A study of nickel and cobalt silicides formed in the Ni/Co/Si(1 0 0) system by thermal annealing

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In this work, the Ni/Co/Si system was annealed at temperatures ranging from 300 °C to 800 °C. The samples were characterized by means of X-ray diffraction (XRD), Raman spectroscopy, Rutherford backscattering spectroscopy (RBS), atomic force microscopy (AFM) and sheet resistance measurement. The XRD and Raman spectroscopy results showed that the formation of nickel and cobalt silicides (CoSi, Co₂Si, Ni₂Si, NiSi, NiSi₂, CoSi₂) is an annealing temperature dependent diffusion process. The diffusion phenomenon was evidenced by RBS. The low values of the sheet resistance which were correlated with the films surface roughness were attributed to the formation of both CoSi and NiSi phases.

Keywords: Ni/Co/Si system; nickel silicide; cobalt silicide; XRD; RBS; Raman spectroscopy; AFM

1. Introduction

Metal silicides play an important role as low-resistive interconnects in the microelectronic field [1–3]. They can be used to reduce both the resistance of source/drain region and gate level interconnection of CMOS. Self-aligned silicide technology, in which silicide is formed simultaneously on the source/drain and gate regions of MOS devices, has been widely used in very large and ultra large integrated circuits fabrication. A great interest has been given to TiSi₂, CoSi₂ and NiSi materials due to their low resistivity, high-temperature stability, compatibility for self-aligned process, and self-passivating nature in oxygen-rich environment [4–6]. TiSi₂ was the first used silicide [7]. However, its electrical resistance increased abruptly with the line width for narrow lines (below 0.25 μm) [8, 9]. For CoSi₂, it was found that this silicide consumed a relatively large amount of silicon resulting in a thick silicide layer [10]. In addition, above 800 °C,

the CoSi₂/Si interface became exceedingly rough due to agglomeration and excessive reaction of Co with native SiO₂ which requires extensive surface cleaning process [11–13]. NiSi has a low resistivity compared with that of CoSi₂ and its formation and growth require less silicon consumption. However, its thermal stability is relatively poor since, at temperatures above 700 °C, the silicide transforms into resistive NiSi₂ [14]. This poor thermal stability was partly addressed by the insertion of a thin Co or Ir interlayer at the Ni/Si interface [15] and by addition of alloying elements such as Co, Pt, and Au [16] inducing the formation of ternary silicide.

Recently, a great interest has been given to ternary silicide Co_xNi_{1-x}Si₂ because of its good electrical conductivity (resistivity of 16 μΩ · cm to 20 μΩ · cm) and, in addition to that, its formation and growth temperature is lower than that of CoSi₂ and its thermal stability is better than that of NiSi [17]. Moreover, Co_xNi_{1-x}Si₂ promotes the safeguarding of the crystallographic structure of CoSi₂ with virtually the same lattice parameter.

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In this work, we studied the dependence of different Co and Ni silicides on the annealing temperature of the Ni/Co/Si system by analyzing the results of X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS), Raman spectroscopy and atomic force microscopy (AFM) techniques in addition to the measurements of the sheet resistance using the four point probe technique.

2. Experimental

Ni and Co thin films were deposited on n-type Si(1 0 0) substrates using the vacuum evaporation method. 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. The Ni and Co thicknesses were controlled to be 50 nm and 20 nm, respectively. The annealing of the deposited films was carried out in a conventional furnace, at temperatures between 300 °C and 800 °C. The annealing time was maintained at 20 min. The identification of the formed phases was done using an X'Pert Pro diffractometer with a CuK α radiation. The films thickness and the atomic depth profiling were determined by means of the Rutherford backscattering spectroscopy (RBS) using 2 MeV $^4\text{He}^+$ delivered by a Van de Graaf electrostatic accelerator; the backscattered particles were collected with a particle detector placed at 160° from the incident beam. The universal RUMP program [18] was used for the simulation of recorded RBS spectra. Raman spectra 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 $\times 50$ objective with short-focus working distance. The lateral resolution on the sample was approximately 2 μm . Atomic force microscopy (AFM) was used in the plan view to examine the surface morphology of the formed films. For the sheet resistance measurements at room temperature, the Jandel four point probe connected with a Keithley 2400 source meter was used.

3. Results and discussion

The XRD pattern of the as-deposited Ni/Co/Si sample is shown in Fig. 1.

Fig. 1. XRD pattern of the Ni/Co films deposited onto Si(1 0 0) substrate.

We can see the presence of three diffraction peaks located at about 32.48°, 45.29° and 51.79° corresponding to the silicon substrate, the cobalt layer and the nickel layer, respectively. The difference between the Co and the Ni related peaks intensity may be due to the fact that the nickel material amount is greater than that of cobalt material since the Co film thickness (20 nm) is smaller than that of Ni film (50 nm). Fig. 2 shows the X-ray diffraction patterns of Ni/Co/Si system annealed at temperatures extending from 300 °C to 800 °C. After annealing at 300 °C, we notice the formation of two main phases, the phase rich in cobalt Co_2Si (2 1 1) detected at the angle of 39.74° along with CoSi (1 1 1) and CoSi (2 1 1) positioned at 34.84° and 50.57°, respectively.

Also, it is noted that no nickel silicide phase has been detected at this temperature in spite of the disappearing of the Ni related peak. This may suggest that all the nickel diffused into the formed cobalt silicide, thus leading to possible formation of a ternary $(\text{Co}_x\text{Ni}_{1-x})_2\text{Si}$ phase. This suggestion will be argued further in the RBS analysis part. For the sample annealed at 400 °C, all the cobalt silicides disappeared while the nickel silicides appeared. The analysis of the diffusion of atoms of

Fig. 2. XRD patterns of the Ni/Co/Si system annealed at different temperatures (the phases corresponding to the peaks are shown on the top).

Co and Ni will be detailed basing on the results of RBS simulation. Also, it must be stated that the nickel rich silicide Ni_2Si has formed at 400 °C instead of 250 °C [19]. This delay is typically due to the presence of the cobalt layer which plays the role of a nickel diffusion barrier to the silicon substrate. In addition, the monosilicide NiSi has been detected simultaneously with the Ni_2Si phase, which suggests that the transformation between these two phases begins at this temperature. For the sample annealed at 500 °C, we notice the disappearance of all the peaks corresponding to the Ni_2Si phase, indicating that the transformation of this latter towards the NiSi phase has been completed at this temperature. The NiSi (2 1 0) peak located at 44.04° is more intense, and two new peaks appearing in the angular positions of 38.27° and 50.90° correspond to the NiSi (2 0 1) and NiSi (1 0 3), respectively. After annealing at 600 °C, we note that the NiSi phase still exists with a slight increase in the intensity of the (2 1 0) line; the position of this line undergoes a slight shift. This displacement may be explained by the diffusion of Co atoms into NiSi phase. At this temperature, the phase transformation of NiSi into Ni_2Si has not occurred yet. With the increase of the temperature to 700 °C, the XRD pattern is almost similar to the previous

sample which reflects that the same phases have been detected with only changes in the intensity of their corresponding peaks. The NiSi phase always exists which indicates that this phase always remains stable at this temperature in addition to a peak located at 56.81° and related to CoSi_2 (3 1 1). From the XRD pattern of the sample annealed at 800 °C, we can see that the NiSi phase completely disappears leaving the place to the NiSi_2 phase. Also, at this temperature, the CoSi_2 phase always exists with the presence of a more intense peak located at 28.79° . Fig. 3 shows the RBS spectra of the Ni/Co/Si system annealed at different temperatures.

Fig. 3. RBS spectra of the as-deposited and the annealed Ni/Co/Si system.

As it can be seen, the as-deposited RBS spectrum is composed of two distinct signals corresponding to the Si substrate surface (Channel 450) and the associated Ni/Co bilayer (Channel 650). It should be noticed that Co and Ni metals are very close neighbors in the periodic table that's why their peaks signals have merged within a single peak. The RUMP simulation of the as-deposited sample (Fig. 4a) indicates only the presence of pure metals and Si substrate.

The simulated values of Ni and Co films thickness have been estimated and found to be equal to 50 nm and 20 nm, respectively, which is consistent with the nominal values. Fig. 4 shows that the intensity of the Ni/Co peak decreases as a function of

Fig. 4. Simulation of RBS spectra of the Ni/Co/Si system (a) as-deposited; (b) annealed at 800 °C.

annealing temperature. This decrease of the Ni/Co peak intensity is accompanied with a shift of the corresponding Si surface channel to 500. This indicates that both Co and Ni atoms have diffused into the silicon substrate which involved the formation of both Co and Ni silicides. Indeed, the decrease in the Ni/Co corresponding peak intensity correlates with the increase in the peaks corresponding to Co and Ni silicides. It is in a good agreement with the XRD analysis results. For the annealing temperatures between 300 °C and 500 °C, no significant changes in the Ni/Co peak shape were observed

which means that the diffusion process induced by thermal annealing in this temperature range is slow since the intensity of channel 500 is very low. However, for the annealing at temperatures between 600 °C and 800 °C, the Ni/Co peak shape changes considerably with the increase of the new layer (Channel 500) related signal intensity. In this range of temperatures, the diffusion of both Co and Ni atoms is pronounced. The simulation of the RBS spectra (Fig. 4b) gave us atomic concentrations of Co, Ni and Si in the appearing layer indicating a possible formation of the ternary $(\text{Ni}_{1-x}\text{Co}_x)\text{Si}_2$ silicides. This is to be excluded since XRD patterns (Fig. 2) show the presence of only binary silicides, such as CoSi, NiSi, Ni_2Si . Fig. 5 shows the Raman spectra of the Ni/Co/Si samples annealed at temperatures up to 800 °C.

Fig. 5. Raman spectra of the Ni/Co/Si system annealed at temperatures up to 800 °C.

The reports on Raman spectra of metal silicides are very few [20], and part of the reason might be the lattice vibration frequencies which are too low to be detected [21]. The Raman spectrum of the sample annealed at 300 °C includes a weak peak located at 150 cm^{-1} corresponding to Co_2Si phase [22]. The Raman peak of Ni_2Si phase in the samples treated at 400 °C and 500 °C is located at 139 cm^{-1} [23]. Also, we note the presence of NiSi in the samples treated at temperatures ranging between 400 °C and 700 °C. The positions of Raman signals associated to NiSi phase are 197 cm^{-1} and 217 cm^{-1} . For the CoSi phase, Raman

spectroscopy shows a peak situated at 240 cm^{-1} for the samples annealed at temperatures between $500\text{ }^{\circ}\text{C}$ and $700\text{ }^{\circ}\text{C}$ and a peak at 223 cm^{-1} for the sample annealed at $800\text{ }^{\circ}\text{C}$ [21]. Raman spectroscopy is sensitive to the presence of CoSi and Co_2Si phases, but not to the CoSi_2 phase even with a more sensitive Raman spectroscopy apparatus [24, 25]. One can deduce that the results of the Raman spectroscopy are consistent with those of the XRD in spite of the absence of information about the CoSi_2 phase.

The AFM observations have been performed on square surfaces of about $8\text{ }\mu\text{m} \times 8\text{ }\mu\text{m}$. AFM images of some samples are shown in Fig. 6. The surfaces are composed of grains having a spheroidal shape. The roughness RMS (root-mean-square) of different samples has been calculated from the AFM images using the software "Nano Rule".

Fig. 6. AFM images of Ni/Co/Si surfaces annealed at: (a) $300\text{ }^{\circ}\text{C}$, (b) $600\text{ }^{\circ}\text{C}$ and (c) $800\text{ }^{\circ}\text{C}$.

The RMS values have been drawn with the sheet resistance as a function of the annealing temperature in Fig. 7. The high values of the sheet resistance for the samples annealed at temperatures of $300\text{ }^{\circ}\text{C}$ and $400\text{ }^{\circ}\text{C}$ may result from the formation of Co_2Si and Ni_2Si phases [26]. For higher temperatures, we can see that the sheet resistance decreases and stabilizes around $4\text{ }\Omega/\text{square}$. This behavior may be related to the presence of CoSi and NiSi phases. The low value of the sheet resistance for the sample annealed at $800\text{ }^{\circ}\text{C}$ in spite of the presence of the resistive CoSi_2 was unexpected. The low RMS value of this sample may be due to the presence of Si atoms on the surface resulting from enhanced diffusion of Ni and Co atoms. The surface roughness affects directly the sheet resistance [27] and this may be the explanation of such behavior.

Fig. 7. Variation of the sheet resistance and surface roughness (RMS), of Ni/Co/Si system, as a function of the annealing temperature.

4. Conclusions

The reaction between Ni/Co bilayer and Si substrate has been investigated as a function of annealing temperature using XRD, RBS, Raman spectroscopy, AFM and the four point probe techniques. XRD and Raman spectroscopy showed that, depending on annealing temperature, the cobalt atoms start first diffusing and reacting with Si to form Co_2Si and CoSi phases. At temperatures higher than $400\text{ }^{\circ}\text{C}$, Ni silicide formation takes place by the formation of NiSi_2 followed by the formation of NiSi. The latter remains stable up to $700\text{ }^{\circ}\text{C}$ but disappears at $800\text{ }^{\circ}\text{C}$ leaving the place to the resistive silicides NiSi_2 and CoSi_2 . The diffusion process was evidenced from RBS spectra analysis. From the simulation of the RBS spectra, the formation of ternary silicides was suspected but excluded basing on the XRD and Raman spectroscopy results. The four point probe technique showed that the sheet resistance decreased as a function of annealing temperature. The decrease of the sheet resistance was attributed to the presence of CoSi and NiSi phases.

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