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Formation of Nickel Self-Aligned Silicide by Using Cyclic Deposition Method

Koichi Terashima[a)], Yoshinao Miura[a)*], Nobuyuki Ikarashi[a)], Makiko Oshida[b)], Kenzo Manabe[a)], Takuya Yoshihara[a)**], Masayasu Tanaka[a)] and Hitoshi Wakabayashi[a)]

[a)] System Devices Research Laboratories, NEC Corporation, 1120 Shimokuzawa, Sagamihara 229-1198, Japan
Phone: +81-42-771-2394 Fax: +81-42-771-2481 e-mail: k-terashima@ay.jp.nec.com
[b)] R&D Support Center, NEC Corporation, 1120 Shimokuzawa, Sagamihara 229-1198, Japan

1. Introduction

Nickel monosilicide (NiSi) has attracted much attention as the contact material of source/drain (S/D) and gate electrode in recent scaled metal-oxide-semiconductor field-effect transistors (MOS-FETs).[1)] However, NiSi transforms easily to nickel disilicide ($NiSi_2$) with high resistivity. The formation of $NiSi_2$ occurs even at low temperature when the thickness of deposited Ni is small.[2)] This means that the formation of NiSi becomes much more difficult when the size of MOS-FETs is progressively shrunk and the thickness of the silicide layer becomes very small.

In this paper, we propose a novel nickel self-aligned silicide (salicide) process, in which less Si atoms in the substrate are consumed and thick NiSi layers can be obtained without elevated S/D. In order to suppress the Si consumption in the substrate, we supplied additional Si atoms by the deposition of Si. We found that the nickel silicide on SiO_2 can be removed selectively under the Ni-rich condition in the deposited layers. The results indicate that our method has the possibility to be applied to the future scaled MOS-FETs of the 22 nm technology node.

2. Experiments

We used p^--type Si (100) substrates in this study. The substrates were implanted with 30-keV As^+ to a dose of 5×10^{15} cm^{-2} and annealed at 1000°C. Some substrates were covered with 70-nm-thick SiO_2 grown by chemical vapor deposition (CVD). We also used the patterned substrates with MOS structures.

After chemically cleaned and dipped in a diluted HF solution, the substrates were introduced to a molecular beam epitaxy (MBE) chamber. Ni and Si were evaporated from effusion cell and electron beam source, respectively. Four-periods of Ni/Si multi-layered structures were fabricated by the cyclic deposition of Ni and Si at the substrate temperature of 50°C. The thickness of one Ni layer was fixed (2.5 nm) and that of one Si layer was varied. The substrates were successively annealed in the MBE chamber at 400-600°C for 30 minutes. After the annealing, the samples were etched by using an etchant which consists of a 1:1:1 volume mixture of HCl, H_2O_2, and H_2O.

The samples were examined by x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and four-point probe sheet resistance measurement.

3. Results and Discussion

Fig. 1 shows XRD spectrum of the typical sample annealed at 400°C. Ni and Si were deposited on the Si substrate under the condition that the Ni/Si ratio in total atomic number is 2. Several peaks in the spectrum are assigned to NiSi as indicated in Fig. 1. From the XRD measurement, we consider that the obtained film is mainly composed of NiSi.

Fig. 2 is a cross-sectional TEM image of the same sample as that in Fig. 1. As can be seen, a uniform silicide layer is grown on Si. The interface between the silicide layer and the substrate is flat and no facets are observed. The TEM image suggests that the uniform NiSi layer is obtained and that the epitaxial growth of $NiSi_2$ does not occur in this sample.

Sheet resistance of the nickel silicide films deposited on the same condition as that in Figs. 1 and 2 is shown as a function of annealing temperature in Fig. 3. In the case of 400°C and 500°C annealing, the sheet resistance is 9.5-10 Ω/sq. Using this value and the thickness of the silicide layer evaluated from the TEM observation (18 nm), we obtain 17-18 μΩcm as the resistivity of the silicide layer. This value is a little higher than the reported resistivity of NiSi (14 μΩcm)[1)] but low enough for the contact material. After the annealing at 600°C, sheet resistance becomes higher. We consider that this is due to the formation of $NiSi_2$.

Considering the above results, we conclude that the NiSi films can be obtained by the cyclic deposition method. The obtained films have the low resistivity, thickness uniformity, and good morphology.

Then we investigated the etching properties of NiSi films grown by our method. We first examined sheet resistance of the samples before and after wet etching and the results are compared in Table I. In these samples, nickel silicide films are grown on the substrates with and without SiO_2 and the Ni/Si ratio is varied. The annealing temperature is 400°C. Sheet resistance of the nickel silicide films grown on Si does not change by wet etching and is almost the same for all the samples. In the case of the growth on SiO_2, sheet resistance becomes higher after wet etching. In the cases of Ni/Si = 1 and 2, sheet resistance after wet etching exceeds the measurable limit of our measurement system. This result suggests

* Present address: NEC Electronics Corporation, 1753 Shimonumabe, Nakahara, Kawasaki 211-8668, Japan
** Present address: Intellectual Asset Operations Unit, NEC Corporation, Shiba 5-33-1, Minato-ku, Tokyo 108-8425, Japan.

that the nickel silicide film on SiO_2 can be removed by wet etching for Ni/Si = 1 and 2.

Ni 2p XPS spectra of some samples listed in Table I are shown in Fig. 4. Ni 2p signal is not observed in the case of the growth on SiO_2 for Ni/Si=2 after wet etching. This indicates that the nickel silicide film on SiO_2 is completely removed for Ni/Si=2. For Ni/Si=1, however, weak Ni 2p signal is observed indicating that the nickel silicide film partially remains on SiO_2.

In our method, silicidation on Si takes place by the reaction of Ni atoms with Si atoms both in the substrate and in the deposited layers. On the other hand, on SiO_2, Ni atoms react only with the deposited Si atoms. Then the nickel silicide formed on SiO_2 is Ni-rich compared to NiSi if Ni/Si>1 and the crystalline quality of nickel silicide on SiO_2 is different from that of NiSi on Si. Although NiSi is a resistant of the etchant used in this work, Ni-rich silicide on SiO_2 can be easily removed by wet etching. If Ni/Si≤1, NiSi or Si-rich nickel silicide is formed also on SiO_2. We conclude that the nickel silicide films formed on SiO_2 can be removed by wet etching if the Ni/Si ratio is lager than unity.

Finally, we fabricated MOS structures with NiSi using our method. In Fig. 5, cross sectional TEM images of the MOS structures with NiSi layers are compared between our method (Ni/Si=2) and the conventional salicide process. In this figure, we can observe that nickel silicide on the side wall is removed. The thickness of consumed Si in the substrate is ~$0.5 \times T_{NiSi}$ for our method and ~$0.8 \times T_{NiSi}$ for the conventional method, where T_{NiSi} is the thickness of the NiSi layer. We obtained about 25-nm-thick NiSi layer consuming only 13-nm-thick substrate Si. This value of Si consumption satisfies the requirement of the 45 nm technology node and the thicker NiSi layer can be obtained without elevated S/D. [3] If we use the condition that Ni/Si ratio is slightly larger than unity, Si consumption becomes much lower and our method has the possibility to satisfy the requirement of the 22 nm technology node.[3]

4. Conclusions

NiSi films with the low resistivity, thickness uniformity, and good morphology can be obtained after annealing of Ni/Si multi-layered structures fabricated by the cyclic deposition of Ni and Si. The nickel silicide formed on SiO_2 can be removed easily by wet etching if the Ni/Si ratio in total atomic number of the deposited layer is lager than unity. The results indicate that our method has the possibility to be applied to the future scaled MOS-FETs of the 22 nm technology node.

References

1) T. Morimoto et al., IEEE Trans. Electron Devices **42**, 915 (1995).
2) J. L. Batstone et al., Appl. Phys. Lett. **52**, 828 (1988).
3) International Technology Roadmap for Semiconductors 2001, 2003.

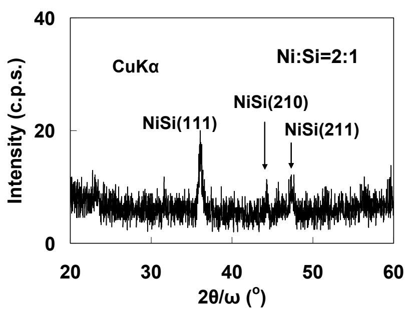

Fig. 1. XRD spectrum of nickel silicide grown on Si.

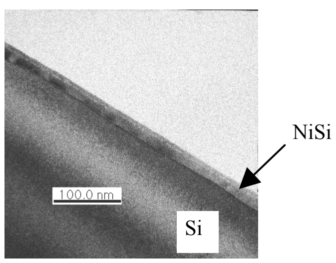

Fig. 2. A cross sectional TEM image of nickel silicide grown on Si.

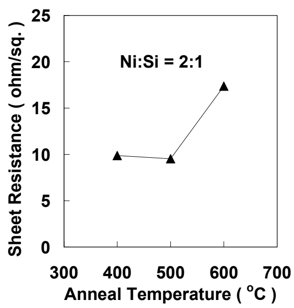

Fig. 3. Sheet resistance of nickel silicide films as a function of annealing temperature.

Table I. Ni/Si ratio and sheet resistance of the nickel silicide films.

sample#	substrate	Ni/Si (deposition)	Sheet Resistance (ohm/sq.) Before etching	After etching
1	Si	0.7	11.24	11.39
2	SiO_2	0.7	13.37	22.28
3	Si	1.0	12.07	12.74
4	SiO_2	1.0	24.80	>500k
5	Si	2.0	12.22	12.53
6	SiO_2	2.0	74.37	>500k

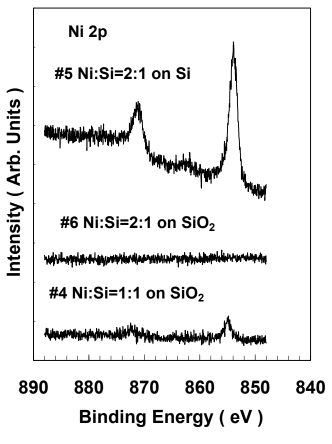

Fig. 4. Ni 2p XPS spectra of some samples listed in Table I after wet etching.

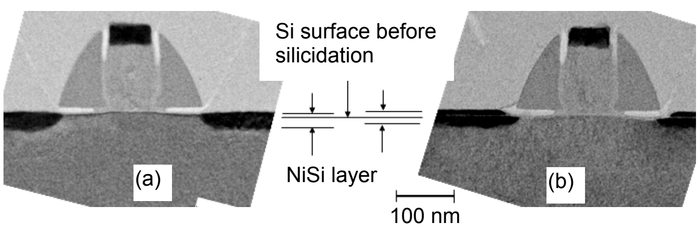

Fig. 5. Cross sectional TEM images of nickel silicide films grown on MOS structures; (a) conventional method (deposition of Ni) and (b) our method (deposition of Ni and Si, Ni/Si = 2).