



Rapid communication

Formation of $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ ternary silicide by thermal annealing of evaporated Co/Ni thin films on Si substrate

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ABSTRACT

In this work, we studied the formation and the thermal stability of a ternary silicide $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$, obtained by thermal annealing. Ni and Co thin films were deposited on Si(100) substrate. The performed annealing of 30 nm-Co/15 nm-Ni/Si(100) samples is carried out by means of a conventional furnace during 20 min and a temperature range 300–800 °C. The obtained specimens were investigated using X-ray diffraction (XRD), Raman spectroscopy and Rutherford backscattering spectroscopy (RBS). XRD data showed that the formation temperature of the ternary $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ phase was relatively lower compared with those of the NiSi_2 and CoSi_2 disilicides and it maintained its sheet resistance below 4.5 Ω/sq. Furthermore, the formation of this ternary silicide was confirmed by a shift in peaks position in the Raman spectra toward the lowest wavenumbers when the temperature is increased up to 500 °C. RBS results indicated that the thickness of the formed $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ layer was approximately 28–52 nm.

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Transition metal silicides, which are attractive materials for applications in electronic and optoelectronic devices, have been intensively studied during the past few years [1–3]. Titanium silicide TiSi_2 was the first silicide which has been used for these applications, mainly because of its low resistivity [4]. However, it has been found that the sheet resistance of titanium silicide may increase significantly as the line width decreases [5]. Recently, academic interest has focused on the CoSi_2 and NiSi compounds due to their low resistivity, high-temperature stability, compatibility for self-aligned process, and self passivating nature in an oxygen-rich environment [6–8]. For CoSi_2 , the gate sheet resistance may increase at very narrow width due to the thinning of CoSi_2 films at the edge of polysilicon line. At the same time, the formation of CoSi_2 consumes more Si in comparison with the one of TiSi_2 . This last is unfavorable for ultra-shallow junction. NiSi has a similar low resistivity as TiSi_2 and CoSi_2 , but it requires a low post-silicide processing temperature. When the annealing temperature is above

750 °C, NiSi will transform into NiSi_2 , which is characterized by an undesirable high resistivity. $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ compound can be formed by the solid reaction of Ni and Co bilayers with silicon atoms of Si substrate on which Co and Ni have been deposited. In the 1980's, d'Heurle et al. [9] have investigated the electrical properties of $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ thin Films. They have found that low resistivity thin films could be formed with up to 50% Ni in the $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ solid solution. Together, with the lower temperature formation for this mixed phase [10], this leads to the industrial interest in the $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ phase as a possible candidate to replace CoSi_2 in sub-100 nm CMOS technology [11–13]. Chamirian has evaluated the use of $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ for sub-45 nm CMOS technology and has concluded that the compound suffers from the same line-width effects as CoSi_2 [14]. Therefore, the interest in $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ for CMOS applications is fainting. Nevertheless, silicides formed from CoNi-alloys are still being evaluated in other fields. For example, Liu et al. have investigated the work function tuning with fully silicided Co–Ni metal gates [15], after Zhu et al. have studied the Schottky barrier characteristics of $(\text{Co}_x\text{Ni}_{1-x})\text{Si}_2$ on Si [16].

In this work, we studied the formation of silicides and phase transition in the Co/Ni/Si thin films at different temperatures using

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XRD, RBS and Raman spectroscopy techniques. The study was expected to provide a better understanding of the formation and thermal stability of the Co–Ni–Si alloys which is promising for technological applications.

In the present work, Co and Ni thin films were deposited using a thermal evaporator on a n-type (100) Si wafer. Prior to the deposition, the Si wafers were cleaned with an RCA solution and HF to remove any organic surface contaminants and native silicon oxide. During the thermal evaporation high purity materials (99.99% Ni and Co wire chips) were used. 15 nm thick Ni film was first deposited followed by a 30 nm Co film. Annealing of the samples was carried out in a conventional furnace between 300 and 800 °C under N₂ ambient atmosphere. Four Point Probe was adopted to measure the sheet resistance of these samples. XRD measurements were carried out using the Bruker-Axs D8 X-ray Diffractometer using Cu_K α radiation, for identification of the formed phases. RBS measurements were carried out using 2 MeV ⁴He⁺ delivered by a Van de Graaff electrostatic accelerator, the backscattered particles are collected with partial detector placed at 160° from the incident beam. RBS technique allows determining layer thickness and atomic depth profiling. The universal RUMP program [17] was used to further assist in the simulation of the recorded RBS spectra. Raman measurements were recorded using a RENISHAW in Via Raman micro analytical spectrometer equipped with a motorized x–y stage and autofocus. The experiments were realized at room temperature employing an excitation wavelength of 633 nm (He–Ne laser) with an accumulation time of 20 s. The laser spot was focused on the sample surface using a 50 × objective with short-focus working distance. The lateral resolution on the sample was approximately 2 μ m. A scanning electron microscopy was used in the plan view to examine the morphology and the structure of the formed films.

Fig. 1 shows the X-ray diffraction pattern of Co/Ni/Si(100) structures after heat treatment at different temperatures. For the as-deposited sample, only the diffraction peaks of Ni(111) and Co(200) were observable with the Si(200) line corresponding to silicon substrate.

At 300 °C, the peak assigned to Co(200) was still unchanged attesting the non reaction of the cobalt film with silicon Si, and

several Ni₂Si diffraction peaks were recorded [18] resulting from the reaction between Ni and Si atoms. The XRD data for the sample annealed at 500 °C have shown a diffraction peak related to Co₂Si [19]. It means that the presence of Ni interlayer did not prevent the formation and growth of Co₂Si phase at this temperature.

This later was formed by the diffusion of Si atoms through the Ni-related silicide layer following the grain boundaries, and the reaction with the Co atoms to form the Co disilicide phase. Also, the presence of nickel monosilicide NiSi was detected and it was formed to the detriment of the transformation of Ni₂Si phase, as it's predicted by theory in such solid reaction, the first compound to be formed are rich metal silicides, followed by mono-silicide and the final one to be formed are disilicides [20,21]. Besides to the Co₂Si and NiSi silicides, XRD data have revealed diffraction peaks assigned to the ternary (Co_xNi_{1-x})Si₂ silicide [22]. The appearance of this phase was attributed to the diffusion of Co atoms into Ni-related silicide. With the increase of temperature to 800 °C, it was found that CoSi₂ was formed and the ternary phase still exists with a significant increase in the peaks intensity.

Fig. 2 shows the sheet resistance measurements obtained for Co/Ni/Si and Ni/Si systems annealed at different temperatures. For the Co/Ni/Si samples, the increase in sheet resistance occurs before 400 °C resulting from the formation of Ni₂Si phase [23]. For higher temperatures, the NiSi monosilicide is formed resulting in rapid decrease in sheet resistance. The trend toward decreasing is stopped at annealing temperature of 600 °C, and it is remained around 4.5 Ω /sq as the annealing temperature increases. According to the XRD analysis, the (Co_xNi_{1-x})Si₂ ternary silicide is the main phase in the system at temperatures ranging between 500 and 800 °C. The Ni/Si samples exhibit a sharp rise in sheet resistance for temperatures higher than 700 °C due to the formation of the NiSi₂ disilicide [23]; Co/Ni/Si samples, however, did not show a noticeable rise in resistance around 700 °C, which is a great improvement over the Ni/Si system.

Fig. 3 shows the RBS spectra of the Co/Ni/Si(100) samples annealed at different temperatures.

The tables of rump data of these samples are inserted into Fig. 3(a–d).

As it can be seen, the energetic RBS spectrum of the un-annealed (as deposited) sample is composed of two distinct and sharp signals corresponding to the Si substrate plateau at low energy and the associated Ni/Co bi-layer at higher energies, it should be noticed

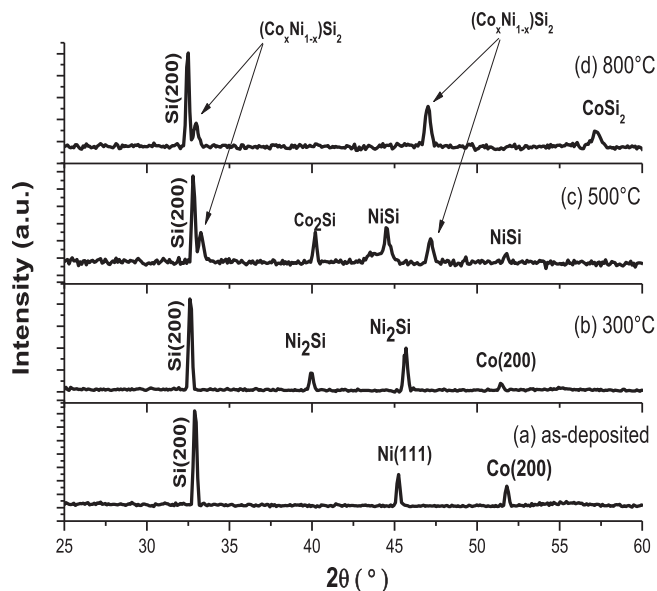


Fig. 1. XRD spectra of the Co/Ni films annealed at different temperatures.

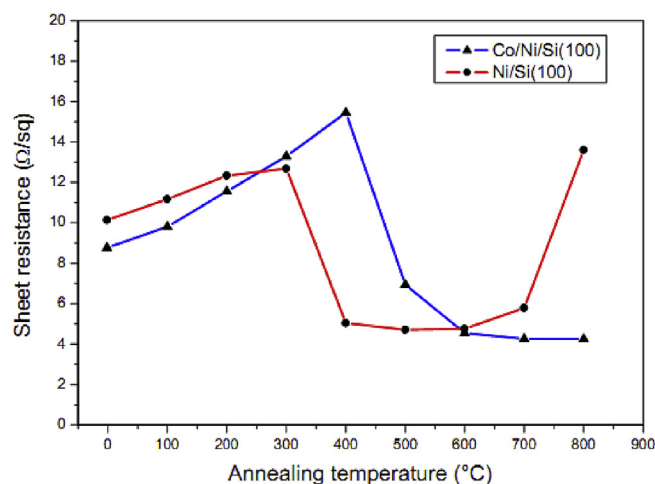


Fig. 2. Sheet resistance of the Co/Ni/Si and Ni/Si samples after annealing at different temperatures.

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