Layer Inversion of Ni(Pt)Si on Mixed Phase Si Films

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The formation of Ni silicides has been improved with Ni(Pt)-silicidation on the mixed phase Si films which were grown using the rapid thermal chemical vapor deposition technique. The Ni(Pt)Si was stabilized up to 800°C and layer inversion was retarded beyond 600°C. The enhanced stability of Ni(Pt)Si is attributed to the change in Gibbs free energy. The reduced layer inversion is due to the modification of the Si microstructure that has played an important role in the layer inversion. The enlarged poly-Si grains from the mixed phase films are due to the silicide enhanced mediated crystallization using $NiSi_2$ precipitates as seeds besides the preexisting Si crystallites.

Silicides are essential in complementary metal oxide semiconductor (CMOS) technology as local interconnect and contacts application. The once commonly used $TiSi_2$ has been replaced by $CoSi_2$ due to the sheet resistance of $TiSi_2$ that shows linewidth dependence as a result of incomplete phase transformation on narrow lines. Nevertheless, Co has high Si consumption that has caused problems in ultrashallow junction. $CoSi_2$ junctions may suffer high diode leakage because of nonuniform $CoSi_2$/Si interfaces or Co spiking. A replacement silicide material is needed to form uniformly at low temperatures. NiSi is a promising candidate for future integrated circuits (IC) generations due to its linewidth independent low resistivity, low temperature one-step annealing, and low silicon consumption.[1] However, NiSi is thermally stable only up to a temperature of 750°C at which the high resistivity phase $NiSi_2$ starts to nucleate.[2] In addition, Ni silicide tends to suffer from layer inversion on poly-Si at temperatures as low as 550°C, at which the topological inversion of the silicide and poly-Si bilayer occurs.

It has been reported that by alloying with a small amount of Pt, the stability of NiSi was improved.[3] This should greatly favor the use of NiSi for deep sub-quarter micrometer CMOS technologies. Nevertheless, the addition of Pt has not shown much effect on the inversion tendency on low pressure chemical vapor deposition (LPCVD) deposited poly-Si.[4,5] This paper aims to investigate the Ni(Pt)Si formation on a mixed phase Si films in order to modify the layer inversion behavior.

Rapid thermal chemical vapor deposition (RTCVD) was used to grow the mixed phase films (coexistence of a-Si and c-Si). The RTCVD process was carried out in a single wafer *in situ* processing multichamber cluster tool, which allows the sequential growth of thin gate oxide and mixed phase Si film without breaking vacuum. The gate stack comprises 24 Å gate oxide and a 2000 Å Si film which was grown at 680°C for 130 s with a deposition pressure of 60 Torr. Rapid changes in the substrate temperature during initiation and termination of the RTCVD process provides precise control of the process time down to a few seconds. After the Si deposition and HF cleaning to remove native oxides, the sputtering of Ni(Pt) with 5 atom % was done using an alloy target. Silicidation was done using rapid thermal anneal (RTA) in N_2 ambient for 60 s. The phase formation was checked using Raman spectroscopy and X-ray diffraction (XRD). Composition analysis was done using Rutherford backscattering (RBS). Cross-sectional transmission electron microscopy (XTEM) and electron diffraction analysis were used to analyze the resultant films.

Figure 1 shows the XTEM micrographs of the mixed phase films formed by RTCVD. The top layer of the Si film is amorphous in nature as confirmed with electron diffraction that shows a diffuse halo. Small Si crystallites are present at the film/substrate interface with a small number of elongated elliptical grains exist in the film. It has been considered that the amorphous Si (a-Si) was first formed and the growth of the elliptical grains followed a certain waiting time due to bulk induced crystallization.[6] Therefore, a mixed phase Si film with the coexistence of a-Si and c-Si was produced.

Figure 2 shows the phase changes of Ni(Pt) on RTCVD-Si after annealing at various temperatures using Raman spectroscopy. The finger print Raman spectrum of NiSi has been studied using Raman spectroscopy on Si(100).[7] The formation of Ni(Pt)Si was observed up to 800°C as signified by the presence of NiSi peak at wavenumber 215 cm^{-1}. This confirms the enhanced stability of Ni(Pt)Si above the nucleation temperature of $NiSi_2$ at 750°C.

The RBS results of the Ni(Pt)-silicided films on RTCVD-Si are shown in Fig. 3. At 600°C, the composition ratio corresponds to Ni(Pt)Si with 5 atom % Pt. The morphology stability was improved compared to NiSi or Ni(Pt)Si on the conventional LPCVD poly-Si substrates at which full inversion has occurred at 600°C.[5] As temperature increases, the gradually lowered Ni and Pt yield with the extended peak tailing may be due to the start of layer inversion. At 750°C, the RBS spectrum shows the higher Ni yield at the bottom layer compared to the surface layer that is a result of layer reversal. The higher Si yield relative to metal is due to the poly-Si intrusion into silicide layer and extended to the surface. Figure 4 shows the XTEM analysis of Ni(Pt)Si on RTCVD-Si at 600°C. The silicide layer was rather uniform on top of the poly-Si layer that comprises large Si grains. Interestingly, some silicide-like grains were seen to have settled on the oxide interface. Diffraction analysis was performed on the top and bottom silicide grains as shown in Fig. 4a and b. It was confirmed that the top silicide layer corresponds to the formation of monosilicide whereas $NiSi_2$ is identified at the oxide interface.
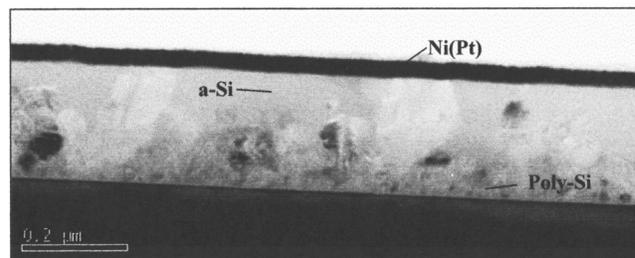
Figure 1. Bright field XTEM analysis of an as-deposited Ni(Pt) film on RTCVD-Si.

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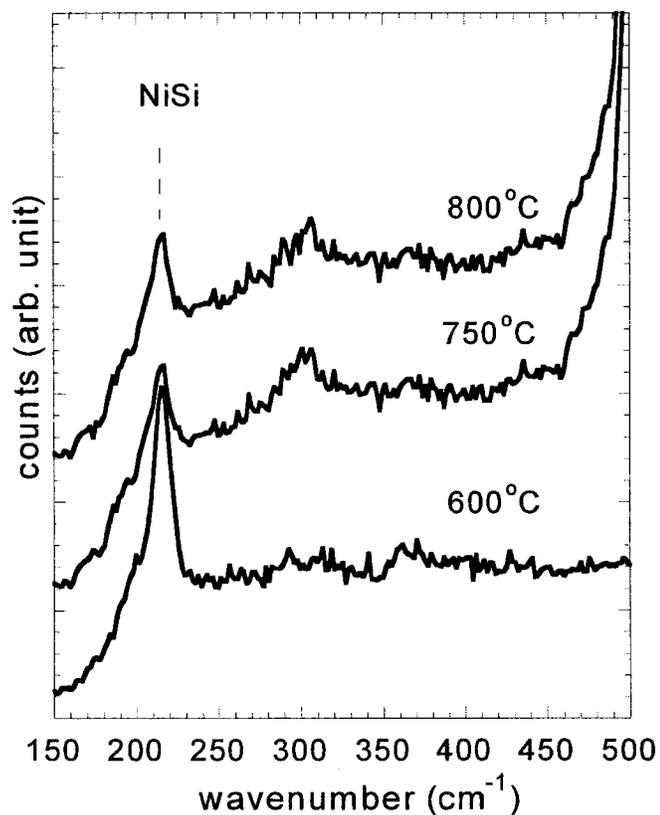
Figure 2. Raman analysis of Ni(Pt)/RTCVD-Si after annealing at various temperatures.

Figure 4. XTEM analysis of Ni(Pt)/RTCVD-Si after annealing at 600°C. Insets (a) and (b) are the diffraction analysis of top and bottom silicide grains, respectively.

NiSi and PtSi are orthorhombic silicides and have close lattice mismatch, which allows the formation of Ni(Pt)Si solid solution formation. The enhanced stability of Ni(Pt)Si can be attributed to the change in interfacial energy (σ) or Gibbs free energy (G) according to the classical nucleation theory where the nucleation rate, $N \propto \exp(-\Delta\sigma^3/\Delta G^2)$. From the TEM analysis at 600°C, Ni(Pt)Si is polycrystalline in nature with no texture formation being observed.

Figure 3. RBS analysis of Ni(Pt)/RTCVD-Si after annealing at various temperatures.

The resulting enhanced stability of Ni(Pt)Si up to 800°C is therefore attributed to the dominant role in the change of Gibbs free energy of NiSi with the addition of Pt.

From the XTEM analysis, it was observed that the poly-Si grains are large and the silicide film does not undergo layer inversion. For a pure a-Si film, the crystallization proceeds through nucleation and grain growth. In the initial stage of crystallization, nucleation occurs randomly within the a-Si matrix, and the orientation of the nuclei determines the orientation of the initial crystal structure and the subsequent growth of the crystallites. For a completely amorphous film, to crystallize at low temperature, a long crystallization time (*i.e.*, longer than 40 h at 550°C) is needed due to a low nucleation rate. Crystallization of electron-beam deposited a-Si required temperatures ~700°C for nucleation.[8] For mixed phase films, upon annealing, a shorter crystallization time was found (9-14 h at 550°C)[9] and is due to the growth of pre-existing crystallites in the mixed phase films. The amorphous regions trapped throughout the volume of the film will start to transform to polycrystalline phase with random nucleation and growth (producing elliptical grains) and a lesser extent of some lateral growth of the pre-existing crystallites (producing rounded grains). A quantitative model was presented by Voutsas and Hatalis[10] for the crystallization of the composite film.

It has been found that the solid phase crystallization temperature of a-Si can be lowered by the addition of certain metals. There are two kinds of crystallization mechanisms related to silicide formation[11]: stress-induced and silicide-mediated crystallization. The stress induced by silicide formation is due to the difference in Si mass density between a-Si and silicide. The silicide-mediated crystallization requires the formation of a silicide with the same lattice structure and a similar lattice constant with the ones of Si, which is the case for $NiSi_2$. From the results obtained, the detection of $NiSi_2$ compounded with the fast and early crystallization of large poly-Si grains from the initial mixed phase Si films strongly suggests the occurrence of the silicide-mediated crystallization during the silicidation of Ni(Pt) on the mixed phase films.

With Ni(Pt) deposited on the mixed phase Si consisting of a-Si

on c-Si layer, octahedral $NiSi_2$ precipitates may formed on the top a-Si layer upon annealing.[12] Following the substantial diffusion of Ni (or Ni-silicide nuclei) in the a-Si toward the a-Si/c-Si interface, the formation of $NiSi_2$ can occur at the a-Si/c-Si interface.[11] Crystalline silicide precipitates serve as crystallization centers for Si atoms from the a-Si matrix. It has been shown that solid phase epitaxial regrowth (SPER) proceeds from the (a-Si/c-$NiSi_2$) interface with the {111} edges from the surfaces of the crystalline Ni silicide precipitates serving as seeds. This develops a $NiSi_2$ /c-Si/a-Si structure and when the Si interlayer between a precipitate and an amorphous region reaches certain thickness, the precipitates begin to dissolve and Ni atoms migrate toward the advancing (a-c) interface.[12] This leads to the formation of needlelike polycrystalline Si grains. Therefore, needlelike crystallites are formed as a result of the migration of the $NiSi_2$ precipitates through the a-Si network.[13] For the lateral growth of the Si crystallites, sufficient spacing between $NiSi_2$ precipitates is needed.[12]

The presence of large poly-Si grains at 600°C is therefore due to the significantly enhanced crystallization of the mixed phase films in the presence of the $NiSi_2$ precipitates via silicide mediated crystallization and/or the crystallization from the pre-existing c-Si embedded in the mixed phase films. The recrystallization might have occurred before inversion and results in the enlarged poly-Si grains. The larger poly-Si grains are more stable and are certainly the cause for the lower extent of the layer inversion of the silicide film on RTCVD-Si. The larger poly-Si grain size has lower grain boundary energies and therefore a reduced driving force for the layer reversal to occur. This further shows that the driving force for the layer inversion is the reduction of the grain boundary energy and surface energy of the underlying poly-Si grains. This finding cohorts the claim that modifying the Si substrate is effective in tailoring layer inversion.[14]

In this paper we have shown that the Ni(Pt)Si can be stabilized up to 800°C on RTCVD-Si and the stabilization was attributed to the preponderant role of the change in Gibbs free energy. Layer inversion was retarded due to the larger resultant poly-Si grains upon heat-treatment of the mixed phase films in the presence of Ni(Pt). Formation of $NiSi_2$ grains has been detected at the oxide interface and this has led to the silicide enhanced mediated crystallization of the mixed phase films besides the Si crystallization via the pre-existing seed of Si crystallites. The enlarged poly-Si grains have led to a reduced tendency for layer inversion to occur. By changing the Si deposition conditions and therefore the Si microstructure, it is viable to modify the layer inversion behavior with Ni silicides.

References

1. T. Morimoto, H. S. Momose, T. Iinuma, I. Kunishima, K. Suguro, H. Okano, I. Katakabe, H. Nakajima, M. Tsuchiaki, M. Ono, Y. Katsumate, and H. Iwai, *Tech. Dig. Int. Electron Devices Meet.,* **1991**, 654.
2. F. M d'Heurle, *J. Mater. Res.,* **3**, 167 (1988).
3. D. Mangelinck, J. Y. Dai, J. S. Pan, and S. K. Lahiri, *Appl. Phys. Lett.,* **75**, 1736 (1999).
4. S. Nygren, D. Caffin, M. Ostling, and F. M. d'Heurle, *Appl. Surf. Sci.,* **53**, 87 (1991).
5. P. S. Lee, D. Mangelinck, K. L. Pey, J. Ding, D. Z. Chi, T. Osipowicz, J. Y. Dai, and A. See, *Microelectron. Eng.*, In press.
6. H. Wee, C. Lee, and S. C. Shin, *Thin Solid Films,* **376**, 38 (2000).
7. P. S. Lee, D. Mangelinck, K. L. Pey, Z. X. Shen, J. Ding, T. Osipowicz, and A. See, *Electrochem. Solid-State Lett.,* **3**, 153 (2000).
8. J. L. Balstone, *Bull. Am. Phys. Soc.,* **36**, 577 (1991).
9. Y. N. Erokhin, R. Grötzschel, S. R. Oktyabrsky, S. Roorda, W. Sinke, and A. F. Vyatkin, *Mater. Sci. Eng., B,* **12**, 103 (1992).
10. A. T. Voutsas and M. K. Hatalis, *J. Appl. Phys.,* **76**, 777 (1994).
11. S. Y. Yoon, S. J. Park, K. H. Kim, J. Jang, and C. O. Kim, *J. Appl. Phys.,* **87**, 609 (2000).
12. B. Mohadjeri, J. Linnros, B. G. Svensson, and M. Östling, *Phys. Rev. Lett.,* **68**, 1872 (1992).
13. C. Hayzelden and J. L. Batstone, *J. Appl. Phys.,* **73**, 8279 (1993).
14. W.-M. Chen, S. K. Banerjee, and J. C. Lee, *Appl. Phys. Lett.,* **64**, 1505 (1994).