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Effect of Rapid Thermal Annealing Ambient on Gettering Efficiency and Surface Microstructure in 300mm CZ Silicon Wafers*

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Abstract: The effect of rapid thermal annealing (RTA) ambient on denuded zone and oxygen precipitates in Czochralski (CZ) silicon wafers is studied in this paper. N_2 and a N_2/NH_3 mixture are used as RTA ambient. It is demonstrated that a high density of oxygen precipitates and thin denuded zone are obtained in N_2/NH_3 ambient, while a relatively lower density of oxygen precipitates and thicker denuded zone are observed in N_2 ambient. As the RTA duration times increased, the oxygen precipitate density increased and the denuded zone depth decreased. X-ray photoelectron spectroscopy (XPS) data and atomic force microscope (AFM) results show that there was a surface nitriding reaction during the N_2/NH_3 ambient RTA process, which can explain the different effect of RTA ambient.

Key words: 300mm CZ silicon wafer; denuded zone; intrinsic gettering; RTA; XPS; AFM
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1 Introduction

During the fabrication process of ultra large-scale integration circuits (IC), metal contaminants such as iron, nickel, and copper *et al.*, are often unintentionally brought into the silicon wafer and are harmful to device performance. Gettering technology is one of the most useful means to remove metal contaminants in the active region of devices. Several gettering techniques, such as intrinsic and external gettering, have been developed in the past decades. Intrinsic gettering (IG) techniques include the conventional high-low-high annealing process and magic denuded zone (MDZ) based on the rapid thermal annealing (RTA) process[1~4]. Extrinsic gettering techniques include backside damage, phosphorous diffusion, and poly-silicon deposit processes[5,6].

The traditional extrinsic gettering techniques are not suitable for 300mm wafers, because 300mm wafers are generally double-side polished to obtain a very flat back surface[5~7], which eliminates the use of the EG process based on the backside surface treatment. As a result, the intrinsic gettering process becomes important for 300mm wafers to remove metal contamination in the device active region.

The conventional high-low-high annealing process[7] has disadvantages such as bad reproduction on the depth of denuded zone, the dependence on the original oxygen concentration in wafers, and high thermal budget[1~7]. The MDZ[1~4] process was developed by Falster *et al.* and is an improved technique based on the traditional high-low-high annealing process. In the MDZ process, RTA replaces the first annealing step of the conventional process. The role of RTA on the formation of the denuded zone and oxygen precipitates has been discussed by Falster and Akatsuka[8,9]. However, more efforts are necessary to decrease the denuded zone depth and increase the oxygen precipitate density.

In this work, the effects of N_2/NH_3 and N_2 on the formation of the denude zone and oxygen precipitates are investigated. Meanwhile, the surface chemical composition and tomography changes during different RTA ambient are investigated by the means of X-ray photoelectron spectroscopy (XPS) and atom force microscope (AFM), and the effect of RTA ambient is explained.

2 Experiment

Samples used in the experiment were p-type, (100) orientation, 300mm polished silicon wafers with an initial interstitial oxygen concentration of about $1.35\times10^{18}cm^{-3}$ (ASTM-76).

RTA was performed at 1200℃ in N_2 and NH_3/N_2 ambient with a ramp-down rate of 90℃/s. After the RTA process, the wafers were annealed (800℃ for 4

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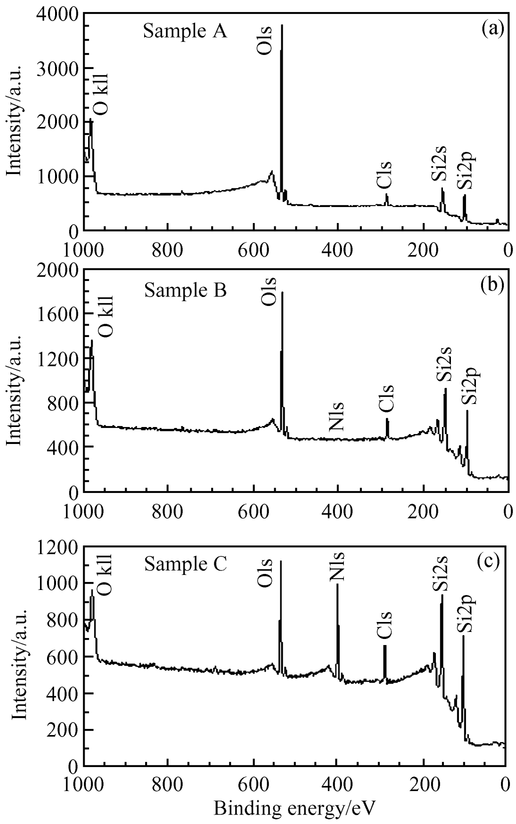

Fig. 1　XPS spectra for as-polished (a), N_2 RTA (b), and N_2/NH_3 RTA wafers (c)

hours + 1000℃ for 16 hours) in pure N_2 ambient. The cross-section of the samples was etched by Wright solution, and then the depth profile of the denuded zone and the oxygen precipitates were observed using an optical microscope. XPS and AFM were used to investigate the wafer surface chemical and tomography variation after RTA.

Initial and post-annealing interstitial oxygen concentration (C_{initial} and C_{post}) were measured using fourier transform infrared spectroscopy. Interstitial oxygen loss ($\Delta O_i = C_{\text{initial}} - C_{\text{post}}$) was introduced to evaluate the oxygen precipitate density.

3　Results and discussion

3.1　Effect of RTA ambient on wafer surface status

Figure 1 shows the wide scan spectra of XPS for the as-polished wafer, and the N_2/NH_3 and N_2 ambient RTA treated wafers. Peaks of Okll, O1s, C1s, Si2s, and Si2p are observed on all three wafers, and Nls is detected only on the wafer with N_2/NH_3 ambient (N atom percentage is 21%). The nitriding reaction may occur during the N_2/NH_3 ambient process.

Figure 2 shows the AFM scan for the as-polished wafer, and the N_2 and N_2/NH_3 ambient RTA treated wafers. The surface micro-roughness increased slightly after the RTA process in both ambient. However, several small pits, 20～80nm in diameter, appear in the surface when the wafer was treated in the N_2/NH_3 ambient. The small pits will deteriorate the wafer surface and influence the GOI in the IC manufacture, and the whole wafer manufacturing process should be redesigned if the RTA process with N_2/NH_3 ambient came to practical application.

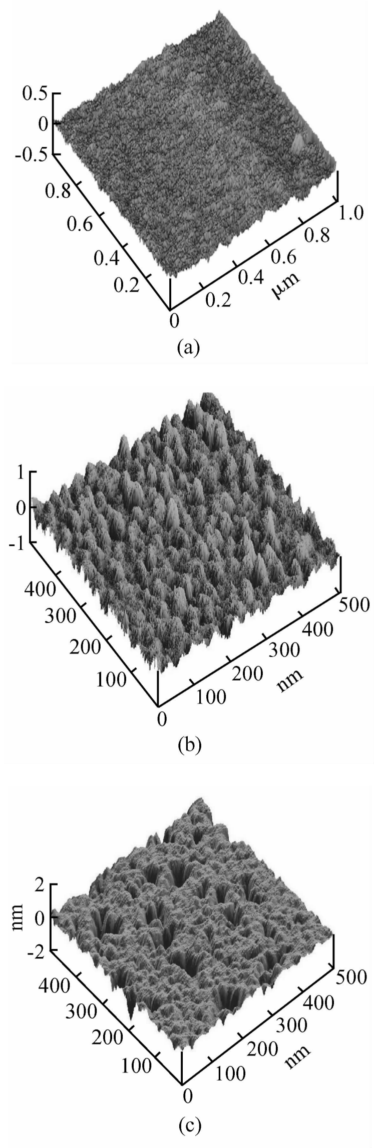

Fig. 2　AFM surface scan of as-polished wafer (a), wafer treated in N_2 ambient RTA treatment with 45s high temperature duration (b), wafer treated in N_2/NH_3 ambient and 32s duration (c)

However, the surface pits were evidence of surface reaction during the RTA process. Combining the present speculation with the XPS result, we conclude that the small pits was formed by the surface erosion by NH_3. During the RTA high temperature holding process, NH_3 decomposed to N and H atoms, which exhibited high activity. The H atom reacted with the surface native silicon oxide and the N atom

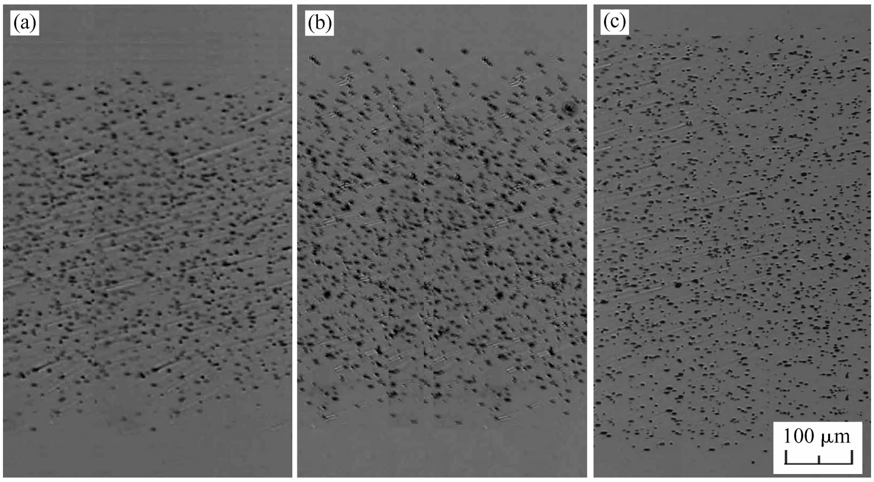

Fig.3 Cross-sectional images of N_2 ambient wafers with RTA duration time (a) 25s;(b) 35s;(c) 45s

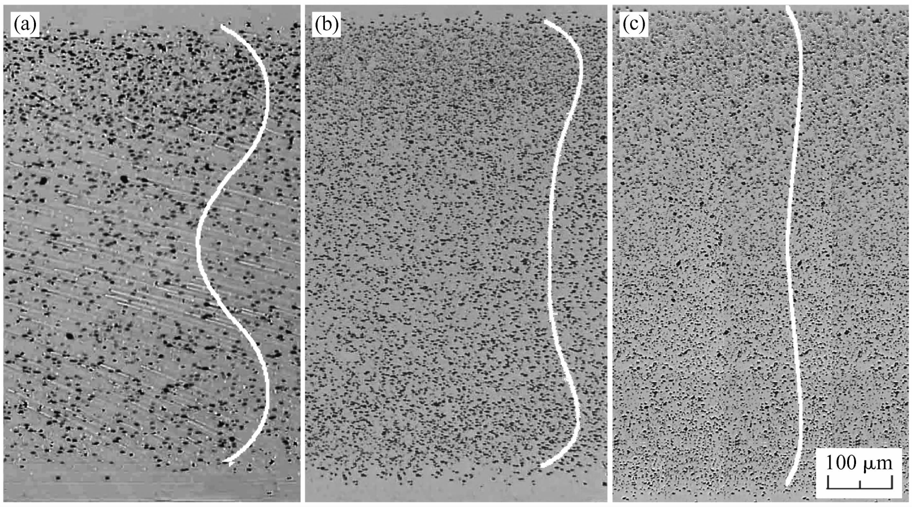

Fig.4 Cross-sectional images of N_2/NH_3 ambient wafers with RTA duration time (a) 12s;(b) 22s;(c) 32s

reacted when a fresh silicon surface that appeared by H atom reduction reaction. Due to the short reaction periods and the slow reduction reaction of the H atom, the nitriding production would be preferentially nucleared on the site of fresh wafer surface, and the H atom continued to react with the wafer surface in the zone uncovered with nitriding reactant. The H atom prefers to react with native oxide, and also can react with bare silicon to form SiH_4 in the surface when the oxide layer had been reduced. As a result, the pits were formed in the position where nitriding reactants were not covered by H atom erosion.

3.2 Effect of RTA ambient on denuded zone distribution

Figure 3 shows the oxygen precipitate depth profile of wafers treated in N_2 RTA ambient. For RTA duration times of 25, 35, and 45s, the depth of the denuded zone is 107, 80, and 40μm, respectively. Thus, the denuded zone depth decreases for prolonged RTA duration time.

Figure 4 shows the oxygen precipitate depth profile of the wafers treated in NH_3/N_2 RTA ambient. For RTA duration times of 12, 22, and 32s, the depth of the denuded zone is 40, 20, and 10μm, respectively. The denuded zone depth decreases for prolonged RTA duration time, as demonstrated in N_2 ambient. Meanwhile, the oxygen precipitate distribution profile in the three samples exhibits an "M" shape, as marked in Fig. 4 with white lines. The precipitate distribution becomes more uniform if the duration time increases.

Figure 5 shows the value of ΔO_i as a function of RTA duration time. ΔO_i increases for prolonged RTA duration time in both N_2 and N_2/NH_3 ambient. ΔO_i increases from 5.39×10^{17} to $5.5\times10^{17}cm^{-3}$ in N_2 ambient. In N_2/NH_3 mixture, ΔO_i increases from 5.3×10^{17} to 1.1×10^{18} cm^{-3}. With the reference of the oxygen depth profile under an optical microscope, the

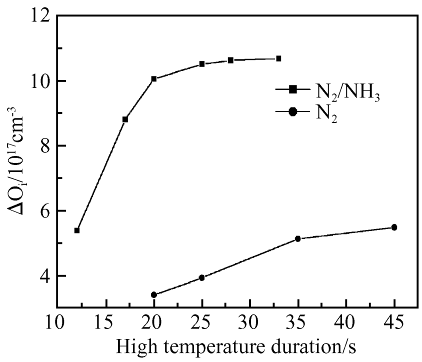

Fig.5 Interstitial oxygen concentration loss (ΔO_i) as a function of the RTA high temperature duration time

value of ΔO_i can be used to evaluate the oxygen precipitate density indirectly, as it is the difference of interstitial oxygen concentration pre- and post- annealing process. An increase in the value of ΔO_i always accompanies the distribution of a thin denuded zone and high oxygen precipitates in the wafer cross-section. By comparison, a relatively thinner denuded zone and higher oxygen precipitate density may be obtained in N_2/NH_3 mixture than in N_2 ambient.

The surface nitriding reaction during the N_2/NH_3 mixture gas RTA process, which had been verified by XPS and AFM, explains the different effects of RTA ambient. A special vacancy distribution[1~4] (low vacancy density in the sub-surface layer, and high vacancy density in the wafer bulk) forms during the RTA process. The special vacancy distribution causes a non-uniform oxygen precipitate profile in the following two step annealing process (800℃, 4h + 1000℃, 16h) since vacancies enhance the non-equilibrium nucleating process of oxygen precipitates[10]. The Frenkel mechanism and surface point defects injection are two main mechanisms that determine the vacancy distribution during the RTA process. The Frenkel mechanism is a thermal equilibrium process that occurs during the high temperature step, and surface point defect injection occurs when there is a surface reaction such as oxidation or nitriding[11~15].

In the present work, N_2 and N_2/NH_3 are used during the RTA process, but the strong nitriding reaction appears only in N_2/NH_3 ambient due to the presence of NH_3. During the N_2/NH_3 ambient RTA high temperature duration stage, vacancies form in the nitride/silicon interface by nitriding reaction diffuse into the wafer bulk. As a result, the vacancy concentration in the N_2/NH_3 RTA wafer is much higher than that in the N_2 RTA wafer. When the wafers are cooled at the same ramp down rate, the vacancy concentration in the N_2/NH_3 RTA wafer bulk is higher than that in N_2 ambient. Consequently, the oxygen precipitation concentration in the N_2/NH_3 RTA wafer bulk is higher than that in N_2 ambient since the vacancies enhance the non-equilibrium nucleating process of oxygen precipitates[10].

The "M" shape oxygen precipitates distribution in Fig.4 (a) and (b) is another important clue to prove the vacancy surface injection. When the duration time is short, vacancies injected into the wafer bulk can not reach the wafer centre zone, and an "M"-like vacancy distribution profile forms after the RTA ramp down process. When the duration time is sufficient, a homogeneous vacancy distribution forms throughout the entire bulk. As a result, we can see homogeneous oxygen precipitates in Fig.4 (c).

4 Conclusion

The depth of the denuded zone is thinner and the oxygen precipitate density is higher in a N_2/NH_3 ambient RTA wafer than in N_2 ambient. Furthermore, the effect of N_2/NH_3 can be explained by the results of XPS and AFM, which prove that NH_3 reacted with silicon. Surface vacancy injection was enhanced by NH_3 reaction. As a result, a thinner denuded zone and higher oxygen precipitate density formed in the N_2/NH_3 ambient RTA wafer in the following two step annealing process.

References

[1] Plummer J D. Silicon VLSI technology fundamentals, practice modeling. Beijing: Publishing House of Electronics Industry, 2003: 151

[2] Falster F, Voronkov V V. Intrinic point defects and their control in silicon crystal growth and wafer processing. MRS Bulletin/JUNE 2000. http://www.mrs.org/ publications/bulletin/

[3] Falster R, Gambaro D, Olmo M, et al. The engineering of silicon wafer material properties through vacancy concentration profile control and the achievement of ideal oxygen precipitation behavior. The Fifth International Symposium on High Purity Silicon V Boston, Massachusetts, 1998: 135

[4] Falster R, Voronkov V V. The engineering of intrinsic point defects in silicon wafer and crystals. Mater Sci Eng, 2000, B73: 87

[5] Tsuya H. Present status and prospect of Si wafers for ultra large scale integration. Jpn J Appl Phys, 2004, 43(7A): 4055

[6] Istravtov A A, Hieslmair H, Weber E R. Advanced gettering techniques in ULSI technology. MRS Bulletin/JUNE 2000. http://www.mrs.org/ publications/bulletin

[7] International Technology Roadmap for Semiconductors 2006 update: Front End Process. http://public.itrs.net

[8] Akatsuka M, Okui M, Sueoka K, et al. Effect of rapid thermal annealing on oxide precipitation behavior in silicon crystal. Nuclear Instruments and Methods in Physics Research B, 2002, 186: 46

[9] Akatsuka M, Okui M, Sueoka K. Effect of rapid thermal annealing on oxide precipitation behavior in silicon wafer. Jpn J Appl Phys, 2001, 40(5A): 281

[10] Liu Bin, Wang Jing, Qin Fu, et al. The influence of RTA on oxygen precipitation in silicon wafer. 6th Sino-Korea Co-Symposium on Advanced Materials, Urumchi, 2002: 8

［11］ Falster R，Pagan M，Gambaro D，et al. Vacancy-assisted oxygen precipitation phenomena in Si. Proceedings of the 7th International Autumn Meeting Gettering and Defect Engineering in Semiconductor Technology，Belgium，1997：129

［12］ Mizuo S，Higuchi H. Anomalous diffusion of B and pin silicon directly masked with Si_3N_4. Jpn J Appl Phys，1982，21(2)：281

［13］ Fahey P，Barbuscia G，Moslehi M. Kinetics of thermal processes in the study of dopant of dopant diffusion mechanisms in silicon. Appl Phys Lett，1985，46(8)：784

［14］ Hu S M. Vacancies and self-interstitials in silicon：generation and interaction in diffusion. J Electrochem Soc，1992，139(7)：2066

［15］ Feng Quanlin，Shi Xunda，Liu Bin，et al. Effect of rapid thermal annealing ambient on denuded zone and oxygen precipitates in 300mm silicon wafer. Chinese Journal of Semiconductors，2006，27(1)：68

快速退火气氛对 300mm CZ 硅片吸杂效应和表面微观结构的影响*

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摘要： 研究了 N_2 和 N_2/NH_3 混合气两种不同气氛快速退火处理硅片对洁净区和氧沉淀分布的影响.研究发现：N_2/NH_3 混合气氛处理的硅片在后序热处理中表层形成很薄的洁净区同时体内形成高密度的氧沉淀；而 N_2 气氛处理的硅片的洁净区较厚、氧沉淀密度较低.但是两种气氛下延长恒温时间都可以降低洁净区厚度，增加氧沉淀密度.X 射线光电子能谱和原子力显微镜扫描的结果显示 N_2/NH_3 混合气氛处理使表面出现了强烈的氮化反应，利用氮化反应可以解释快速退火气氛对洁净区分布的影响.

关键词： 300mm CZ 硅片；洁净区；本征吸杂；快速退火；X 射线光电子能谱；原子力显微镜

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