Nickel silicide formation by electroless technique for ULSI technology

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Abstract

In this paper we report on the formation of nickel silicide by electroless process. The nickel plating solution was composed of a mixture of NiSO 4·6H 2 O, NaH 2 PO 2·H 2 O, Na 2 C 6 H 5 O 7 , and NH 4 Cl, where NiSO 4·6H 2 O is the main nickel source and NaH 2 PO 2·H 2 O is the reducing agent. The nickel silicide formation was carried out by heating the deposited samples in vacuum at temperatures from 100 °C to 800 °C. The evolution of NiSi phase from the nickel film was verified using the X-ray diffraction technique and Raman spectroscopy. The surface morphology was studied using AFM technique. The electroless plating technique can provide a cheap and easy process for forming nickel silicide, and has potentiality of application for the electronic device industries.

1. Introduction

With the advent of ULSI, silicides have gained very high importance because of their low resistivity, self alignment, good diffusion barrier properties, low process temperature, and strong tolerance for high temperatures [1]. Recently Nickel silicide has been demonstrated to be a promising material for deep submicron CMOS devices. It can be formed by solid state reaction of metal and Si at high temperature and yields high quality ULSI compatible, thin film deposits [2,3]. NiSi has many advantages over CoSi 2 and TiSi 2 in terms of thermal stability, low silicon consumption, and low stress. However, NiSi is not stable at high temperatures above the 650 °C. Many efforts were provided to improve the thermal stability of NiSi by adding alloying element as: Pt, Pd, Zr, W, and BF 6 .

2. Experimental details

Single crystal (1 0 0) silicon wafers were used in present study. Prior to the electroless plating process, it is necessary to pretreat the silicon surface. The pretreatment of Si consisted of the following four steps; (1) degreasing the surface using acetone by ultrasonic; (2) then cleaned in RCA1 solution containing NH 4 OH, H 2 O 2, and H 2 O in 1:1:5 and RCA2 solution containing HCl, H 2 O 2, and H 2 O in 1:1:5 solution for 10 min; (3) sensitizing in a solution of SnCl 2/HCl (40 g/l SnCl 2 + 40 ml/l HCl) for 2 min; and (4) activating by deposition of Pd in a mixed solution (0.15 g/l PdCl 2 + 3 ml/l HCl + 83 ml/l HF) for 10 s. The sensitization and activation steps were carried out at room temperature. A rinse with DI water was carried out at the end of each step. The plating solution was composed of a mixture of NiSO 4·6H 2 O, NaH 2 PO 2·H 2 O, Na 2 C 6 H 5 O 7 , and NH 4 Cl, with NiSO 4·6H 2 O as the main nickel source, NaH 2 PO 2·H 2 O as the reducing agent, Na 2 C 6 H 5 O 7 and NH 4 Cl as complexing and buffer agent for nickel. Since NaH 2 PO 2·H 2 O is used as a reducer, the electroless plated nickel structures were always incorporated with phosphorus. The composition of plating solution is listed in Table 1. The 50 nm thin NiP film was deposited by dipping the Si wafer in the bath for 100 s. Although the contaminants and native
oxide were removed by dilute HF before sensitizing, it is inevitable to form oxide layer on wafer surface during sensitization, activation, and deposition. All deposited samples were annealed in vacuum furnace at 100–800°C, the annealing time at each temperature was 30 min. After the thermal treatment, the unreacted metal was etched with a mixture of NH4OH and H2O2 for several minutes. A four-point probe method was used for measuring the sheet resistance of the deposited films. The thickness of electroless deposited films was measured by the stylus Profiler (AMBIOS XP-1). Variation of the crystal structures of the films caused by the annealing process was observed with X-ray diffractometer (XRD, Panalytical's X'Pert Pro) and Raman spectroscopy (WiTec CRM 2000 Raman spectrometer coupled with a high resolution Confocal optical microscope). The surface morphology of the film was characterized by the Atomic Force Microscope Model Pro 47, NT MDT.

3. Results

The variation of sheet resistance as a function of annealing temperature is shown in Fig. 1. The sheet resistance of as deposited 50 nm NiP film was 4.112 ohm/square. After annealing of the structure at 100°C, the sheet resistance drops to 40% of its original value. The continuous decrease in sheet resistance was observed at higher annealing temperatures. The sheet resistance falls by about 75% after annealing at 600°C and becomes about 1.1 ohm/square.

The XRD analysis was carried out twice: first with unreacted top Ni film present and then after removal of unreacted Ni from the
top. Fig. 2a shows the XRD spectrum of the Si/NiP samples annealed at various temperatures and unreacted Nickel is still present on top of the structure. In the case of as deposited samples there is only one peak at 2θ = 44.5° corresponding to the Ni. When the samples were annealed at 400 °C, this peak sharpens and a new peak has emerged which corresponds to NiSi(1 0 3). The emergence of this peak indicates that the silicidation has started at 400 °C. Further annealing at 500 °C indicates new peaks corresponding to NiSi(0 0 2), δ-Ni2Si(2 2 1), NiSi(1 0 2), and NiSi(2 0 2), respectively. The annealing at 600 °C results in the growth of all these monosilicided orientations along with the appearance of new peaks NiSi(2 0 0), NiSi(1 1 1), and NiSi(1 1 0), respectively. The δ-Ni2Si(2 2 1) phase disappeared at 600 °C.

Fig. 2b exhibits the XRD spectrum after removing the top unreacted nickel metal. The peaks were observed corresponding to NiSi(1 1 0), NiSi(0 0 2), NiSi(2 0 0), NiSi(1 1 1), NiSi(1 0 2), NiSi(2 0 2) in the samples annealed at 400 °C. No new peaks were observed when the samples are annealed at 600 °C. Further annealing at 800 °C resulted in development of a new peak at 2θ = 28.5° which corresponds to NiSi2(1 1 1). The disappearance of NiSi(1 1 0) peak at 800 °C was also observed.

The Raman spectra obtained after removing the unreacted Ni film is shown in Fig. 3. The peaks at 212, 255, 303, 320, 360, and 396 cm−1 were observed for the nickel silicide thin film. NiSi formed at 400 °C has one major peaks at 212 cm−1 with minor peaks at 255, 303, and 360 cm−1. The NiSi2 which nucleate at 800 °C has weak and broad peaks at 320 and 396 cm−1 [6]. According to factor group analysis, the peaks at 212 and 360 cm−1 can be assigned to the A2g symmetry, while peaks at 255 and 303 cm−1 may belong to B2g or B3g symmetry [7].

Fig. 4. (a) AFM surface morphology of as deposited Si/NiP sample. (b) AFM surface morphology of 500 °C annealed Si/NiP sample. (c) AFM surface morphology of 600 °C annealed Si/NiP sample.
The AFM surface morphologies of as deposited Si/NiP sample are shown in Fig. 4a. The three dimensional image is also shown. The surface is smooth and root mean square roughness is of the order of 20 nm. The annealing of samples at 500°C and 600°C results in the growth of grains as visible from Fig. 4b and c, respectively.

4. Discussion

The diffusivity of nickel inside silicon is about 10 times more as compared to diffusivity of Si into nickel [8]. The Ni3Si phase which forms at low temperature is normally considered as unstable and high resistivity phase. NiSi phase formation takes place either at the same annealing temperature with longer annealing time or at higher temperature with similar annealing time. NiSi phase is thermally stable up to 700°C and then it begins to transform to another high resistivity phase NiSi2 at about 800°C. NiSi is orthorhombic structure with lattice parameters a = 0.523 nm, b = 0.326 nm, and c = 0.566 nm [9]. NiSi2 is a cubic calcium fluoride structure with lattice parameter a = 0.5395 nm.

As reported in literature, the nickel silicide formed by annealing of sputtered Ni/Si film at 800°C resulted in the disappearance of monosilicide phase and only NiSi2 phase was present [10]. Almost similar results were reported by Young-Woo Ok et al. where NiSi2 was the only available phase after annealing at 750°C [11]. The sheet resistance in their study also indicated increasing trend after annealing of the sample at 650°C. They supposed that increase in the sheet resistance is due to the presence of only high resistivity NiSi2 phase after annealing. In our study, the sheet resistance did not show any increasing trend even after annealing at 800°C. XRD results indicated that nickel monosilicide phase (low resistivity phase) is still present along with NiSi2 (high resistivity phase) phase after annealing at 800°C (Fig. 2b). It is clear from our data that complete transformation from NiSi to NiSi2 phase has not taken place even after annealing of the samples at 800°C.

Electroless deposition of Ni normally results in the incorporation of some phosphorus in the film which may have some influence on the nucleation process required for the formation of NiSi2 phase at high temperatures. So, the presence of phosphorus in electroless deposited nickel film may be responsible for the delay in complete phase transformation from NiSi to NiSi2.

In order to have detailed understanding of the effect of phosphorus concentration on the phase transformation, further studies need to be carried out with different chemical composition of the nickel deposition bath which results in different concentration of phosphorus in the film. Moreover, the characterization using SEM and TEM is still required to understand the influence of agglomeration during annealing on the phase transformation process. The results obtained from these characterization tools will be reported in a separate communication.

5. Conclusion

The formation of nickel silicide using electroless process was reported. The nickel plating on silicon substrate was carried out in a solution which was composed of NiSO4·6H2O, NaH2PO2·H2O, Na3C6H5O7, and NH4Cl, where NiSO4·6H2O is the main nickel source and NaH2PO2·H2O is the reducing agent. XRD and Raman analysis confirms the formation of nickel silicide. The presence of unstable phase Ni2Si also detected in XRD spectrum. NiSi phase was found to be most stable phase in the structure. At high temperature transformation of NiSi phase to NiSi2 was observed. Further studies related to effect of phosphorous concentration on phase transformation need to be carried out.

References