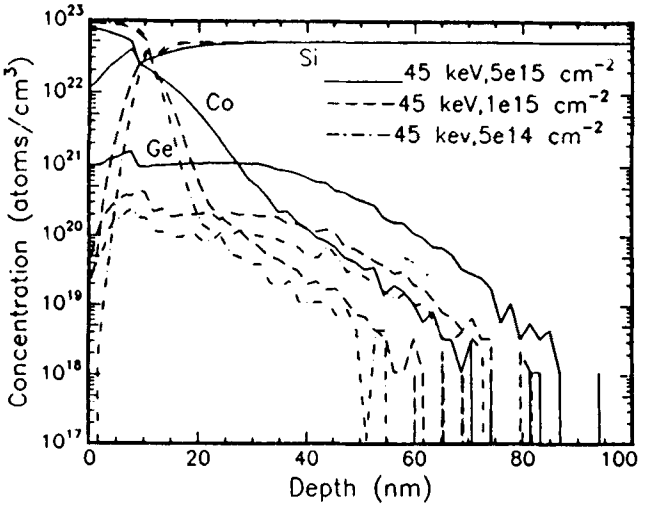

Figure 1. Dynamic Monte Carlo (T-DYN) simulated concentration profiles of Ge, Co and Si after ion-beam mixing of Ge.

After Co sputtering, the as-deposited samples were implanted with Ge ions at an energy of 45 keV. The energy was chosen from the simulation results with the dynamic Monte-Carlo program TRIM (T-DYN) (Biersack *et al* 1991). The simulation was done for germanium implantation in 10 nm cobalt film deposited on single crystal Si substrate. Concentration profiles of Ge, Co and Si are calculated from T-DYN data and the results are shown in figure 1. The Ge concentration necessary for Si amorphization is $\sim 2{\cdot}7 \times 10^{19}$ atoms/cc (Kasko *et al* 1992). The thickness of the amorphous silicon layer after implantation of Ge at dose $1{\cdot}0 \times 10^{15}\,cm^{-2}$ is about 48 nm. During the $CoSi_2$ silicidation process, silicon will be consumed and the thickness of the $CoSi_2$ layer obtained from 10–12 nm Co is ~ 35–42 nm. Thus the silicidation reaction will take place completely in amorphized Si for the Ge mixing dose of $1{\cdot}0 \times 10^{15}\,cm^{-2}$. The Ge^+ ion mixed Co deposited wafers were subsequently annealed in a rapid thermal annealing system (Heat Pulse 610, AG Associates) in Ar ambient at a peak temperature of 700°C for 45 sec. The first annealing process leads to the formation of thin Co_2Si film between the Si substrate and the unreacted Co layer on the top. The unreacted Co-layer was etched using a selective Co etch solution (5 HCl:4 H_2O_2:20 H_2O) at a temperature of 30°C for 30–60 sec. A second thermal treatment followed using RTA at a higher temperature of 800–1000°C for 10 sec to form the final $CoSi_2$ phase. The process sequence for silicide preparation is shown in figure 2.

3. Characterization of the $CoSi_2$ film

To understand the progress of the reaction after the RTA process, the sheet resistance of $CoSi_2$ was measured by Four-Point Probe measurements. X-ray diffraction (XRD) employing Cu K_α radiation ($\lambda = 1{\cdot}5418$ A) was used to identify the silicide phases that were present in the film. The metallurgical analysis was performed by Rutherford back scattering spectroscopy (RBS) with a 2·0 MeV $^4He^+$ ion-beam.

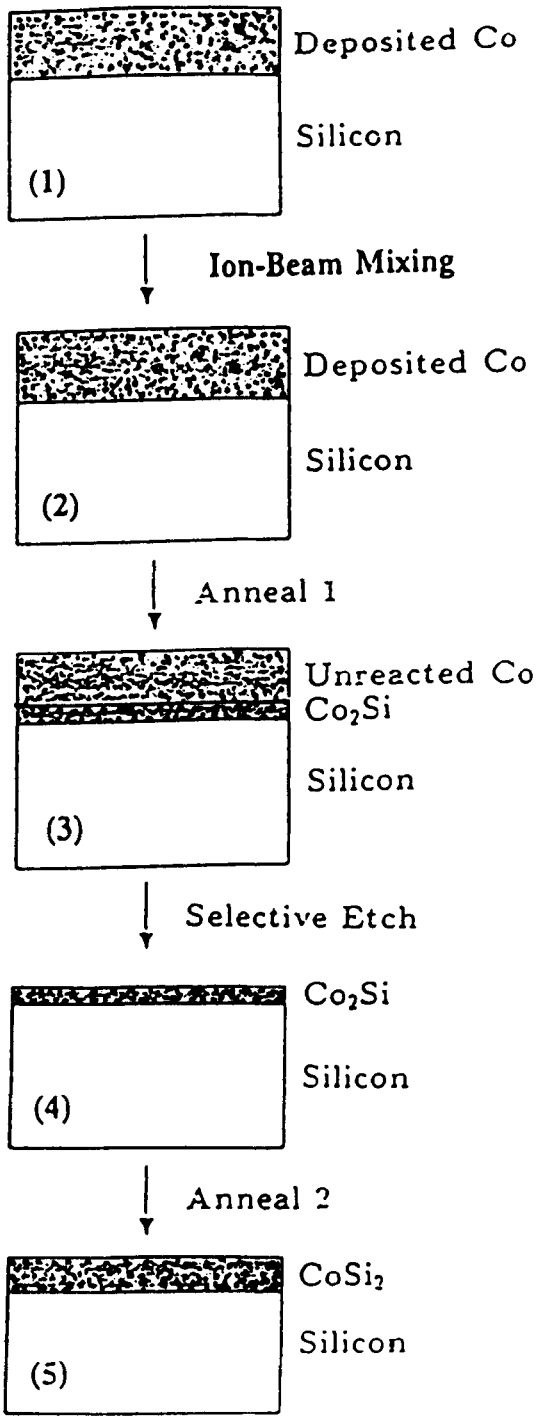

Figure 2. Process sequence of ion-beam mixed cobalt silicide.

3.1 *Sheet resistance measurements*

Sheet resistance of the Co film on Si were measured at different stages of $CoSi_2$ formation using 4-point resistivity method and the results are shown in table 1. The results indicate that the sheet resistance of the ultra-thin (~ 35 nm) $CoSi_2$ is a little bit higher (5·67 Ω/sq) compared to that of thick cobalt silicide (3–4 Ω/sq). It was observed from the available literature that sheet resistance increases as the silicide thickness goes down (Maszara 1992). It was also noted that sheet resistance of the samples after second anneal treatment remained almost same as the values obtained after first RTA. It was observed that, if the second anneal was performed at 1000°C for 10 sec (as is used in case of thick silicide formation (Kasko *et al* 1992; Xiao *et al* 1992)), $CoSi_2$ colour changed to gray and the sheet resistance could not be measured. This change was probably due to the formation of large grains of $CoSi_2$ embedded in Si which is also confirmed from the XRD analysis in the following section. The results indicated that in case of thin silicide (< 50 nm), the anneal temperature should be within 900°C and we had chosen the second RTA parameter as 800°C for 10 sec.

Sheet resistance mapping of sputter deposited Co film on Si after ion-beam mixing of Ge were measured using Four Dimension Auto Probe Model 280 and is shown in figure 3a. The mean value of sheet resistance was found to be 47·0 Ω/sq and the corresponding resistivity was obtained as 47 μΩcm taking the average value of Co thickness as 10 nm. The range of variation of sheet resistance was 1·68 Ω/sq and the standard deviation was 1·106%. Figure 3b shows the sheet resistance mapping of the final $CoSi_2$ film after second anneal treatment. $CoSi_2$ was removed at one edge of the wafer to compare the sheet resistance variation from $CoSi_2$ to single crystal Si. The final sheet resistance was much uniform over the entire surface of 4 inch dia wafer. The resistivity of the $CoSi_2$ film after the second RTA was found to be 19·87 μΩcm.

3.2 *X-ray diffraction (XRD) analysis*

The X-ray diffraction patterns were measured using Philips HR XRD instrument and *d* values of the intensity peaks were found using Philips diffraction software. The as-deposited Co film shows intensity peaks of Co, Si, Co_2Si and $CoSi_2$ (figure 4a). Figure 4b shows the X-ray diffraction pattern after 2nd RTA of 800°C, 10 sec and only $CoSi_2$ phase is present. Thus silicidation reaction seems to be completed after the second anneal treatment. The results of the XRD pattern of the silicide samples annealed at a temperature of 1000°C, 10 sec (shown in figure 4c) indicate that Si intensity peaks are dominant along with $CoSi_2$ and CoSi phases. It is presumably due to the formation of large grains of

Table 1. Sheet resistance (Ω/sq) of $CoSi_2$ films at different stages of silicide formation.

Process steps	Sheet resistances (Ω/sq)
After Ge^+ ion-beam mixing 45 keV, 1×10^{15} cm^{-2}	47
After first RTA: 700°C, 45 sec	5·82
After second RTA: 800°C, 10 sec	5·67

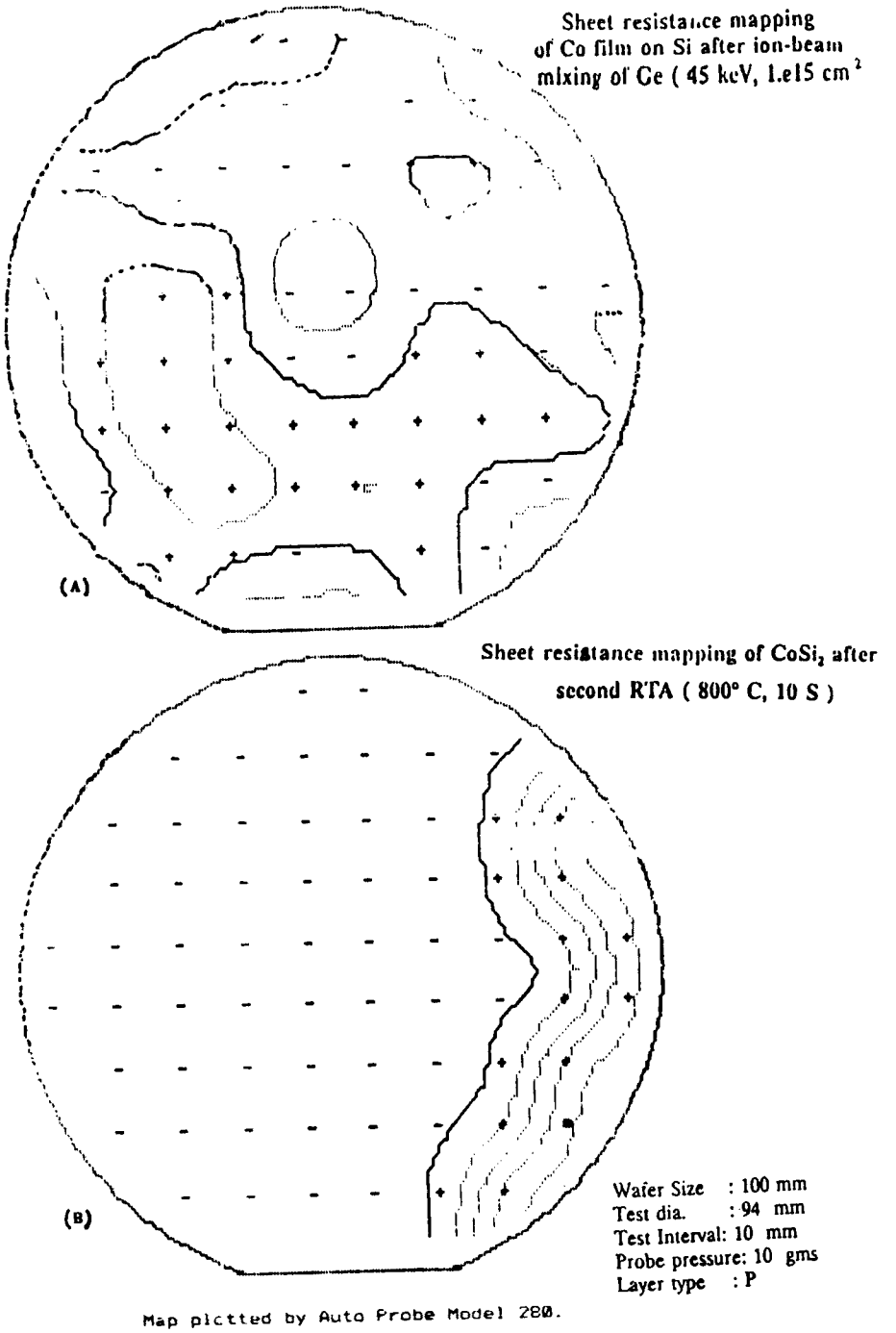

Figure 3. Sheet resistance mapping of (A) sputter deposited Co film on Si and (B) final $CoSi_2$ layer.

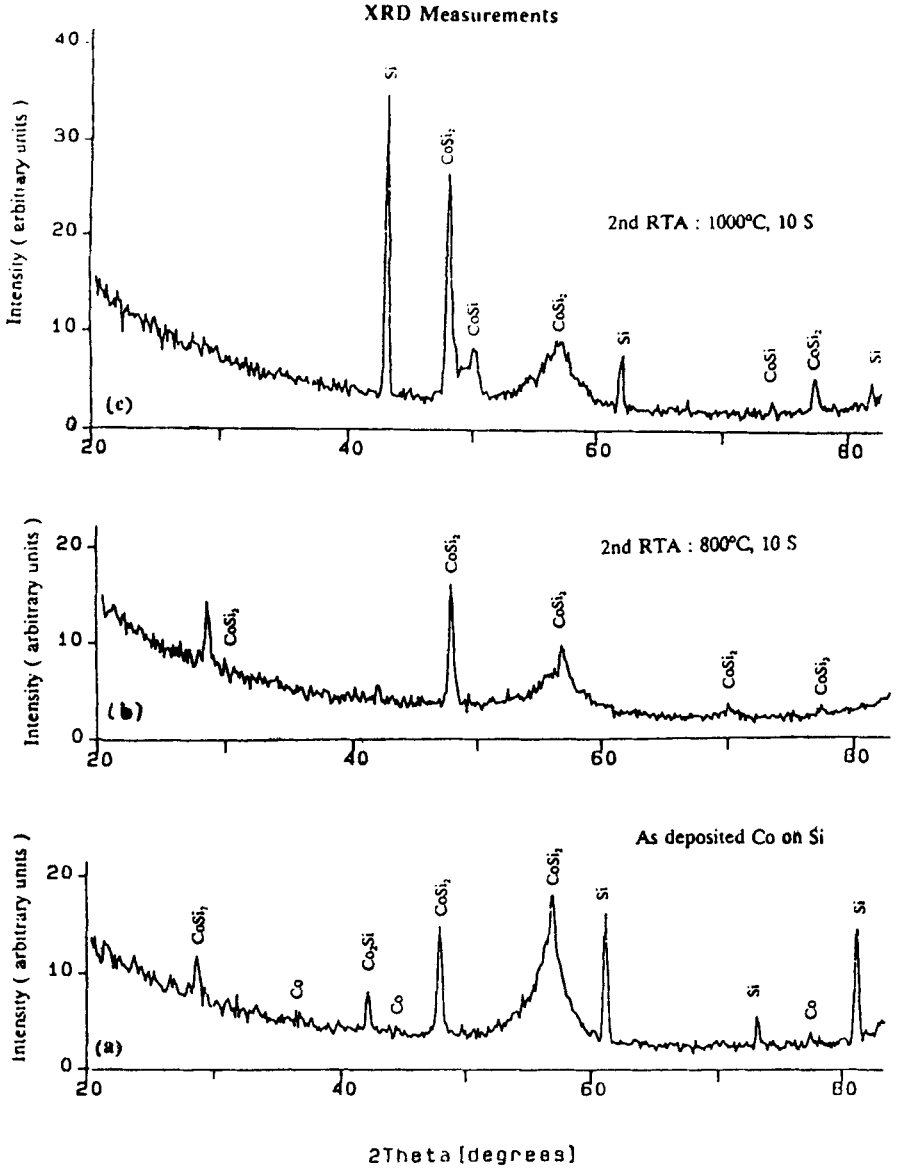

Figure 4. The X-ray diffraction patterns of $CoSi_2$ at various annealing conditions.

$CoSi_2$ and CoSi, which are embedded in silicon. As a result, the colour changes to gray. Sheet resistance at this stage could not be measured.

3.3 *Rutherford back scattering (RBS) analysis*

Rutherford back scattering (RBS) analysis with 2 meV $^4He^+$ ions was used for detection of silicide reaction. The samples were tilted at an angle of 10° in respect to the He beam.

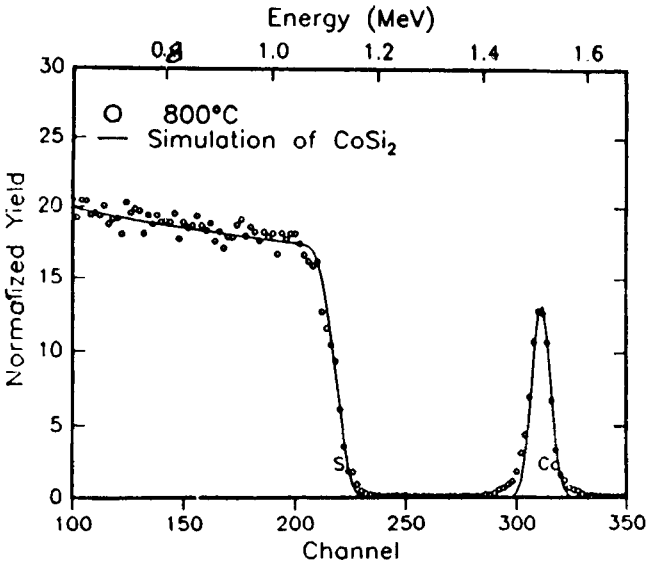

Figure 5. RBS spectra of thin $CoSi_2$ layer.

Typical RBS spectra of 10 nm Co on Si after ion beam mixing of Ge and two-step RTA at 700°C, 45 sec and 800°C, 10 sec are shown in figure 5. Simulated RBS spectra of $CoSi_2$ (obtained using RUMP software) is also plotted in the same figure for comparison. The results indicate that the experimental and simulated spectra exactly match after second anneal treatment of 800°C 10 sec. The equal slope at the left and right sides of the Co peak indicates uniform and homogeneous formation of $CoSi_2$. The thickness of the Co film was calculated from the RBS data and was found to be 11 nm. For RBS measurements, some samples were tilted at an angle of 60° in respect of He beam for improved depth resolution, but the step at the silicon surface of the yield curve, which was normally found in case of thick (> 50 nm) silicide, was not observed because of the thin layer of the cobalt silicide.

4. Conclusions

In this work, thin cobalt silicides were prepared from sputtered deposited 10 nm cobalt film by the solid phase reaction of Co and Si using rapid thermal annealing. The cobalt layers were mixed using 45 keV Ge^+ ions for homogeneous silicidation. A two-step annealing process at 700°C for 45 sec and 800°C for 10 sec was necessary to achieve $CoSi_2$ formation. The sheet resistance of the thin (~ 35 nm) $CoSi_2$ layer was found to be 5·67 Ω/sq. XRD analysis revealed that Si and CoSi phases were present in addition to $CoSi_2$ phase if the final RTA temperature was increased to 1000°C for 10 sec. The sheet resistance of the samples annealed at 1000°C, was very high and was difficult to measure. RBS measurements also indicated complete silicidation reaction at an RTA of 800°C for 10 sec. It is concluded from the investigations under this study that ultra-thin $CoSi_2$ layers needs RTA temperature of 800°C, 10 sec for homogeneous thermal silicidation.

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