Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 296-297

F-3-6L

New Finding of Pt Segregation at the NiSi/Si Interface by Atom Probe

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1. Introduction

Nickel monosilicide (NiSi) is used for lowering the parasitic resistances in source/drain. However, NiSi has a disadvantage of thermal instability such as $NiSi_2$ nucleation and agglomeration. It was found that Pt doped Ni-silicide has rather good tolerance of thermal agglomeration. [1] [2]

Three possible mechanisms have been reported for the improvement in thermal stability of the NiSi as follows. (1) the addition of Pt appears to influence the texture of NiSi film, thus affecting the interface energy, (2) the expansion of the NiSi lattice due to the addition of Pt may result in the transformation of the MnP-type structure into more stable NiAs-type structure, and (3) the nucleation of $NiSi_2$ will be more difficult because of the expulsion of Pt from the nucleation region.[1][3] T. F. Kelly et al. analyzed Ni(Pt)Si/Si(As doped) interface with Atom Probe(AP). They found the As segregation at the NiSi/Si interface and Pt redistribution to the NiSi surface in the 1-D profile. [4]

In this work, we have successfully found the Pt segregation at a NiSi/Si interface by AP analysis. Moreover, Pt was clearly found to segregate in higher concentration near the grain boundaries of NiSi by nanometric 3-D spatial distribution analysis. From these results, we discuss the role of Pt in the Ni(Pt)Si for improvement of thermal stability.

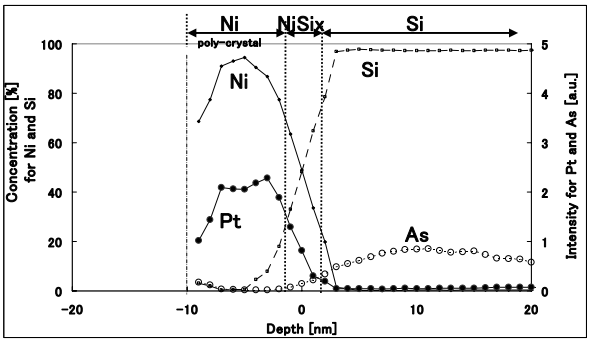
2. Experiments

Ni-Pt alloy film of about 10nm in thickness were sputter deposited on As implanted (100)Si substrates. Some of the samples were annealed to form Ni silicide in N_2 after Ni sputtering. As deposited sample and the sample after silicidation were prepared for Atom Probe(AP) analysis using LEAP3000(IMAGO). Special resolution was 0.2 nm×0.2 nm×0.4 nm . Detection efficiency was about 50 atomic %. Sensitivity was about 0.5 atomic %. To complement AP analysis, TEM observation was carried out.

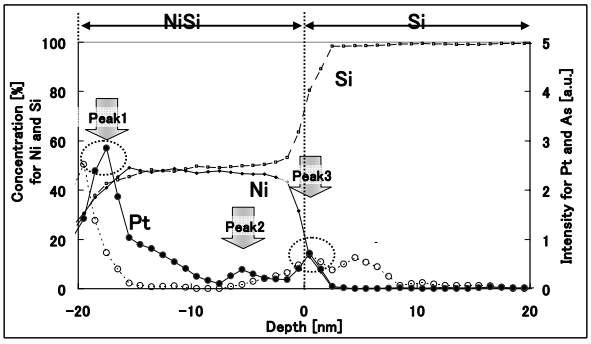
3. Results

The depth profile through the Ni(Pt)/Si interface of the as deposited sample analyzed by AP is shown in Fig.1(a). It is clear that a NiSix alloy layer is formed below an unreacted Ni layer. Figure 1(b) shows that of the after silicidation sample.

There are three peaks in the profile of Pt as shown in Fig.1 (b). Peak 1 locates at the top surface, Peak 2 is about 6nm above the NiSi/Si interface and Peak 3 is at the NiSi/Si interface.



(a) as deposited sample. Depth=0 means the center of the interfacial NiSix alloy layer on Si (100).



(b) after silicidation sample. Depth=0 is $NiSi_x$/Si(100) interface.

Fig. 2 Depth profiles of Si, Ni, As and Pt by Atom Probe.

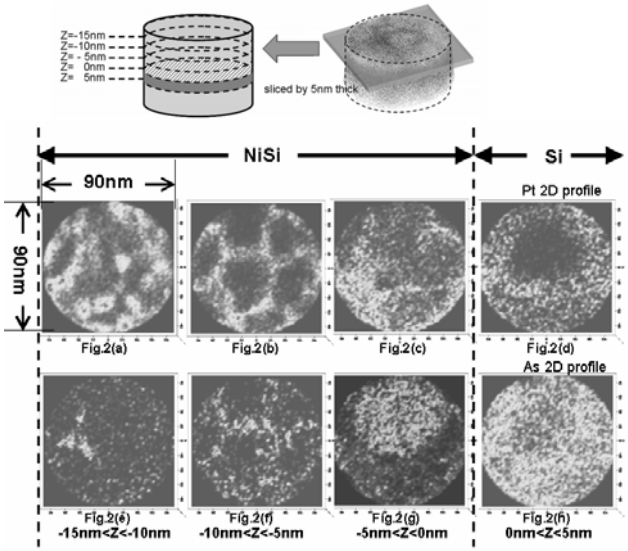
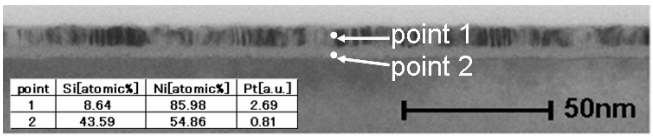


Fig2. 2D concentration mapping of Pt,As in 5nm thick slices. (Z=0nm means the interface of NiSi/Si. (a)~(d) indicate Pt distribution of the each slice. (e)~(h) indicate As distribution.)

To analyze the Pt distribution in after silicidation sample more properly, we processed the 3D image as follows: a cylindrical part is extracted from the 3D image; it is divided into 5nm thick slices; and 2D images depicting density-distribution of Pt and As in the slices are calculated as shown in Figs. 2(a) to 2(h). Fig. 2(b) shows that Pt atoms segregate around grains of NiSi. Fig. 2(d) shows that Pt atoms exist below the NiSi/Si interface. Fig. 2(f) and 2(h) also shows that As atoms segregate at grain boundaries of NiSi and the interface of NiSi/Si.

Fig.3(a) shows results of TEM & EDX on the as deposited sample , and Fig.3(b) shows a result of TEM on the after silicidation sample. As shown in Fig. 3(a), the as deposited sample has a NiSi amorphous layer on the substrate and a Ni poly-crystal layer on the amorphous layer. The thickness of amorphous layer is about 4nm from the TEM observation. While in Fig.1(a), the dashed line 1 is placed at Ni 80% compared with the Ni-poly-crystal region. The dashed line 2 at Ni 20%. The thickness between these two lines is about 4nm and corresponds to the Fig.3(a). This region is an amorphous-NiSi layer. As shown in Fig. 3(b), NiSi grains grow by annealing.



point	Si[atomic%]	Ni[atomic%]	Pt[a.u.]
1	8.64	85.98	2.69
2	43.59	54.86	0.81

Fig. 3(a) The Results of TEM & EDX on the as deposited sample.

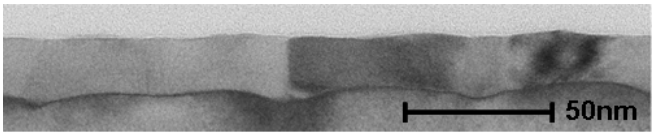


Fig. 3(b) The Result of TEM on the sample after silicidation.

4. Discussion

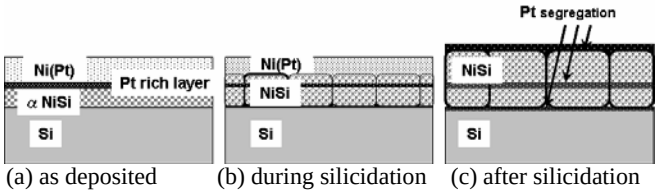
Fig. 1(a) shows that Pt atoms are localized at the interface between the Ni poly crystal layer and the amorphous layer in the as-sputtered sample. On the other hand, Fig. 1(b) shows that there are three peaks in the depth profile of Pt after the annealing in sample B. Figs. 2(a)~(d) show Pt atoms distribution in detail. The 2D image of Fig. 2(a) corresponds to the depth of Peak 1 in Fig. 1(b). In view of Peak 1 which is at the top surface of the NiSi grains, Fig. 2(a) shows that Pt atoms are snowplowed out of the NiSi grains during the silicidation. The 2D image of Fig .2(b) corresponds to the depth of Peak 2. In view of Peak 2, Fig. 2(b) shows that Pt atoms are piled up at the side faces of the NiSi grains due to the segregation of Pt atoms.

The 2D image of Figs. 2(c) and (d) correspond to the depth of Peak 3. In view of Peak 3, Figs. 2(c) and (d) show that Pt atoms are uniformly distributed at the bottom of the NiSi grains. From these results, it is evident that Pt atoms segregate around the NiSi grains. At the same way As atoms also segregate around the NiSi grains.And these results lead to the following assumption about Ni(Pt) silicidation scheme.

(1) While Ni(Pt) atoms are sputtered on the Si substrate, Ni atoms diffuse much faster than Pt atoms in the Si matrix. [5] As the result, the Pt rich layer is formed at the top of α NiSi layer.

(2) In the annealing step, Pt atoms are unstable in NiSi grains so that Pt atoms are piled up at the grain boundaries of the NiSi grains.

(3) Consequently, as shown in Fig. 4(c), Pt segregate at the grain boundaries of the NiSi grains and Pt profile has 3 peaks in the NiSi.



(a) as deposited (b) during silicidation (c) after silicidation

Fig.4 Schematic diagrams of Pt segregation during Ni silicidation.

We also point out that there are few Pt atoms in a NiSi grain. Pt atoms were found to exist around NiSi grain-boundaries. It suggests that Pt does not change a material property of a bulk-NiSi because Pt does not exist inside a NiSi grain. Pt atoms at the interface can reduce the interface energy of NiSi/Si interface. Since Pt has rather strong electron affinity as compared with Ni and Si, the existence of Pt atoms at the NiSi/Si interface would deform a lattice structure of the interface. As a result, Pt atoms work as barriers against the diffusion or reaction of NiSi and Si atoms. In this way, we speculate that the thermal agglomeration and $NiSi_2$ nucleation can be suppressed by the existence of Pt atoms. Therefore, the thermal stability of NiSi can be drastically improved by adding Pt to Ni.

5. Conclusions

We first found that Pt was segregated at NiSi grain boundaries during NiSi formation for Pt doped Ni on Si by Atom Probe. We speculate that segregated Pt atoms can decrease the interface energy of Ni(Pt)Si/Si interface and improve the thermal stability of NiSi films.

Acknowledgements

We acknowledge T. Iba (NOAH), R. M. Ulfig (IMAGO), K. Tomoda and K. Mori (TNA) for cooperation for Atom Probe analysis. We also acknowledge Y. Tsunashima, T. Yamauchi, A. Shimazaki, Y. Toyoshima, K. Ohuchi of Toshiba Corporation for fruitful discussion.

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