Growth of oxide-mediated ternary silicide controlled by a Si cap layer by rapid thermal annealing

M. Xu^{a,b,*}, A. Vantomme^b, K. Vanormelingen^b, S.D. Yao^{b,c}

^aLaboratory for Low-dimensional Structure Physics, Institute of Solid State Physics, Sichuan Normal University, Chengdu 610068, PR China

^bInstituut voor Kern-en Stralingsfysica, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium

^cSchool of Physics, Beijing University, Beijing 100871, PR China

Received 27 March 2007; received in revised form 26 June 2007; accepted 3 July 2007

Available online 7 July 2007

Abstract

We reported a simple method to grow good-quality CoSi_2 film by using Si cap technology and introducing moderate Ni. First, a cobalt layer of ~ 15 nm with a Si cap layer with a different thickness deposited onto the Si surface with a thin silicon oxide buffer is applied to investigate the formation of CoSi_2 by *ex situ* rapid thermal annealing. It was found that a 13 nm thick Si cap layer could significantly improve the crystal quality of oxide-mediated CoSi_2 film. Setting the Si cap thickness at 13 nm, we revealed that introduction of Ni can further improve the crystal quality of the silicide film in comparison to the pure Co silicide, and a ratio of Ni to Co at round 1:8 causes the lowest sheet resistance, $\sim 5 \Omega/\text{sq}$.

© 2007 Elsevier B.V. All rights reserved.

PACS: 61.10.Nz; 68.35.-p; 68.37.-d

Keywords: Silicide film; Si cap layer; Rapid thermal annealing

1. Introduction

In the past 20 years, the study on the epitaxial metal silicides has received much interest due to their applications in very large-scale integration technology. Among the silicide materials, the CoSi_2 has been considered to be one of the most attractive materials for contact and interconnect in the next generation devices because of its low resistance, high-thermal stability and process compatibilities [1]. Generally, the small lattice mismatch with Si is expected to grow a good epitaxial CoSi_2 . Indeed, this has been demonstrated by using template [2] or oxide-mediated epitaxy technology [3] in the case of very thin CoSi_2 film. For the thicker CoSi_2 film, i.e., cobalt thickness > 10 nm, one has to apply Ti buffer [4] or repeated growth technology [3]. However, the silicides suffer from the generation of large voids in the epitaxial CoSi_2 layers near

the edges of field oxide and an inability to grow uniform epitaxial CoSi_2 layers with thickness of less than 40 nm. Alternatively, epitaxial CoSi_2 can be fabricated by meso-taxi, using high-energy, high-dose, Co implantations [5,6], but these techniques require dedicated tools not commonly available in modern Si processing facilities. To solve these problems, the ternary epitaxial silicides ($\text{Co}_x\text{Ni}_{1-x}\text{Si}_2$) may prove to be a better choice than pure CoSi_2 due to the smaller lattice mismatch of NiSi_2 compared to Si substrate. Especially, the bulk material of the ternary silicides ($\text{Co}_x\text{Ni}_{1-x}\text{Si}_2$, $0.5 < x < 1$) has electrical resistance nearly identical to that of CoSi_2 [7]. The smaller lattice mismatch of $\text{Co}_x\text{Ni}_{1-x}\text{Si}_2$ to Si compared to CoSi_2 has proved to successfully grow thin single crystal $\text{Co}_x\text{Ni}_{1-x}\text{Si}_2$ layers on $\text{Si}(111)$ [7]. In this paper, we explored a simple method to grow good-quality CoSi_2 by using Si cap technology and introducing moderate Ni. We first revealed that there exists an optimal Si cap thickness to grow oxide-mediated CoSi_2 on $\text{Si}(001)$, i.e., a 13 nm thick Si cap layer can achieve the best crystal quality of oxide-mediated CoSi_2 on $\text{Si}(001)$ by assuming a 15 nm Co layer and by rapid thermal annealing

*Corresponding author. Institute of Solid State Physics, Sichuan Normal University, Chengdu 610068, PR China.

E-mail address: hsuming_2001@yahoo.com.cn (M. Xu).

(RTA) in the N_2 ambient. Furthermore, we showed that the introduction of moderate Ni does not only improve the crystal quality of $Co_xNi_{1-x}Si_2$, but also decreases the sheet resistance.

2. Experimental

P-type Si(100) substrates were used in this study. Substrates were cleaned chemically and dipped in a dilute HF solution to remove the native oxide. A thin SiO_x layer was then grown by submerging the substrates in a hot $NH_4OH:H_2O_2:H_2O = 1:1:4$ solution for 25 min (ammoniacal oxide). Substrates were then loaded in an UHV evaporation system. Co was evaporated at rate typically, 0.015 nm/s and Ni was grown at rates 0–0.015 nm/s. Subsequently, a Si cap layer with the thickness of 0–30 nm was deposited in the same UHV system in order to improve the quality of silicide film. Rapid thermal annealing from 550 to 1050 °C was performed to study the formation of $Co_xNi_{1-x}Si_2$. Before reaching the higher annealing temperature, each sample is first heated and kept at 300 °C for 15 s in order to achieve a uniform mixture of Co, Ni and Si.

The film structure was characterized by X-ray diffraction (XRD) and Rutherford backscattering (RBS). Cu $K\alpha$ radiation is used for the XRD measurements. High-angle diffraction was carried out from 27° to 75° with a step size 0.01°. Rutherford backscattering spectroscopy (RBS)/channeling experiment was carried out using a 1.57 MeV He^+ ion beam.

3. Results and discussion

First, we investigated the effect of an amorphous Si cap layer with a different thickness on the formation of $CoSi_2$ by depositing a cobalt layer of ~ 15 nm onto the Si(001) covered with a thin silicon oxide layer and following *ex situ* rapid thermal annealing. From the high-angle X-ray diffraction (HAXRD) of the films annealed up to 1050 °C, no $CoSi_2$ (111) or (220) diffraction peak is observed except $CoSi_2$ (400) diffraction peak. Fig. 1 shows HAXRD of the Co disilicide film around (400) diffraction peak after annealing at 1050 °C. To obtain obvious $CoSi_2$ (400) peak, $(\theta + \delta) - 2\theta$ scan was applied, where δ is a small constant angle. One can see that the $CoSi_2$ (400) diffraction peak appears only when the thickness of Si cap layer is not too thick, i.e., 150 Å or thinner. It should be pointed out that, for the sample without a Si cap layer, $CoSi_2$ (400) diffraction peak disappears as the temperature is increased up to 1050 °C and in the sample with a Si cap layer up to 30 nm, no $CoSi_2$ (400) diffraction peak is observed after annealing from 550 to 1050 °C. Moreover, seen from Fig. 1, the $CoSi_2$ (400) peak position shifts from 70.5° to 70.85° when the cap layer thickness increases from 0 to 13 nm; as the cap layer is 15 nm, the $CoSi_2$ (400) peak slightly shifts back to the lower angle. The diffraction peaks correspond to a perpendicular strain from

Fig. 1. (a) High-angle X-ray diffraction (HAXRD) spectrum of the oxide-mediated $CoSi_2$ films on Si(100) with different Si cap layer thickness, 0–30 nm from the up curve to the down one after annealing at 1050 °C. (b) Variation of the perpendicular strain of $CoSi_2$ film formed by RTA at 1050 °C with a different Si cap layer thickness.

$\epsilon^{\perp} = -1.60\%$ to -2.19% , indicating that the $CoSi_2$ becomes more coherent as the Si cap layer is increased up to 13 nm. When the anneal temperature was reduced to 700 °C, the $CoSi_2$ (400) diffraction peak was observed only for capping layers of 10 and 13 nm. This further evidences that too thin or thick Si cap impedes the formation of Co disilicide.

The crystalline quality of the silicide film has been checked by measuring the RBS/channeling spectra. The polycrystalline Co silicide is determined for all the samples,

but a minimum value of $\chi_{\min}$ occurs in the case with 13 nm cap layer when the anneal temperature is up to 1050 °C. The minimum value of $\chi_{\min} \sim 29\%$ is obtained, which is a bit higher than that of Co disilicide formed by reaction deposition epitaxy (RDE) [8,9] or with Ti interlayer [4].

Fig. 2 displays the random RBS spectrum of Co silicide with a different Si cap thickness. It is interesting to note that, without cap layer, the silicidation of Co atoms is obviously accompanied by a tail on the low-energy side. As the Si cap layer thickness increases, the Co peak narrows, indicating that silicidation becomes more difficult. When the thickness of Si cap layer is above 13 nm, the Co peak is almost the same. As is known, the Ti interlayer acts as a diffusive barrier, which retards the formation of CoSi₂ up to a higher temperature. In our experiment, Si cap layer acts similarly to the Ti interlayer, the existence of which slows the silicidation process or raises the formation temperature of CoSi₂. It was found that the Si cap layer of a certain thickness not only improved the quality of the CoSi₂ but also decreased the formation temperature of CoSi₂. Since Si is one of the reactive elements for CoSi₂, the existence of amorphous Si cap layer should be able to further induce the silicidation. The opposite is true as the amorphous Si cap layer slows the diffusion. This is because, as a new Si source, the amorphous Si cap layer slows the diffusion rate of Co atoms into the Si substrate by first forming Co₂Si or CoSi due to the lower heat of formation between Co atoms and amorphous Si.

In order to check the detailed formation of oxide-mediated CoSi₂ with a Si cap layer, we performed the measurement and simulation of X-ray reflectivity. As is well known, X-ray specular reflection is very sensitive to the distribution of

electrons at the heterointerface. By theoretically fitting the measured specular reflectivity curve at grazing angle condition, we are able to extract the electron density profile across the heterointerface. In other words, the information on the atomic density and thickness of each layer, surface and interfacial roughness, etc., can be obtained. In Fig. 3, we displayed the X-ray grazing angle specular reflectivity curves of the samples (open circles). Based on the formalism given by Parrot [10], we simulated the measured specular reflectivity, shown by solid curves in Fig. 3.

It was found, with the increase of the cap thickness, the surface and interfacial roughness decreases, also evidenced by the variation of bumps in the reflectivity curves. From our simulated results, the shift of the CoSi₂ (400) peak position and variation of crystalline quality of the silicide films can be understood as follows: without a Si cap, a Si rich Co silicide layer formed on the Si substrate, indicating that there exists a significant atomic interdiffusion between Co layer and Si substrate, which reasonably results in a rough interface between the silicide layer and substrate. When a 13 nm Si cap layer is applied, the composition of Si rich silicide layer becomes closer to the atomic ratio of CoSi₂. As such, the silicide layer becomes more coherent in comparison to the bulk CoSi₂ and hence has higher crystalline quality. When the cap layer is thickened up to 300 Å, the Si content in the silicide layer is found to further decrease. This indicates a decrease in the atomic interdiffusion between Co layer and Si substrate, in accordance with the decrease of the interface roughness. In this case, the silicide is formed mainly by consuming the amorphous Si cap layer, and so the crystalline quality of the silicide degrades.

Fig. 2. 1.57 MeV ⁴He backscattering spectra of the oxide-mediated CoSi₂ films on Si(100) with a different Si cap layer thickness after annealing at 1050 °C. The scattering angle is 170°.

Fig. 3. Specular X-ray reflectivity curves (open circle) and simulated results (solid line) of the CoSi₂ films on Si(100) formed by RTA at 1050 °C with different Si cap layer thickness: curve a—0 nm; curve b—13 nm; curve c—30 nm.

After knowing the optimal Si cap thickness for the growth of oxide-mediated CoSi_2 from this particular thickness of Co, we turn to the further improvement in the crystalline quality of CoSi_2 film by introducing moderate Ni content during the deposition of Co layer.

Due to the miscibility of NiSi_2 and CoSi_2 , it has been shown that the formation temperature of CoSi_2 can be decreased by introducing Ni content. On the other hand, since both NiSi_2 and CoSi_2 have a CaF_2 -type structure and very close lattice constant (0.5406 and 0.5364 nm, respectively), the introduction of Ni is expected to reduce the stress between CoSi_2 and Si substrate, and hence to improve the crystal quality of CoSi_2 .

In Fig. 4, we displayed the XRD spectra of MSi_2 (M is $\text{Co}_{1-x}\text{Ni}_x$, $x = 0-0.385$) after annealing at 1050°C . To obtain obvious MSi_2 (400) peak, $(\theta + \delta) - 2\theta$ scan was still applied. Except for the CoSi_2 (400) diffraction peak appearing at 70.73° , we do not observe any other peaks relevant with CoSi_2 or NiSi_2 . It is noted that, the position of MSi_2 (400) diffraction peak is almost independent of the Ni content, indicating that the lattice constant of MSi_2 is not affected by the Ni introduction. This is a bit different from the results reported by Mo et al. [11]. In their work, a ternary silicide $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ formed by Ni and Co thin films or Ni, Co and Ti thin films deposited on a Si(100) substrate was found to have a lattice constant between that of CoSi_2 and NiSi_2 . One possible reason is that, when the Ni concentration is much lower than that of Co, the lattice of $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ keeps the same as that of CoSi_2 . The ongoing work on the compositional analysis along the growth direction will possibly give a further interpretation.

The RBS/channeling measurements were performed to check the crystal alignment of CoSi_2 . The variation of $\chi_{\min}$ with the Ni concentration is displayed in Fig. 5. Shown in the inset in Fig. 5 is the random/channeling RBS spectra of $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ with $x = 0.24$ in $\text{Co}_{1-x}\text{Ni}_x$. As can be seen

Fig. 4. High-angle X-ray diffraction (HAXRD) spectrum of the oxide-mediated $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ films on Si(100) with different Ni concentration after annealing at 1050°C .

Fig. 5. Variation of $\chi_{\min}$ with Ni concentration. The inset shows the random/channeling RBS spectra of $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ formed by RTA at 1050°C with $x = 0.24$ in $\text{Co}_{1-x}\text{Ni}_x$.

Table 1

Formation temperature and annealing time of $\text{Co}_x\text{Ni}_{1-x}\text{Si}_2$ with the best crystallinity

Ni concentration (%)	0	11.5	24.0	38.5	100
Temperature ($^\circ\text{C}$)	1050	1050	1050	1050	800
Annealing time (s)	60	60	30	30	60

from Fig. 5, the introduction of Ni improves the crystal quality, $\chi_{\min}$ decreases with increasing Ni concentration. It was also noted that the temperature and time required for silicide formation was also influenced by the Ni concentration and is summarized in Table 1. The latter is in good agreement with that reported by Park et al. [12] and Detavernier et al. [13]. The decrease of formation temperature or time with increasing Ni concentration can be attributed to the influence of mixing entropy on the nucleation of CoSi_2 . The improvement of crystal structure obtained by introducing Ni is attributed to the reduced diffusion rate of Co into Si substrate. Vantomme et al. [14] explained the growth mechanism of CoSi_2 by considering concentration controlled phase selection. It was thought that, in the case of low deposition rate of Co on Si, the slow supply of Co reduces the effective concentration of Co at the growth interface to a value lower than about 33 at% Co, so CoSi_2 forms directly as the first phase due to the most negative heat of reaction. In our case, the diffusion rate of Co into Si substrate is lowered due to the dilution of Co by Ni so that the formation of CoSi_2 phase is easy. On the other hand, the first formed $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ phase will act as a better template than CoSi_2 phase for the following growth of $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ phase. As such, the $\chi_{\min}$

Fig. 6. Variation of sheet resistance of $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film formed by RTA at 1050°C with Ni concentration.

characterizing the crystalline quality of silicide decreases with increasing Ni concentration.

For the possible application of the $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ films, we measured the sheet resistance of the samples. It was found that, as the Ni concentration increases, the sheet resistance of $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film first decreased, followed by an increase (Fig. 6). This is possibly due to the formation of a little high-resistance NiSi_2 phase (undetectable by XRD) at the surface of Si substrate as more Ni is added, since Ni is easier to diffuse into the Si substrate in comparison to Co. The sheet resistance reaches a minimum ($\sim 5.0 \Omega/\text{sq.}$) as $x = 0.115$. In this case, the $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film thickness is estimated to be round 55 nm. As such, the resistance of the sample with the Ni concentration $x = 0.115$ is rather close to the normal value of CoSi_2 [15], demonstrating the feasibility of fabricating the applicable $\text{Co}_{1-x}\text{Ni}_x\text{Si}_2$ film by the simple method mentioned above.

4. Conclusion

In a summary, we explored a simple method to grow good-quality CoSi_2 by using Si cap technology and

introducing moderate Ni. First, it is revealed that a 13 nm thick Si cap layer can significantly improve the crystalline quality of oxide-mediated CoSi_2 film formed from a cobalt layer of ~ 15 nm. Keeping the Si cap thickness at 13 nm, we showed that the introduction of Ni can further improve the crystal quality of the silicide film in comparison to the pure Co silicide, and a ratio of Ni to Co at round 1:8 results in the lowest sheet resistance, $\sim 5 \Omega/\text{sq.}$

Acknowledgments

This work is supported by IUAP P5/1 GOA (KU Leuven). We thank Mr. B. Oppendoes, Dr. A. Falepin, and Mr. Q. Zhao for their help in MBE experiment, XRD and RBS measurements, respectively.

References

- [1] R.T. Tung, K. Inoue, *Inst. Phys. Conf. Ser.* 157 (1997) 487.
- [2] R.T. Tung, F. Schrey, S.M. Yalisove, *Appl. Phys. Lett.* 55 (1989) 2005.
- [3] R.T. Tung, *Appl. Phys. Lett.* 68 (1996) 3461.
- [4] M.L.A. Dass, D.B. Fraser, C.S. Wei, *Appl. Phys. Lett.* 58 (1991) 1308.
- [5] H. Vanderstraeten, Y. Bruynseraede, M.F. Wu, A. Vantomme, G. Langouche, J.M. Phillips, *Appl. Phys. Lett.* 57 (1990) 135.
- [6] M.F. Wu, J. De Wachter, A.-M. Van Bavel, H. Pattyn, G. Langouche, J. Vanhellemont, H. Bender, K. Temst, B. Wuyts, Y. Bruynseraede, *J. Appl. Phys.* 75 (1994) 1201.
- [7] R.T. Tung, F. Hellman, J.M. Gibson, T. Boone, *Mater. Res. Soc. Symp. Proc.* 91 (1987) 451.
- [8] A. Vantomme, S. Degroote, J. Dekoster, G. Langouche, *Appl. Surf. Sci.* 91 (1995) 24.
- [9] D.K. Sarkar, I. Rau, M. Falke, H. Giesler, S. Teichert, G. Beddies, H.-J. Hinneberg, *Appl. Phys. Lett.* 78 (2001) 3604.
- [10] L.G. Parrot, *Phys. Rev.* 95 (1954) 359.
- [11] H.X. Mo, X.P. Qu, J.H. Liu, G.P. Ru, B.Z. Li, in: *Proceedings of the 5th International Conference on Solid State and Integrated Circuit Technology*, Category No. 98EX105, 1998, p. 271.
- [12] S.J. Park, J.H. Huh, H. Jeon, in: *MRS Spring Meeting*, San Francisco, CA, 2000.
- [13] C. Detavernier, R.L. Van Meirhaeghe, F. Cardon, K. Maex, *Phys. Rev. B* 62 (2000) 12045.
- [14] A. Vantomme, S. Degroote, J. Dekoster, G. Langouche, R. Pretorius, *Appl. Phys. Lett.* 74 (1999) 3137.
- [15] K. Maex, *Mater. Sci. Eng. R* 11 (1993) 53.