第27卷 第4期
2006年4月

半 导 体 学 报
CHINESE JOURNAL OF SEMICONDUCTORS

Vol.27 No.4
Apr. ,2006

Effect of Nickel Contamination on Formation of Denuded Zone in Czochralski Silicon *

Wu Dongdong[1], Yang Deren[1,†], Xi Zhenqiang[1], Que Duanlin[1], and Zhong Yao[2]

(1 State Key Laboratory of Silicon Materials, Zhejiang University, Hangzhou 310027, China)
(2 Beijing Institute of Control Engineering, Chinese Academy of Space Technology, Beijing 100080, China)

Abstract: The effect of nickel contamination under rapid thermal processing (RTP) on the magic denuded zone (MDZ) in Czochralski silicon is investigated. It is found that the bulk defects can effectively getter nickel atoms once the MDZ forms. However, if the silicon sample is initially contaminated with nickel, the MDZ cannot form during the subsequent RTP, and a high density of precipitates occurs near the surface. In conventional IG processes, the DZ can form regardless of the nickel contamination sequence. Based on the facts, we propose that the formation of nickel silicide (Ni_3Si) at the surface keeps the concentration of vacancies in the near-surface zone still higher than the critical concentration for oxygen precipitation under the subsequent RTP, which prevents MDZ formation.

Key words: silicon; nickel; denuded zone
PACC: 7280C; 6155F; 6170Y
CLC number: TN304.1+2 **Document code:** A **Article ID:** 0253-4177(2006)04-0623-04

1 Introduction

It is widely recognized that 3d transition metals are harmful contaminants in silicon devices and degrade device performance either by forming metal silicides or by acting as recombination centers[1,2]. The removal or gettering of these metal contaminants is critical for proper device operation. An intrinsic gettering (IG) mechanism that occurs by oxygen precipitation is widely used to reduce impurity content in electrically active devices[3~5]. Thus a defect-free zone, called denuded zone (DZ), is created in devices. Conventionally, the DZ is created by the high-low-high processes due to the out-diffusion of oxygen during the first high temperature annealing. Recently, the creation of what is called a magic denuded zone (MDZ), formed by high temperature rapid thermal processing (RTP) has been reported[6~8]. Unlike conventional IG processes, the formation of an MDZ is determined by the out-diffusion of vacancies. It has been reported that many factors, such as the protective gas or the RTP temperature, have a great influence on the MDZ[6]. However, to our knowledge, no report has been made on the effects of metal contamination on an MDZ.

An important impurity, nickel (Ni) is one of the fastest diffusing elements in silicon and can be easily contaminated during device processing or wafer preparation[9]. It was found that Ni degrades the gate oxide integrity or effectively kills minority carriers[10]. In this paper, we have investigated the effects of Ni contamination on an MDZ in CZ silicon wafers. On the basis of the experiments, the mechanism by which nickel contamination affects the MDZ is discussed.

2 Experiment

The samples used in this work were cut from 200mm (100)-orientated, boron-doped, Czochralski-grown silicon wafers with a thickness of about 620μm and a resistivity of about 10Ω·cm. The initial oxygen concentration in the wafers was about 10.5×10^{17} atoms/cm^3 as measured by a Bruker IFS 66v/S Fourier transform infrared (FTIR) device with a calibrated coefficient of 3.14×10^{17} cm^{-2}.

* Project supported by the Research Fund for the Doctoral Program of Higher Education (RFDP), the Program for New Century Excellent Talents in Universities, and the National Natural Science Foundation of China (No. 90307010)

† Corresponding author. Email: mseyang@zju.edu.cn

Received 27 October 2005, revised manuscript received 24 December 2005

©2006 Chinese Institute of Electronics

Then the samples were divided into two groups, A and B. The detailed annealing processes for the samples are shown in Table 1. The difference between samples A1 and A2 in group A is the sequence of Ni contamination, as shown in Table 1. The Ni contamination level is about 5×10^{17} atoms/cm^3, which results from the solubility of Ni at 1000 ℃. The annealing processes of the samples of group B are similar to those of group A, but the DZ is formed by high-low-high processes in group B. The cooling rate of the RTP is about 40 ℃/s. All annealing was performed under argon atmosphere. After annealing, optical microscopy (Olympus MX50) combined with Sirtl solution was used to observe the cleaved surfaces of the samples. The etching time was 4min. Nickel silicides that formed at the surfaces of the samples were characterized by X-ray diffraction (XRD) (Phermo Arl Xtra).

Table 1 Annealing processes of samples

Sample		Annealing process for different nickel contamination sequences
Group A	A1	MDZ(formation) (RTP 1250 ℃for 50s + 750 ℃for 4h + 1050 ℃for 16h) + Nickel contamination (RTP 1000 ℃for 50s)
	A2	Nickel contamination (RTP 1000 ℃for 50s) + MDZ (formation) (RTP 1250 ℃for 50s + 750 ℃for 4h + 1050 ℃for 16h)
Group B	B1	Conventional DZ(formation) (1150 ℃for 2h + 750 ℃for 4h + 1050 ℃for 16h) + Nickel contamination (RTP 1000 ℃for 50s)
	B2	Nickel contamination (RTP 1000 ℃for 50s) + Conventional DZ(formation) (1150 ℃for 2h + 750 ℃for 4h + 1050 ℃for 16h)

3 Results and discussion

Figure 1 shows optical micrographs of a cross section of the group A samples followed by Sirtl etching for 4min. From Fig. 1 (a), an MDZ with a thickness of about 100μm clearly exists in sample A1 in spite of the subsequent nickel contamination. This result indicates that oxygen precipitates or their induced defects formed in the bulk become effective gettering sites for subsequent nickel contamination, resulting in the formation of a good MDZ in the sample A1. However, if the sample was initially contaminated, the MDZ could not form during the following RTP, and many etching pits would occur near the surface, as shown in Fig. 1 (b). Furthermore, we also observe from Fig. 1 (b) that the density of etching pits near the surface is much lower than that in the bulk. A noticeable difference between the MDZ quality of the two samples suggests that the sequence of nickel contamination has a strong influence on the MDZ. It has been reported that nickel atoms tend to diffuse out to the surface and precipitate there under slow cooling or air cooling[11,12]. The cooling rate of the RTP in our experiment is slow enough for the supersaturated nickel atoms to diffuse out to the surface, resulting in the formation of a nickel precipitate-free zone near the surface. Therefore, it is reasonable to deduce that the etching pits near the surface in Fig. 1 (b) come from the oxygen precipitates.

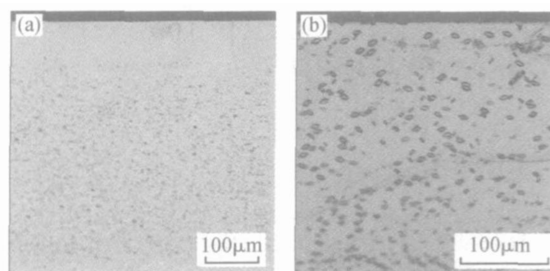

Fig. 1 Optical micrographs of a cross-section of the group A samples subjected to different nickel contamination sequences during MDZ annealing (a) MDZ formation (RTP 1250 ℃for 50s + 750 ℃for 4h + 1050 ℃ for 16h) + Nickel contamination (RTP 1000 ℃ for 50s); (b) Nickel contamination (RTP 1000 ℃for 50s) + MDZ formation (RTP 1250 ℃for 50s + 750 ℃for 4h + 1050 ℃for 16h)

Unlike the formation of the MDZ, the formation mechanism of the conventional DZ is mainly due to the out-diffusion of oxygen at high temperature annealing. The effect of nickel contamination on the conventional DZ was also investigated. Figure 2 shows optical micrograph of the cross section of the group B samples. Before or after nickel contamination, the samples were treated by the high-low-high processes to form the DZ. From Figs. 2 (a) and (b), it could be observed that good DZs of about 20～30μm exist in both samples regardless of the sequence of nickel contamination, which means that nickel contamination almost has no effect on the formation of the DZ through conventional IG processes. Furthermore, the different effects of nickel contam-

ination on the MDZ and the DZ formed by conventional processes suggest that nickel precipitates at the surface may increase the concentration of vacancies near the surface, preventing the formation of the MDZ.

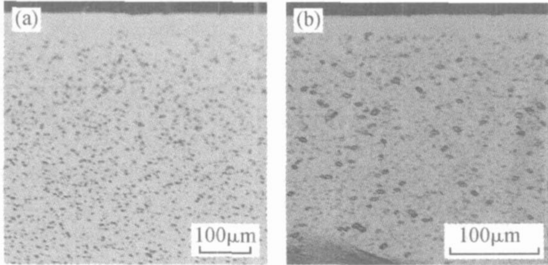

Fig. 2 Optical micrographs of a cross-section of the group B samples subjected to different nickel contamination sequences during conventional DZ annealing
(a) DZ formation (1150 ℃ for 2h + 750 ℃ for 4h + 1050 ℃ for 16h) + Nickel contamination (RTP 1000 ℃ for 50s); (b) Nickel contamination (RTP 1000 ℃ for 50s) + DZ formation (1150 ℃ for 2h + 750 ℃ for 4h + 1050 ℃ for 16h)

The creation of an MDZ by RTP is controlled by the point defect profiles induced by RTP, and the oxygen out-diffusion can generally be omitted[6,13]. RTP under Ar ambient will result in supersaturated vacancies. Due to the fast out-diffusion of vacancies during cooling, the concentration profile of vacancies decreases gradually from the bulk to the surface. The concentration of vacancies in the bulk is much higher than the critical concentration, so these supersaturated vacancies bind oxygen atoms to form the relatively immobile O_2V complex, resulting in the enhancement of oxygen precipitation in the bulk. Near the surface, however, the concentration is lower than the critical concentration, and thus the oxygen precipitation near the surface is suppressed. In this case, the MDZ near the surface occurs during the following annealing. Oxygen precipitates or their induced defects in the bulk have a strong ability to getter the subsequently contaminated nickel atoms, resulting in good DZs (Fig. 1 (a)). However, if the samples were initially contaminated by nickel, nickel atoms tend to precipitate at the surface, and the nickel-precipitate-free zone forms near the surface[11,12]. By X-ray diffraction pattern, nickel silicide (Ni_3Si) with a cubic structure is found to form at the sample's surface, as shown in Fig. 3. In comparison with the silicon matrix, Ni_3Si has a much smaller lattice parameter (about 0.35nm). When the sample underwent RTP at 1250 ℃ for 50s again, nickel precipitates at the surface were dissolved partly due to the short annealing time. A large number of vacancies are generated during cooling because of a great volume difference between Ni_3Si and the silicon matrix, hence keeping the vacancy concentration near the surface still higher than the critical concentration. As a result, oxygen precipitation near the surface can also occur in spite of the lower density, as shown in Fig. 1(b).

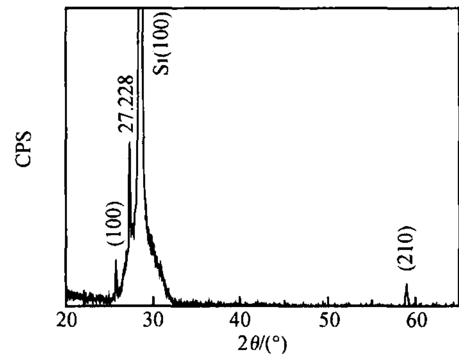

Fig. 3 XRD pattern of Ni_3Si formed at the surface of the sample annealed at 1000 ℃ for 50s under Ar atmosphere

During the conventional processes, the formation of the DZ is mainly due to the out-diffusion of oxygen at the first annealing step (1150 ℃, 2h). Generally, transition metals, including nickel, have a slight enhancement on the diffusion of oxygen in silicon[14]. Thus, the initial nickel contamination cannot affect the DZ formation, as shown in Fig. 2 (a). On the other hand, once the oxygen precipitates or their induced defects form in the bulk, they can become effective gettering sites for nickel atoms, leading to a good DZ near the surface, as shown in Fig. 2(b).

4 Conclusion

In summary, the effect of nickel contamination on the MDZ and conventional DZ in CZ silicon wafers has been investigated with optical microscopy and X-ray diffraction in this paper. After DZ formation, whether through RTP or conventional IG processes, nickel contamination has no effect on the DZ, and nickel atoms can be gettered by the bulk microdefects (BMDs). Otherwise, in silicon wafers initially contaminated with nickel, the MDZ could not form, and many precipitates occurred near the

surface of the sample. Based on the facts, we propose that the interface between nickel silicides at the surface and silicon matrix generate a high enough vacancy concentration to enhance the oxygen precipitation near the surface during RTP, preventing the formation of the MDZ.

References

[1] Myers S M, Seibt M, Schroeter W. Mechanisms of transition-metal gettering in silicon. J Appl Phys, 2000, 88(7): 3795

[2] Bergholz W, Gilles D. Impact of research on defects in silicon on the microelectronic industry. Phys Status Solidi B, 2000, 222(1): 5

[3] Tan T Y, Garnde E E, Tice W K. Intrinsic gettering by oxide precipitate induced dislocations in Czochralski Si. Appl Phys Lett, 1977, 30(4): 175

[4] Gilles D, Weber E R, Hahn S K. Mechanism of internal gettering of interstitial impurities in Czochralski-grown silicon. Phys Rev Lett, 1990, 64(2): 196

[5] Falster R J, Fisher G R, Ferrero G. Gettering thresholds for transition metals by oxygen-related defects in silicon. Appl Phys Lett, 1991, 59(7): 809

[6] Falster R, Vorokov V V, Quast F. On the properties of the intrinsic point defects in silicon: a perspective from crystal growth and wafer processing. Phys Status Solidi B, 2000, 222(1): 219

[7] Falster R, Vorokov V V. The engineering of intrinsic point defects in silicon wafers and crystals. Mater Sci Eng B, 2000, 73: 87

[8] Akatsuka M, Okui M, Morimoto N, et al. Effect of rapid thermal annealing on oxygen precipitation behavior in silicon wafers. Jpn J Appl Phys, 2001, 40: 3055

[9] Graff K. Metal impurities in silicon device fabrication. Berlin, Heideiberg, New York: Springer, 1995

[10] Hoelzl R, Huber D, Range K J, et al. Gettering of copper and nickel in p/p$^+$ epitaxial wafers. J Electrochem Soc, 2000, 147: 2704

[11] Xi Z, Yang D, Chen J, et al. Nickel precipitation in large-diameter Czochralski silicon. Physica B, 2004, 344: 407

[12] Gay N, Martinuzzi S. External self-gettering of nickel in float zone silicon wafers. Appl Phys Lett, 1997, 70(19): 2568

[13] Falster R, Cornara M, Gambaro D, et al. Effect of high temperature pre-anneal on oxygen precipitates nucleation kinetics in Si. Solid State Phenom, 1997, 57: 123

[14] Newman R C. Oxygen diffusion and precipitation in Czochralski silicon. J Phys: Conden Matter, 2000, 12(25): R335

单晶硅中过渡族金属镍对洁净区形成的影响*

吴冬冬[1] 杨德仁[1,†] 席珍强[1] 阙端麟[1] 钟 尧[2]

(1 浙江大学硅材料国家重点实验室, 杭州 310027)

(2 中国空间技术研究院北京控制工程研究所, 北京 100080)

摘要: 研究了过渡族金属镍在快速热处理作用下对直拉单晶硅中洁净区形成的影响. 实验结果发现: 硅中魔幻洁净区(MDZ)形成后, 氧沉淀及其诱生缺陷能有效地吸杂金属镍; 而沾污金属镍的硅中, 随后的快速热处理工艺不能形成MDZ, 硅片近表面出现大量沉淀. 采用传统的内吸杂工艺, 镍沾污的次序对洁净区的形成没有影响. 实验表明由于硅片表面形成的镍硅化合物的晶格常数比硅小, 所以在硅片近表面产生高浓度的空位, 导致近表面的氧依然能够在MDZ工艺中形成沉淀.

关键词: 硅; 镍; 洁净区

PACC: 7280C; 6155F; 6170Y

中图分类号: TN304.1$^+$2 **文献标识码**: A **文章编号**: 0253-4177(2006)04-0623-04

* 教育部博士点基金, 高校新世纪人才基金, 及国家自然科学基金(批准号: 90307010)资助项目

† 通信作者. Email: mseyang@zju.edu.cn

2005-10-27 收到, 2005-12-24 定稿

©2006 中国电子学会