Abnormal oxidation in nickel silicide and nickel germanosilicide in sub-micro CMOS*

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After post-silicidation annealing at various temperatures for 30 min, abnormal oxidation and agglomeration in nickel silicide and nickel germanosilicide are investigated under different conditions of NiSi, with As-, In-, and Sb-doped Si substrates of nickel germanosilicide without any dopants. The NiSi thickness, dopant species, doping concentration, and silicide process conditions are dominant factors for abnormal oxidation and NiSi agglomeration. Larger dopants than Si, thinner NiSi thickness and SiGe substrates, and higher dopant concentrations promote abnormal oxidation and agglomeration.

Keywords: NiSi, NiSiGe, oxidation, metal–oxide semiconductor field-effect transistor, sub-micro IC process

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1. Introduction

NiSi and Ni germanosilicide attract much attention in the almost sub-micro ultra-large scale integration (ULSI) process node development due to the merits of low formation temperature, low resistivity, less silicon consumption, and insensitive line width effect. The requirements for NiSi are miscellaneous, and include low sheet resistance, stable phases, good thermal reliability, and uniformity within the wafers, with no piping, spiking, abnormal oxidation or agglomeration, etc. Otherwise, this will cause higher contact resistance, low ion or high junction leakage, or high standby leakage issues. The poor thermal stability is the top obstacle that needs to be overcome. Moreover, since it is a potential candidate for the metal gate, how to adjust the positive channel metal–oxide semiconductor (PMOS) and negative channel metal–oxide semiconductor (NMOS) working function and become comparable with high k gate oxidation is another topic. Post-silicidation annealing is an effective method to test NiSi quality and evaluate the process in the NiSi loop.

Recently, SiGe technology was introduced into high-performance strain-induced CMOS technology.[1,2] A high quality of nickel germanosilicide is necessary as well. In this paper, the abnormal oxidation and agglomeration on Si and SiGe substrates are discovered after high-temperature post-silicide annealing. By adjusting the Ni deposition thickness, dopant, substrate species, and dopant concentration, the main factors influencing abnormal oxidation and agglomeration are found.

2. Experiments

As shown in Table 1, different implant conditions are designed for comparison. The process flow follows the common two-step silicidation process. Dilute HF etch up native oxide. Then 200 Å (1 Å = 0.1 nm) and 50 Å Ni/TiN is sputtered in an RF magnetron sputtering system without breaking vacuum. Rapid thermal process 1 (RTP) is carried out at various temperatures for 30 s. After the H_2SO_4 and H_2O_2 admixture (SPM) removes the unreacted Ni and capping TiN layer, RTP 2 changes unstable Ni silicide into NiSi. Finally, the samples test the thermal stability by high-temperature 30 min post-silicidation annealing in N_2 ambient. A cross-section transmission electron microscope (TEM) and field-emission scanning electron microscope (FESEM), from the Jeon–Ju branch of the

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Korea Basic Science Institute, are used to show the silicide characterization.

Table 1. Implant conditions.

Dopant	Dose/10^{15} ions · cm^{-2}	Energy/keV
B11	4	10
BF_2	4	20
P	5	40
As	5	50
Sb	1	5
Bi	1	10

3. Results and discussion

When the Ni thickness is 50 Å, the post silicidation temperature is 600 °C for 30 min. Then, serious agglomeration and coarse oxide are found, as shown in Fig. 1. Both Sb- and Bi-doped samples suffer the same issue. The silicide islands will increase NiSi sheet resistance and contact-to-silicide resistance As to degrade ion and device performance. With the ongoing trend to shrink devices, the source and drain junction depth should be shallower to restrain the short channel effect and improve the gate control ability, so Ni silicide should be thinner as well as dropping silicide-induced junction leakage current. For the ultra-thin junction, Sb and Bi are potentials to replace As as the n-type dopant.[3] Too thin an Ni thickness with Sb or Bi doping will deteriorate the formation of NiSi and easily agglomerate. This experiment demonstrates that the limit is a 50-Å Ni deposition thickness. We should also pay attention to the fact that Sb, Bi, and As atoms are larger than Si atoms. All these larger dopants help accelerate the dissociation of Ni/Si bonds during post-silicidation annealing.

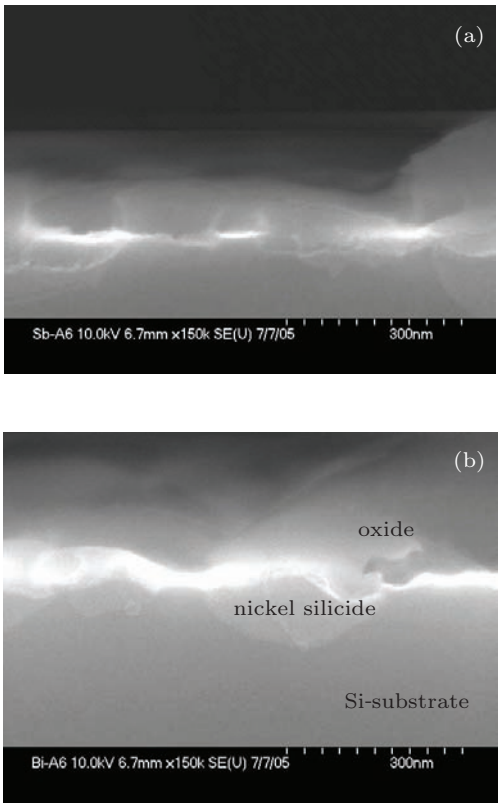


Fig. 1. Cross-section FESEM images of 50 Å Ni deposition samples after 600 °C, 30 min post-silicidation annealing: (a) the Sb-doped substrate and (b) the Bi-doped substrate.

While 200-Å Ni is deposited, no oxide layer was found in any of the samples, including the B_{11}-, BF_2-, P-, and As-doped Si substrates. Then, post silicidation at 700 °C for 30 min is performed. Compared with the B_{11}-, BF_2-, and P-doped samples, only the As-doped wafers with patterns become abnormal, and a non-uniform oxide layer appears, as shown in Fig. 2. However, there is no extra clean step in the process flow to remove the oxide if oxidation occurs in the worst cases, which may cause contact open or high contact resistance issues. While oxygen makes an access to the surface of the Ni silicide, the Si/Ni band will be broken and Si will be consumed to form oxide in the surface. The released Ni will diffuse towards the Si substrate and generate silicide along the NiSi/Si interface. The abnormal oxidation is different with dry oxygen Ti silicide oxidation of more than 800 °C.[4,5]

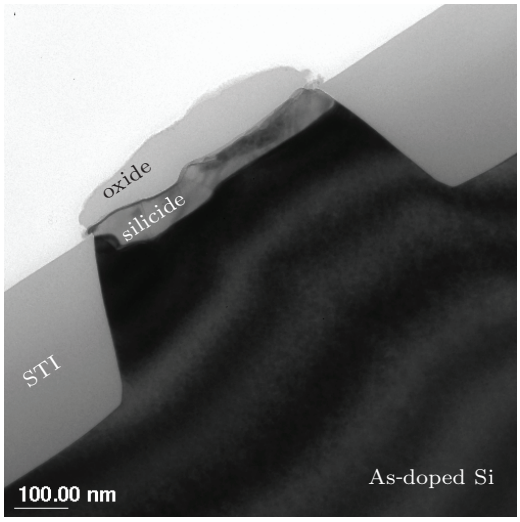


Fig. 2. Cross-section TEM images of 200 Å Ni samples after 700 °C 30 min post-silicidation annealing.

As for SiGe, the abnormal oxidation and agglomeration are worse than Si wafers. After 550-°C 30-min post-silicidation annealing, the sheet resistance of nickel germanosilicide dramatically increases, as shown in Fig. 3. From Fig. 4, it is shown that the abnormal oxide is formed on the Ni germanosilicide agglomerates. This can be explained by the same reason that larger dopants promote abnormal oxidation if Ge atoms are regarded as larger size dopants. Ge

function is more than the other dopants, since it is the lowest post-annealing temperature at 550 °C, and un-doped SiGe substrates suffer from abnormal oxidation. The thermal immunity of Ni germanosilicide is worse than NiSi, and the utilization of abnormal oxide as an insulating over layer was discussed. However, the application is too limited to be impossible as the abnormal oxidation is depended on the substrate dopants.[6,7]

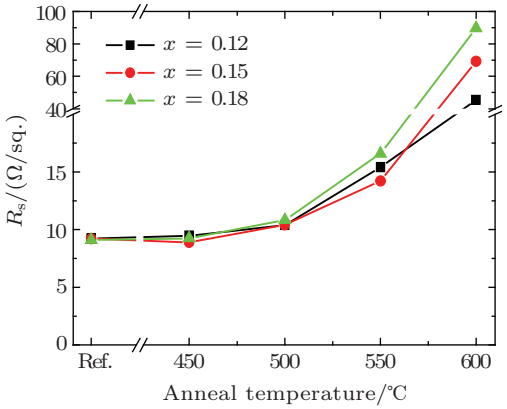


Fig. 3. (colour online) The sheet resistance of Ni germanosilicide in terms of various post-silicidation annealing temperatures.

The concentration of Ge is a key factor. A higher Ge concentration (x) causes higher sheet resistance. After 600 °C 30 min post-silicidation annealing, the sheet resistance ($x = 0.18$) is more than 80 Ω/□, which is 1.5 times larger than that ($x = 0.12$). The FESEM images in Fig. 4 show the cross section characterization that worse agglomeration and oxidation on the sample surfaces occur with higher Ge concentration in the substrates and correspond to a changing trend in sheet resistance. Hence, a lower Ge concentration, for instance 0.12, is recommended for silicide thermal stability. However, a higher concentration may cause higher stress and improve device performance, so it is worth balancing them and re-tuning the silicidation precess.

The summary is listed in Table 2, where all the main factors are concluded. NiSi thickness, dopant species, doping concentration, and silicide process conditions are the dominant factors for abnormal oxidation and NiSi agglomeration for sub-micro CMOS process development. The pre-clean and metal strip after RTP 1 and the clean after RTP 2 and dopant activation are minor factors. A suggestion is to tune the dominant factors to improve the Ni silicide loop for better reliability. How to control sheet resistance and agglomeration, and abnormal oxidation and uniformity within the wafers, are still hot topics.[8−11] A careful tuning process and the balance of all the factors are still a challenge for the 45 nm, 32 nm, and 22 nm technology nodes.

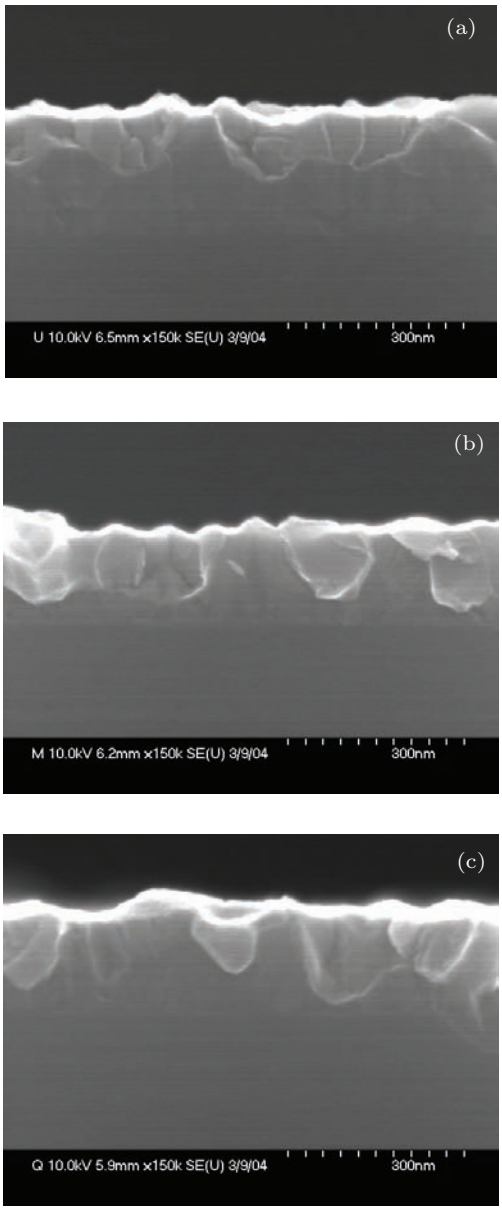


Fig. 4. FESEM images of Ni germanosilicide on $Si_{1-x}Ge_x$ after 600 °C 30 min post-silicidation annealing: (a) $x = 0.12$, (b) $x = 0.15$, and (c) $x = 0.18$.

Table 2. The main factors influencing abnormal oxidation and agglomeration in the Ni silicide process.

Process	Main impact	Other infectors
NiSi thickness	yes	thinner layer
Dopant species	yes	larger atoms
Doping concentration	yes	high concentration
RTP temperature	yes	higher T
RTP time	yes	longer time
Metal for silicidation	yes	low thermal immune property
Substrate species	yes	SiGe

4. Conclusions

After high-temperature post-silicidation annealing, abnormal oxidation and agglomeration of NiSi and Ni germanosilicide degrade low sheet resistance, and may result in junction leakage. Dopants like As, In, Bi, and Ge, whose sizes are larger than Si, facilitate the breakage of metal-Si bonds to release Si atoms to form oxide with oxygen. Thinner Ni suffers worse oxidation and agglomeration than thick Ni. When the dopants are As, thick Ni still involves abnormal oxidation without agglomeration. A higher Ge concentration for SiGe promotes abnormal oxidation and agglomeration.

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