第27卷 第2期 半 导 体 学 报 Vol.27 No.2
2006年2月 CHINESE JOURNAL OF SEMICONDUCTORS Feb.,2006

Study of NiSi/Si Interface by Cross-Section Transmission Electron Microscopy *

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Abstract: Different silicidation processes are employed to form NiSi, and the NiSi/Si interface corresponding to each process is studied by cross-section transmission electron microscopy (XTEM). With the sputter deposition of a nickel thin film, nickel silicidation is realized on undoped and doped (As and B) Si(001) substrates by rapid thermal processing (RTP). The formation of NiSi is demonstrated by X-ray diffraction and Raman scattering spectroscopy. The influence of the substrate doping and annealing process (one-step RTP and two-step RTP) on the NiSi/Si interface is investigated. The results show that for one-step RTP the silicidation on As-doped and undoped Si substrates causes a rougher NiSi/Si interface, while the two-step RTP results in a much smoother NiSi/Si interface. High resolution XTEM study shows that axiotaxy along the Si⟨111⟩ direction forms in all samples, in which specific NiSi planes align with Si(111) planes in the substrate. Axiotaxy with spacing mismatch is also discussed.

Key words: contact interface; NiSi; nickel silicide; solid-state reaction; rapid thermal processing
PACC: 6848; 6855; 7340N
CLC number: O484.1 **Document code:** A **Article ID:** 0253-4177(2006)02-0223-06

1 Introduction

Self-aligned silicide technology is widely used in complementary metal-oxide-semiconductor (CMOS) manufacturing to reduce sheet and contact resistances of the gate, source, and drain areas[1,2]. Recently, NiSi has been considered as a promising candidate for sub-90nm nodes because of its low resistivity, relatively low formation temperature, low silicon consumption, and no resistivity increase on narrow lines[1~4]. As a direct contact to Si, a smooth NiSi/Si interface, which generally yields a better electrical performance of the devices, is always expected[5,6]. The interface may be influenced by the substrate doping[7]. The substrate doping affects the thermal stability of NiSi film, in which the agglomeration is greatly related to the NiSi/Si interface[7]. The specific NiSi formation process, e.g., one-step or two-step rapid thermal process (RTP), may also affect NiSi/Si interface[8]. The possibility of a single-step RTP below 600 ℃ was initially considered to be a significant advantage for NiSi formation[3]. Recent studies, however, have shown that one-step RTP not only results in excess silicidation of gate and junction contacts[9], but also increases the inhomogeneity of the contact interface[8]. A two-step RTP has been proposed, in which some of the deposited Ni reacts during the first annealing (RTP1) at low temperature (< 310 ℃). The unreacted Ni is then removed by chemical etching, and finally a second annealing (RTP2) at 400~600 ℃ is carried out to form the low resistivity NiSi phase[9]. In this paper, different silicidation processes are employed to form NiSi on Si substrates with various dopants, and the NiSi/Si interface corresponding to each case is studied by cross-section transmission electron microscopy (XTEM).

2 Experiment

Blanket 200mm Si(001) substrates with n^+/p

* Project supported by the National Natural Science Foundation of China (No. 60576029), the Shanghai Applied Materials Research and Development Fund (No. 0514), the Science and Technology Commission of the Shanghai Municipality (No. 05ZR14017), and the Bilateral Program Between Flanders and China (No. B/06086/01)

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Received 22 July 2005

or p^+/n junctions ($\sim$50nm junction depth) were prepared by the implantation of As at 4keV and $2\times10^{15}cm^{-2}$ into p-type Si, or of B at 1keV and $2\times10^{15}cm^{-2}$ into n-type Si, respectively, followed by a 1050 ℃ spike annealing to activate the dopants. The junction substrates as well as the undoped substrates were cleaned by a RCA procedure just before the sputter deposition of a 13nm Ni film, during which the wafer temperature was kept at 30 ℃. The silicidation was carried out during a 30s soak annealing at temperatures ranging from 260 to 550 ℃. Our preliminary experiments had shown that a 260 ℃/30s annealing can fully consume a 13nm-thick Ni layer. Hence, no selective etch was used. The sheet resistance (R_s) dependence on annealing temperature for the silicide on undoped-Si (u-silicide), n^+/p (n-silicide) or p^+/n (p-silicide) junctions is compared in Fig. 1. In the low temperature range (260~310 ℃ for u- and p-silicide, 260~330 ℃ for n-silicide) R_s is much higher for u- and p-silicide than n-silicide. The much higher resistivity of the substrate was not responsible for the difference in R_s. According to the R_s behavior on different substrates, to successfully realize NiSi formation, a one-step RTP at 450 ℃ with a 30s soak time and a two-step RTP at 290 ℃ for RTP1 and 450 ℃ for RTP2, each with 30s soak time, were employed. X-ray diffraction (XRD) and Raman scattering spectroscopy (RSS) were used to identify the phase of the formed silicide. XTEM was employed to study the silicide/Si interface.

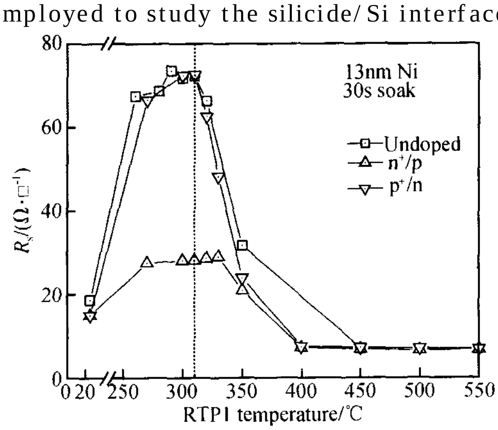

Fig. 1 Sheet resistance (R_s) of the silicide formed on different substrates versus annealing temperature of RTP1

3 Results and discussion

Table 1 lists the samples' process history information. For the two-step RTP a selective etch (SE) is introduced between RTP1 and RTP2, in which a H_2SO_4 : H_2O_2 = 4 : 1 solution is employed as the etching chemical. XRD and RSS are used to analyze the phase of the formed silicide. As can be seen in Fig. 2, XRD (Fig. 2(a)) and RSS (Fig. 2(b)) both demonstrate the successful formation of NiSi in all samples.

Table 1 Process history description for all samples

Sample ID	Process history
# 1	Ni(13nm)/p^+/n-Si(001), one-step RTP, 450 ℃/30s
# 2	Ni(13nm)/n^+/p-Si(001), one-step RTP, 450 ℃/30s
# 3	Ni(13nm)/undoped-Si(001), one-step RTP, 450 ℃/30s
# 4	Ni(13nm)/undoped-Si(001), two-step RTP, 290 ℃/30s + SE + 450 ℃/30s

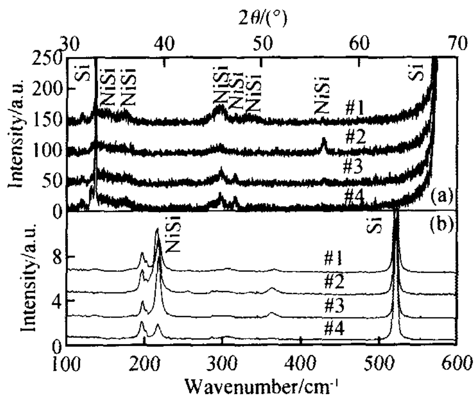

Fig. 2 XRD (a) and RSS (b) results for all samples NiSi formation is demonstrated in all samples.

Figure 3 shows low-resolution XTEM images for all samples with different scales. As can be seen, for all samples annealed by one-step RTP (#1~3) the silicidation on undoped and n^+/p-Si substrates results in a rougher NiSi/Si interface, while a smoother interface is observed on p^+/n-Si substrate. A rougher interface always indicates that the grain size of the formed NiSi is larger, which will cause a poorer thermal stability for thin films[7]. In view of thermodynamics a rougher interface will increase the total contact interface area, which generally means that the NiSi/Si interface energy for u- and n-silicide is smaller than that for p-silicide. In other words, the boron dopant may increase the NiSi/Si interface energy. Hereby the substrate doping does influence the NiSi/Si interface characteristics. In addition, a specific annealing process also affects the NiSi/Si interface. As can be seen from Fig. 3, for u-silicide, compared with one-step RTP (sample #3)

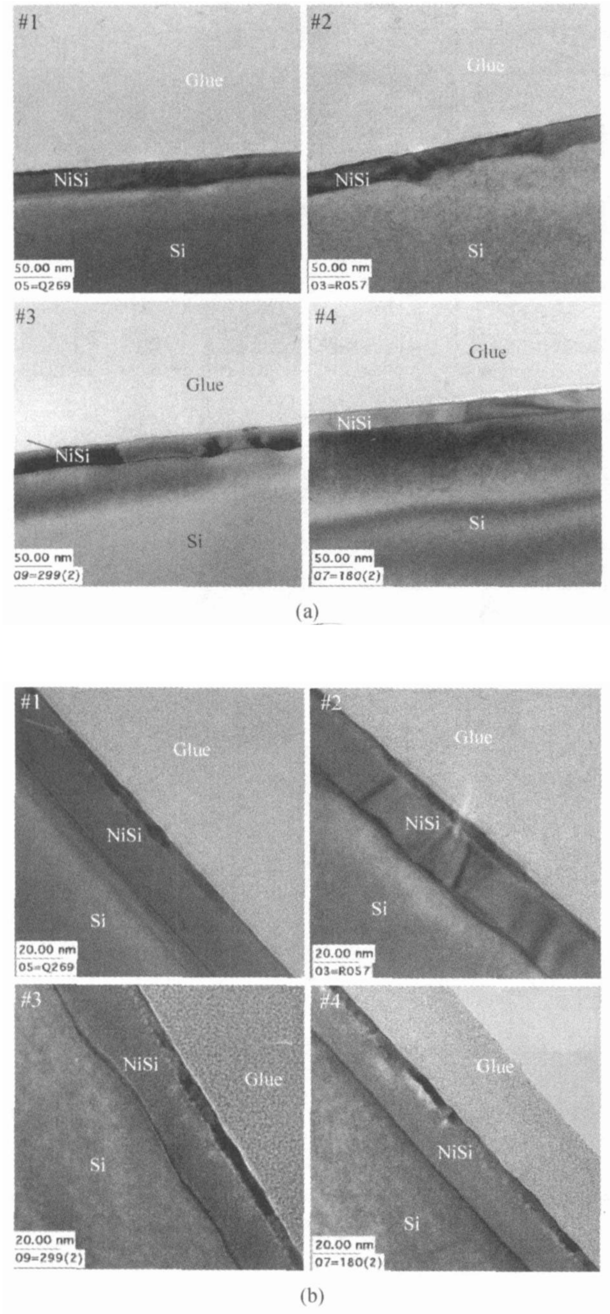

Fig. 3　XTEM images for all samples with different scales　(a) 50nm; (b) 20nm

the two-step RTP (sample #4) yields a much smoother NiSi/Si interface. A similar result is also obtained for p- and n-silicide (not shown here). Although the highest process temperature for one-step and two-step RTP is the same (450 ℃/30s), the heating ramp rate is different. It has been demonstrated that the heating ramp rate does influence the NiSi/Si contact characteristics[10]. For one-step RTP, to reach 450 ℃ the heating ramp rate is generally higher than that to reach 290 ℃. Thus for the two-step RTP with RTP1 soak-annealed at 290 ℃, the required time to reach the same temperature of 290 ℃ should be longer than that for the one-step RTP with a soak temperature of 450 ℃. Therefore Ni atoms have a longer time to laterally diffuse along the formed silicide/Si interface, which generally results in a smoother growing front (interface). Moreover, there is a 30s soak anneal time for RTP1 at 290 ℃ in the two-step RTP, while 290 ℃ is only a transient temperature for the one-step RTP of 450 ℃/30s. So Ni atoms should have a long enough time to laterally diffuse and generate a smooth growing front after RTP1 for the two-step RTP. After SE, the unreacted Ni will be removed. A smooth interface has formed in RTP1, and RTP2 will not only convert the high resistivity silicide phase formed in RTP1 but also generally keep the smooth growing front. Finally a smooth NiSi/Si interface will form. Hence it is demonstrated that the specific annealing process may also influence the NiSi/Si interface characteristics.

Recently, a new type of texture in thin film systems, i.e., axiotaxy, has been reported, which is characterized by the alignment of planes in the film and substrate that share the same d-spacing[11]. This preferred alignment of planes across the interface manifests itself as a fibre texture lying off-normal to the sample surface, with the fibre axis perpendicular to certain planes in the substrate. This texture forms because it results in an interface that is periodic in one dimension and is preserved independently of interfacial curvature. Figure 4 shows high-resolution XTEM images for all samples.

As shown in Fig. 4, after proper image processing the plane alignment between the NiSi film and Si substrate does exist for all samples. It is, however, different from the axiotaxy in Ref. [11]. Although the alignment is observed here, the aligned planes across the NiSi/Si interface do not share the same d-spacing. Moreover, because the incident electron during XTEM imaging is along the Si⟨110⟩ rather than Si⟨100⟩ direction, after Fourier filtering the planes kept in the substrate are the Si(111) planes with a plane spacing of 0.3136nm. Such an alignment is also different from Ref. [11], in which the incident electron is along Si⟨100⟩ and the planes in the NiSi film align

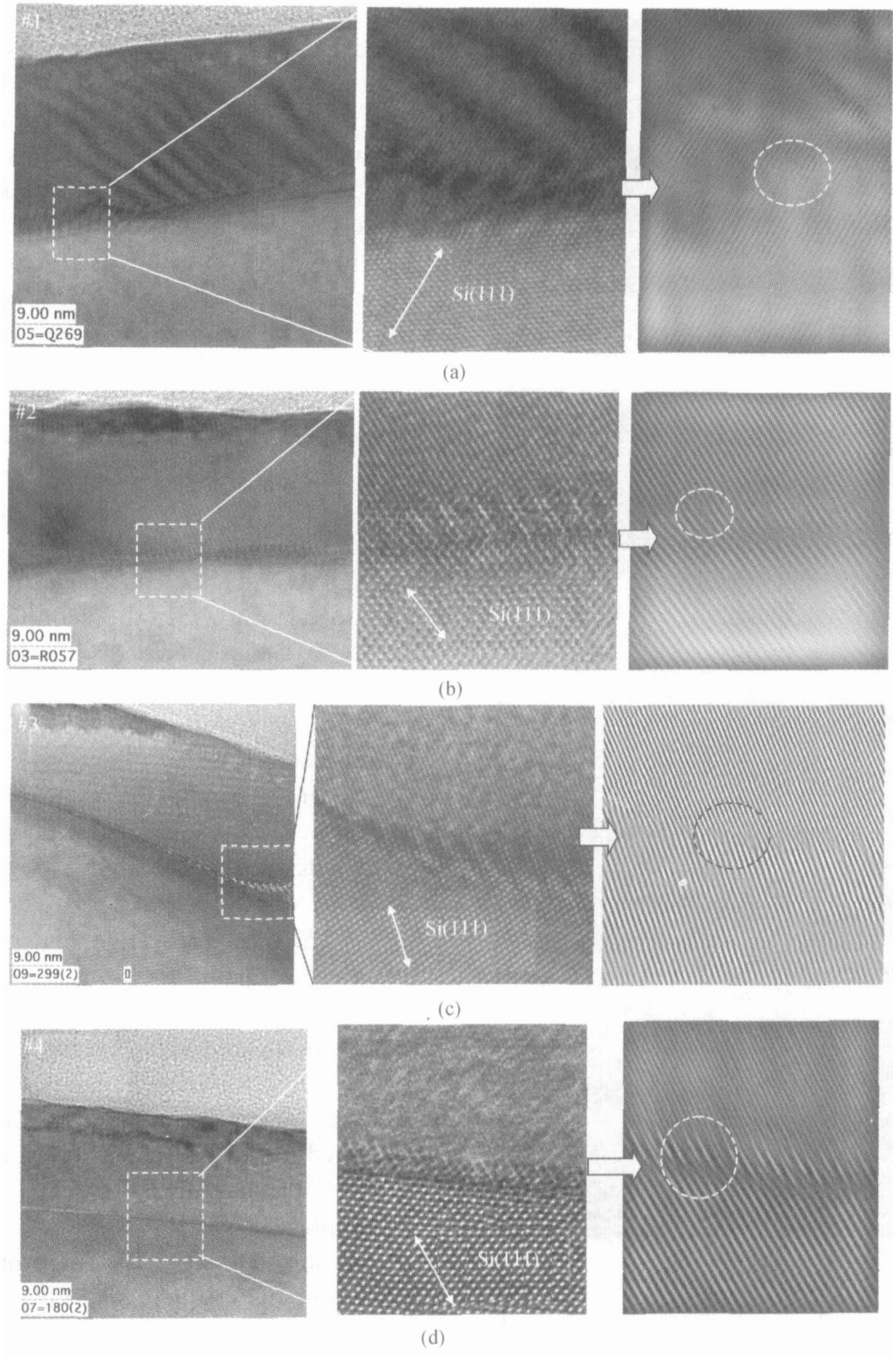

Fig. 4 High resolution XTEM images for all samples (a) Sample # 1; (b) Sample # 2; (c) Sample # 3; (d) Sample # 4 For each image group, the left image is the original high resolution XTEM image, the middle is the amplified image of the selected part on the left; and on the right is the middle image after Fourier filtering. On the right, only planes along Si⟨111⟩ are kept. Besides the alignment between the NiSi film and Si substrate, plane mismatches labeled by the dashed circle are also revealed on the right.

with the Si (110) planes. Due to the different d-spacing, very weak (even no) axiotxay across the NiSi/ Si interface should form, and even if it does form the corresponding lattice planes in the NiSi film should tilt so that each plane in the NiSi film can exactly align with its corresponding Si (111) plane in the substrate[11]. The results shown in Fig. 4, however, demonstrate that the alignment between planes in the NiSi film and Si substrate can still exist even though the d-spacing across the

NiSi/ Si interface is different. Preserving the alignment across the interface plane mismatch along the NiSi/ Si interface is unavoidable when there is no plane tilt. As shown in Fig. 4, after Fourier filtering the dashed circle clearly shows the plane mismatch. Thus the new type of texture, called axiotaxy, is extended to a wider range, which means that the alignment across the NiSi/ Si interface can form even when the planes on each side do not share the same d-spacing. A plane mismatch will occur instead of a plane tilt to preserve the alignment. A plane alignment with a mismatch across the NiSi/ Si interface will make it easier to form a rougher interface, and it may also introduce excessive stress in the NiSi film which is likely related to its thermal stability[12].

4 Conclusion

In this paper nickel thin film silicidation is realized on undoped, As-doped, and B-doped Si substrate by RTP using different annealing processes. XTEM is employed to investigate the NiSi/ Si interface in each case. Low-resolution XTEM images show that for the one-step RTP, the NiSi/ Si interface is the smoothest for the silicidation on B-doped Si substrate. It is also demonstrated that the interface roughness, in principle, can be greatly suppressed by the two-step RTP. For the first time, non-ideal axiotaxy is observed by high resolution XTEM, in which the planes in NiSi film can still align with Si planes in the substrate but with plane mismatches across the NiSi/ Si interface.

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NiSi/ Si 界面的剖面透射电镜研究 *

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摘要：采用不同硅化工艺制备了 NiSi 薄膜并用剖面透射电镜(XTEM)对样品的 NiSi/ Si 界面进行了研究. 在未掺杂和掺杂(包括 As 和 B)的硅衬底上通过物理溅射淀积 Ni 薄膜,经快速热处理过程(RTP)完成硅化反应. X 射线衍射和喇曼散射谱分析表明在各种样品中都形成了 NiSi. 还研究了硅衬底掺杂和退火过程对 NiSi/ Si 界面的影响. 研究表明:使用一步 RTP 形成 NiSi 的硅化工艺,在未掺杂和掺 As 的硅衬底上, NiSi/ Si 界面较粗糙;而使用两步 RTP 形成 NiSi 所对应的 NiSi/ Si 界面要比一步 RTP 的平坦得多. 高分辨率 XTEM 分析表明,在所有样品中都形成了沿衬底硅〈111〉方向的轴延-NiSi 薄膜中的一些特定晶面与衬底硅中的(111)面对准生长. 同时讨论了轴延中的晶面失配问题.

关键词：接触界面；NiSi；镍硅化物；固相反应；快速热处理

PACC：6848；6855；7340N

中图分类号：O484.1 **文献标识码**：A **文章编号**：0253-4177(2006)02-0223-06

* 国家自然科学基金(批准号:60576029)，上海应用材料研究与发展基金(批准号:0514)，上海市自然科学基金(批准号:05ZR14017)和中国-比利时佛拉芒大区科技合作计划(批准号:B/06086/01)资助项目

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2005-07-22 收到