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INVESTIGATION OF Ni SILICIDES FORMATION ON (100) Si BY X-RAY DIFFRACTION (XRD)

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ABSTRACT

In this study NiSi were investigated using XRD (X-Ray diffraction) to observe silicides phase transition from the low sheet resistance phase to the high sheet resistance phase. In the analyzed Ni silicide samples, the transition was observed to occur at the formation temperatures greater than 650-700ºC, according to XRD measurements and sheet resistance measurements performed using the four point probe method (V/I). Agglomerates and precipitated formation on the obtained silicide films were also investigated using SEM (Scanning Electron Microscopy).

1. INTRODUCTION

In microelectronics the constant shrinking of devices dimensions demanded studies for another materials. For the MOS technology, source and drain contacts with low resistivity are necessary. Several metal silicides have been studied to attempt this requirement. The more important silicides are $TiSi_2$, $CoSi_2$, WSi, $TaSi_2$, and NiSi, but each silicide present different formation characteristics. $TiSi_2$ and $CoSi_2$ are formed in two temperature steps and present high silicon consumption [1]. $TiSi_2$ presents a high agglomeration formation showing itself difficult to use in sub-micron interconnections lines [2-3]. $CoSi_2$ is currently being used due to the absence of sheet resistance degradation on deep submicron lines. However, high Si consumption and junction spiking may limit its utilization in the future CMOS technologies [4].

In recent years, nickel silicide has become an attractive candidate material for use in future CMOS device generations, because of its low resistivity, one-step low temperature formation and low consumption of Si, in addition to the fact that its sheet resistance is independent on line width [5]. However, the major concern to use Ni silicide in the process integration resides in its poor phase stability. NiSi is thermally stable only up to the temperatures of 650 ºC - 700ºC, thereafter the high resistivity phase $NiSi_2$ starts nucleating [6-7]. NiSi has been reported to agglomerate during the silicidation process at temperature as low as 600ºC [8]. In this work, we investigate the formation and thermal stability of thin NiSi films on <100> mono crystalline Si in the temperature range from 500 ºC to 700 ºC.

2. EXPERIMENTS

The substrates used in this study were 1-10 Ω.cm <100> p-type Silicon wafers. The wafers were cleaned using a standard RCA cleaning process and dipped in 1:10 HF solution for 30 seconds prior the metal deposition, in order to remove the native oxide. Nickel deposition was performed by e-beam-gun evaporator, 30 nm of nickel was deposited, using base pressure of 4×10^{-9} Torr, pre-chamber pressure of 1×10^{-7} Torr, and deposition rate of 0.8 Å/s. Silicides formation were performed by rapid thermal annealing (RTA) process with 2000 sccm, very pure and dry nitrogen, to avoid strange materials incorporations, flow rate at atmospheric pressure and with RTA annealing time of 30, 60, and 90 seconds. The unreacted metal after silicidation was removed using H_2SO_4: H_2O_2 = 4:1 solution at room temperature. The physical characterization was performed using X-Ray Diffraction Spectrometry (XRD) and Scanning Electron Microscopy (SEM) to identify crystalline phases, structures, and to analyze the surface characteristics of the obtained silicide samples. The electrical characteristics measurements were performed by the four-point probe method.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of Ni silicide formed at temperatures of 500, 600 and 700ºC and annealing time of 60 seconds. The highlighted region in the figure is amplified and it shows the crystalline orientations between 30º and 40º of 2θ. The crystalline orientation displayed are: (200) Si with $2\theta \cong 33º$ and (102) NiSi with $2\theta \cong 37.2º$. The (102) NiSi crystalline orientation intensity increases with temperature. Figure 2 shows the same plot, highlighting a different crystalline orientation region between 40º and 50º of 2θ. The crystalline orientation observed is (112) NiSi with $2\theta \cong 43.2º$. The (112) crystalline orientation intensity decreases with temperature, as opposed of (102). Up to this annealing

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temperature of 500º and 600ºC, the formed silicide samples exhibited no $NiSi_2$ orientation, only the intensity change with the temperature. Figure 3 shows in the highlighted region the first $NiSi_2$ crystalline orientation observed. The 2θ region observed in this plot corresponds to the crystalline orientations between 60º and 70º. The silicide structure formation in this 2θ range was observed to occur only on the samples formed at 700ºC. This only shows that sample has the $NiSi_2$ orientation presence, it doesn't characterize that crystalline phase change completely, but this presence was enough to help increase the sheet resistance. The crystalline orientation exhibited are (020) NiSi at $2\theta \cong 61.8º$, (400) $NiSi_2$ at $2\theta \cong 66º$, and the crystalline orientation (400) Si at $2\theta \cong 70º$ observed to all samples measured. The last crystalline orientation observed in this scanning is (222) NiSi at $2\theta \cong 78.8º$ shown in the highlighted region of Figure 4. The crystalline phase transition confirmation at 700ºC can be observed at figure 5, where the sheet resistance increases in this sample. Figure 5 also shows the influences of the silicide agglomerations and precipitations on the behavior of the sheet resistance of the samples formed above 600ºC [8].

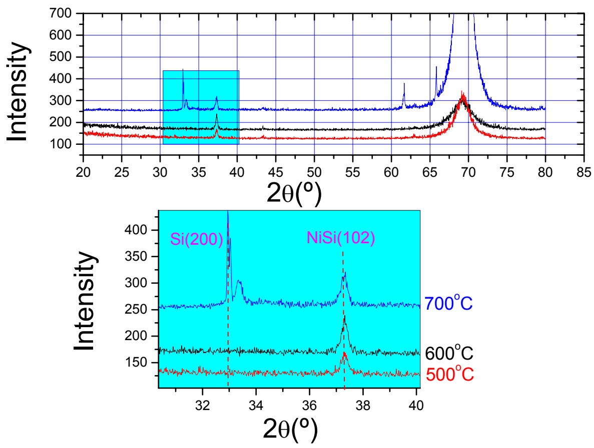

Figure 1 - XRD Spectra of samples formed at 500, 600 and 700ºC, showing the crystalline orientations between 30 and 40º.

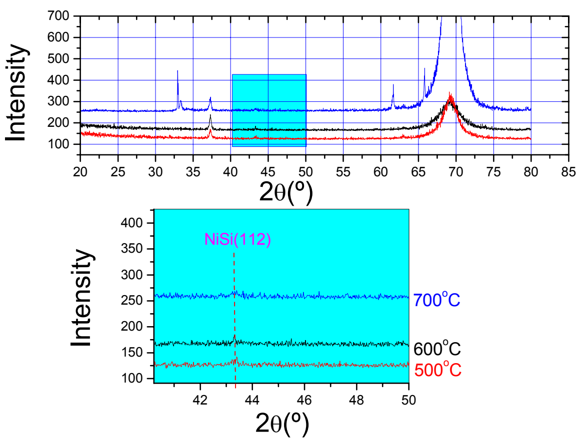

Figure 2 - XRD Spectra of samples formed in 500, 600 and 700ºC, show the crystalline orientation to 2(θ) between 40 and 50º.

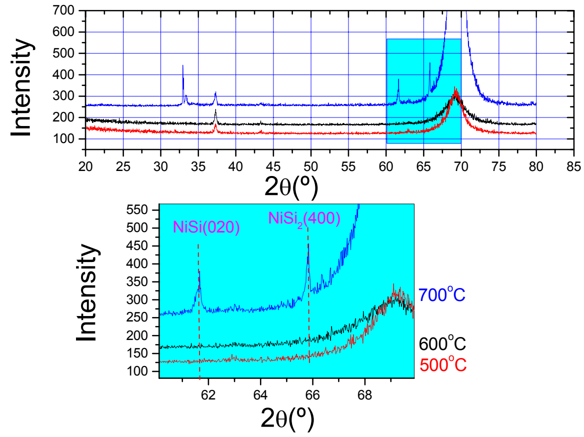

Figure 3 - XRD Spectra of samples formed at 500, 600 and 700ºC, showing the crystalline orientations between 60 and 70º.

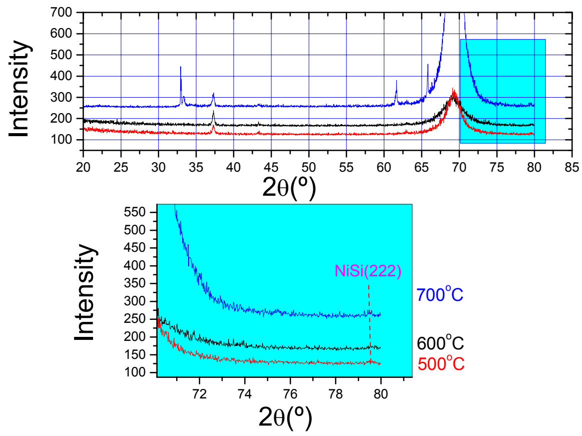

Figure 4 - XRD Spectra of samples formed at 500, 600 and 700ºC, showing the crystalline orientations between 70 and 80º.

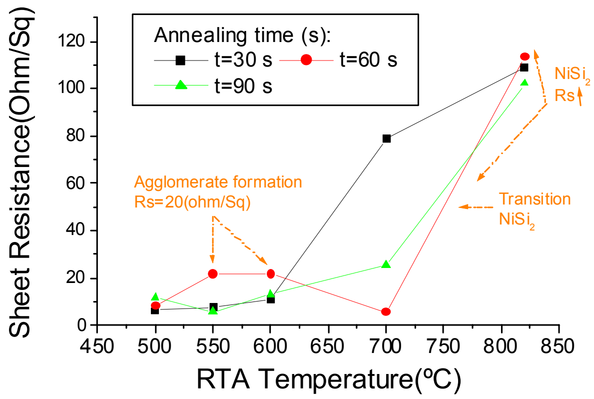

Figure 5 – Sheet Resistance versus RTA temperature of the samples formed at 500, 550, 600 and 700ºC with annealing time of 30, 60 and 90s.

The more reasonable resistance behavior is that of the samples obtained at t=90 s (green curve), where the occurrence of the agglomerate formation was not observed up to the higher anneal temperatures. The sheet resistance starts to change to high values only in the temperatures around 650ºC, due to the beginning of the crystalline phase changes to $NiSi_2$. The agglomerate formation influence on our samples was noticed to be stronger in the t=60 s (red curve) at temperatures of 550ºC and 600ºC. Finally, in Figure 6, SEM images show the agglomerate and precipitate formation. This figure shows the surface micrographs of the samples formed at 600ºC (A), 700ºC (B) and 800ºC (C and D). In the samples of figure 6 (A) and (B) we observe precipitation formation and high roughness, that can be caused by impurities introduced into the process before silicidation. The samples shown in Figures 6 (C) and (D) exhibit agglomerate formation, which may be caused by the weak thermal stability and process impurity. All samples were formed at annealing time of 30 s. Influence of RTA temperatures on the agglomerate formation and sizes were observed in the samples formed since temperature of 600ºC.

4. CONCLUSIONS

This work has investigated silicide formation using Ni. NiSi presented sheet resistance of ≅7Ω/Sq, high surface roughness, and high thermal stability problems. These results indicate that low resistivity phase NiSi formation is limited to the temperature range of 450-700ºC, because of nucleation, , agglomerate, precipitation problem and of course crystalline phase change. This temperature range is very low for the nowadays temperature required for the process integration.

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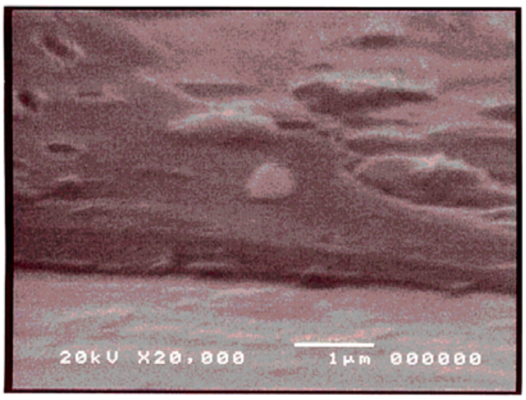
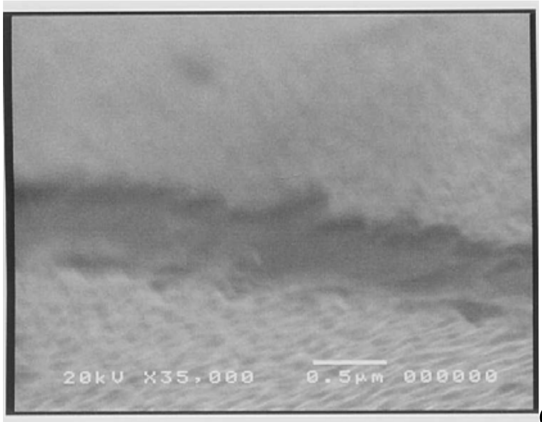
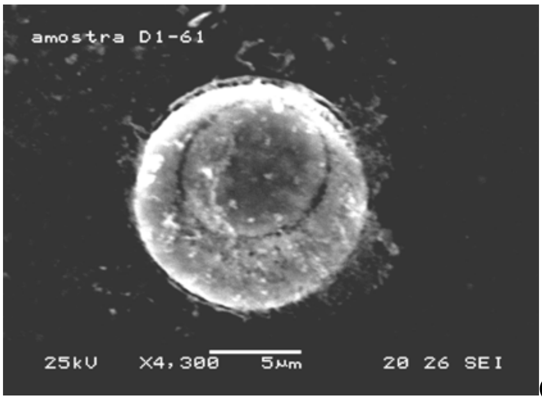


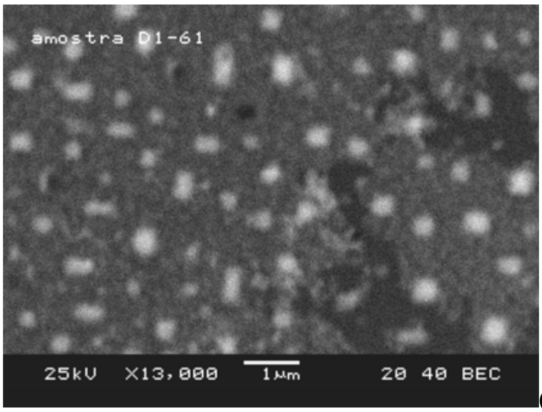
(A)



(B)



(C)



(D)

Figure 6 - SEM micrographs of the obtained silicide samples. (A) sample formed at 600ºC/30s; (B) sample formed at 700ºC /30s; (C) and(D) samples formed at 800ºC/30s. All these images show agglomerate and precipitation formation.

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