Impact of Transition-Metal Contamination on Oxygen Precipitation in Czochralski Silicon Under Rapid Thermal Processing*

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Abstract: The effects of the transition metals copper and nickel on oxygen precipitation in Czochralski silicon under a rapid thermal process are investigated. It is found that interstitial copper has almost no effect on oxygen precipitation, but copper precipitation markedly enhances oxygen precipitation. However, neither interstitial nickel nor nickel precipitation affects oxygen precipitation. The reasons for the effects of copper and nickel contamination on oxygen precipitation are discussed in light of oxygen precipitation nucleation theory.

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1 Introduction

Oxygen is the main impurity in Czochralski (CZ) silicon, with a concentration of about 10^{18} cm^{-3}, which exceeds the solubility of oxygen in silicon at typical device processing temperatures. Most oxygen atoms exist on interstitial sites between two silicon atoms. During thermal treatments at high temperatures, the supersaturated interstitial oxygen atoms tend to agglomerate and form oxygen precipitates.

In the past few decades, the behavior of oxygen precipitation in CZ silicon has been investigated extensively[1]. In the microelectronics industry, oxygen precipitation and defects are intentionally induced to reduce the impurity content in the electrically active device regions, by what is called the internal gettering (IG) mechanism[2~4]. It is well accepted that the IG efficiency strongly depends on the type of defect induced and on the density and size of the oxygen precipitate[5,6]. All these factors are directly related to the behavior of oxygen precipitation nucleation and growth, which is determined not only by the thermal process but also by other factors, such as initial oxygen content, carbon content, nitrogen content, ambient, and metals. Metals, especially 3d transition metals, may contaminate silicon wafers during high-temperature annealing. These metals, their silicides, or defects induced by silicides may have a strong effect on oxygen precipitation. The influence of iron on oxygen precipitation has been researched by several groups[7~9]. However, few papers have reported the impact of copper or nickel on oxygen precipitation[10,11].

Rapid thermal processing (RTP) has emerged as a key manufacturing technique for the fabrication of integrated circuits on silicon. Recently, MEMC, one of the largest world's silicon material companies, has developed a different approach to optimizing the denuded zone (DZ) in IG, called the magic denuded zone (MDZ)[12], which is carried out by means of RTP. The MDZ process has now been widely used in the micro-electronics industry. However, during RTP, silicon is easily contaminated with transition metals, such as copper and nickel. Research about how these metals affect the oxygen precipitation or the denuded zone in the MDZ process is needed. Copper and nickel have a different precipitation behavior in silicon. Further research is needed to know how their different precipitation behaviors affect the nucleation or the growth of oxygen precipitation in silicon. Therefore it is important to study the effects of such metals on oxygen precipitation in silicon both in experi-

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ment and in theory.

In this paper, we report the investigation of the impact of copper and nickel on the behavior of oxygen precipitation in CZ silicon under RTP by means of Fourier transform infrared spectro-scopy (FTIR) and defect etching. In light of the nucleation theory of oxygen precipitation, the mechanism behind the influence of copper and nickel on oxygen precipitation is discussed.

2 Experiment

The samples used in this work are 200mm (100) Czochralski grown, boron-doped silicon wafers with a thickness of about 620μm and a resistivity of about 10Ω·cm. The initial oxygen concentration of the wafers was about $1.0\times10^{18}cm^{-3}$, as determined by a Bruker IFS 66V/S FTIR with a calibrated coefficient of $3.14\times10^{17}cm^{-2}$. All samples were chemically etched to remove surface damage and were cleaned by RCA solute. Then they were divided into two groups, A and B. In group A, the samples were subjected to MDZ annealing, two-step annealing (750℃ for 4h + 1050℃ for 16h), followed by a pre-annealing of RTP at 1250℃ for 50s. To introduce copper and nickel contamination from the surface into the bulk of the silicon, the samples, which were sputtered with copper and nickel on the surface, were annealed by RTP at 1000 or 1200℃ for 50s. According to the solubility of copper and nickel in silicon, the concentrations of copper and nickel in the samples were about $10^{17}\sim10^{18}cm^{-3}$. This contamination level should be much higher than that in actual devices, in which the maximum tolerable metal concentration for important impurities such as copper and nickel is about $10^{11}cm^{-3}$[13]. The cooling rate of the RTP was about 20℃/s. In group B, copper and nickel contaminant was first introduced into the samples by RTP at 1000 or 1200℃ for 50s. Then the same MDZ annealing (RTP 1250℃ for 50s + 750℃ for 4h + 1050℃ for 16h) was performed. All annealing was performed in argon atmosphere. The samples' interstitial oxygen concentration was measured by FTIR at room temperature. Before measurement, all samples were chemically etched to remove about 50μm of the surface and cleaned by RCA processes. Optical microscopy observation (Olympus MX50) combined with Sirtle etchant was used to study the defect distribution at the cleaved surfaces of the samples. The etching time was 4min.

3 Results and discussion

Figure 1 shows the variation of interstitial oxygen concentration in samples with a different copper contaminated sequence during the IG process. In Fig. 1(a), the samples were first subjected to MDZ annealing (RTP 1250℃ for 50s + 750℃ for 4h + 1050℃ for 16h) and were then contaminated with Cu by RTP at 1000 or 1200℃. In Fig. 1(b), the samples were first contaminated with Cu by RTP at 1000 or 1200℃ and were then subjected to MDZ annealing (RTP 1250℃ for 50s + 750℃ for 4h + 1050℃ for 16h). The oxygen concentration loss, defined as the difference in oxygen concentration before and after thermal treatments, was taken as the precipitated oxygen concentration. In Fig. 1 (a), it can be seen that after the MDZ annealing, the oxygen concentration of the samples ranges from the original 10.5×10^{17} to $8.3\times10^{17}cm^{-3}$, and the precipitated oxygen concentration is about $2.2\times10^{17}cm^{-3}$. After the samples were contaminated with copper by RTP, the oxygen concentration dropped slightly, as shown in Fig. 1(a), and the amount of oxygen precipitation changed slightly. In Fig. 1(b), a small increase in the oxygen concentration can be observed in the samples subjected to copper contamination by RTP. This is because high temperature RTP annealing makes the original small oxygen precipitation melt in the silicon, thus increasing the measured oxygen concentration. Due to the short duration of the RTP annealing, the change of oxygen precipitation can be neglected. Then the oxygen concentration drops to about $4.4\times10^{17}cm^{-3}$ after the MDZ annealing (RTP 1250℃ for 50s + 750℃ for 4h + 1050℃ for 16h). Thus the final concentration of oxygen precipitation is about $6.1\times10^{17}cm^{-3}$, which is much higher than the oxygen precipitation concentration shown in Fig. 1(a). For the process shown in Fig. 1(a), the MDZ annealing creates some density of the oxygen precipitation and induced defects in the silicon wafers, which getters the interstitial copper undiffused by the subsequent RTP annealing. Due to the IG mechanism, copper only precipitated at the existing induced defects or oxygen precipitate. Thus they would not affect the oxygen precipitation concentration remarkably. However, for the process shown in Fig. 1(b), during the cooling of RTP, the undiffused copper agglomerates and then forms copper silicides in the silicon wafers due to the great dependence of the solubility of interstitial copper on temperature. These copper silicides should enhance the oxygen precipitation in the subsequent MDZ annealing, so that the amount of oxygen precipitation is greater than those of the samples only subjected to MDZ annealing shown in Fig. 1(a).

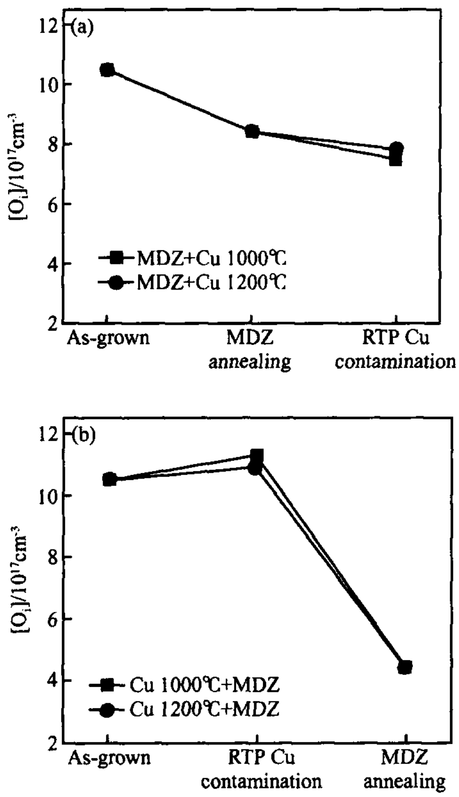

Fig. 1　Variation of interstitial oxygen concentration ([O_i]) in samples with different copper contaminated sequences during IG annealing　(a) MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h) + Cu contamination by RTP (1000 ℃/1200 ℃ for 50s); (b) Cu contamination by RTP (1000 ℃/1200 ℃ for 50s) + MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h)

The variation of the samples' interstitial oxygen concentration with different nickel contamination sequences during the IG process is shown in Fig. 2. The annealing process of nickel is similar to that of copper. In Fig. 2(a), the samples' oxygen concentration shows a big drop after MDZ annealing, and the subsequent in-diffused nickel has a slight impact on the oxygen precipitation, which is similar to that of copper. In Fig. 2(b), the oxygen concentration of the samples ranges from the original 10.5 $\times 10^{17}$ to about 4.2 $\times 10^{17} cm^{-3}$, and the amount of oxygen precipitation is about 6.3 $\times 10^{17} cm^{-3}$, which is as much as the last oxygen precipitation concentration in Fig. 2(a). This indicates that the initial undiffused nickel also has no effect on the subsequent oxygen precipitation, which is obviously different from the effect of copper on oxygen precipitation.

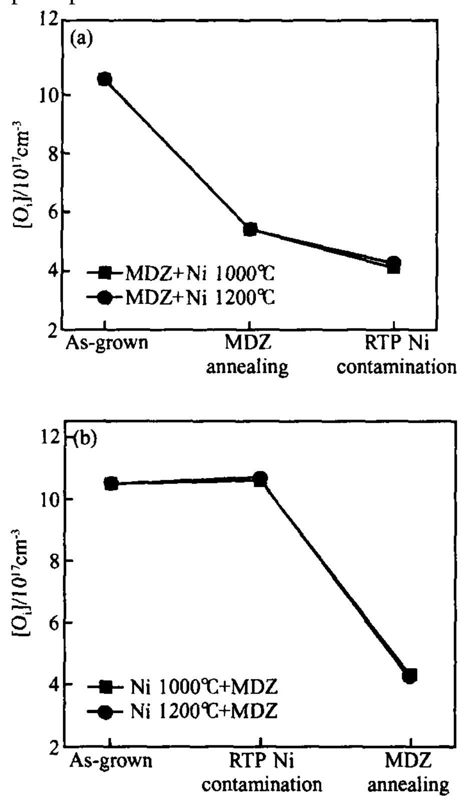

Fig. 2　Variation of interstitial oxygen concentration ([O_i]) in samples with different nickel contaminated sequences during IG annealing　(a) MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h) + Ni contamination by RTP (1000 ℃/1200 ℃ for 50s); (b) Ni contamination by RTP (1000 ℃/1200 ℃ for 50s) + MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h)

To further investigate the impact of copper and nickel on oxygen precipitation behavior during the different annealing processes in silicon, an optical microscope combined with Sirtle etchant was used to observe the defect distribution in the samples. Figure 3 shows the cross-sectional optical micrographs of the samples subjected to Cu annealed in groups A and B. It is clearly seen that there is a high density of etching pits in Fig. 3 (a), but in Fig. 3 (b) large star-like colonies appear in the etching pits. These etching pits reveal oxygen and copper precipitation as well as the induced defects. This type of colony normally forms during slow cooling of annealing of copper precipitation[14]. After subsequent MDZ annealing, the star-like configuration hardly changes because the RTP at 1250 ℃ in the MDZ is short and could not entirely dissolve the copper precipitation. It is reasonably demonstrated that oxygen precipitated at the arm of the colonies and nucleated at the dislocation loops induced by copper precipitation, that is, heterogeneous nucleation of oxygen precipitation should be dominant in this sample[10]. Figure 4 shows cross-sectional optical micrographs of the samples subjected to Ni annealed in groups A and B. There were high densities of etching pits in Figs. 4(a) and (b). No obvious different etching pits can be found in these two micrographs, and they all reveal oxygen and nickel precipitation.

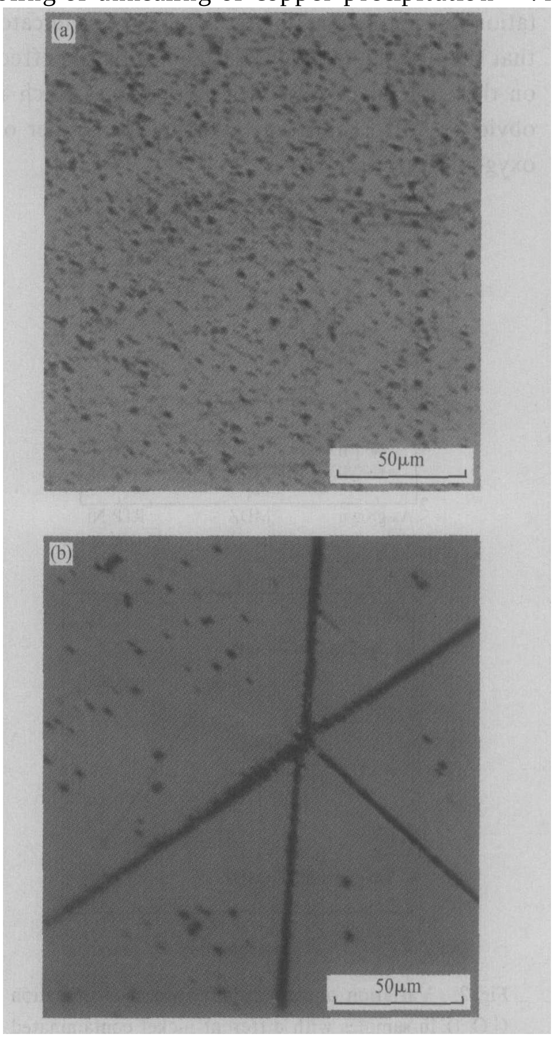

Fig. 3 Cross-sectional optical micrographs of the samples subjected to Cu annealed in groups A and B (a) MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h) + Cu contamination by RTP (1000 ℃ for 50s); (b) Cu contamination by RTP (1000 ℃ for 50s) + MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h)

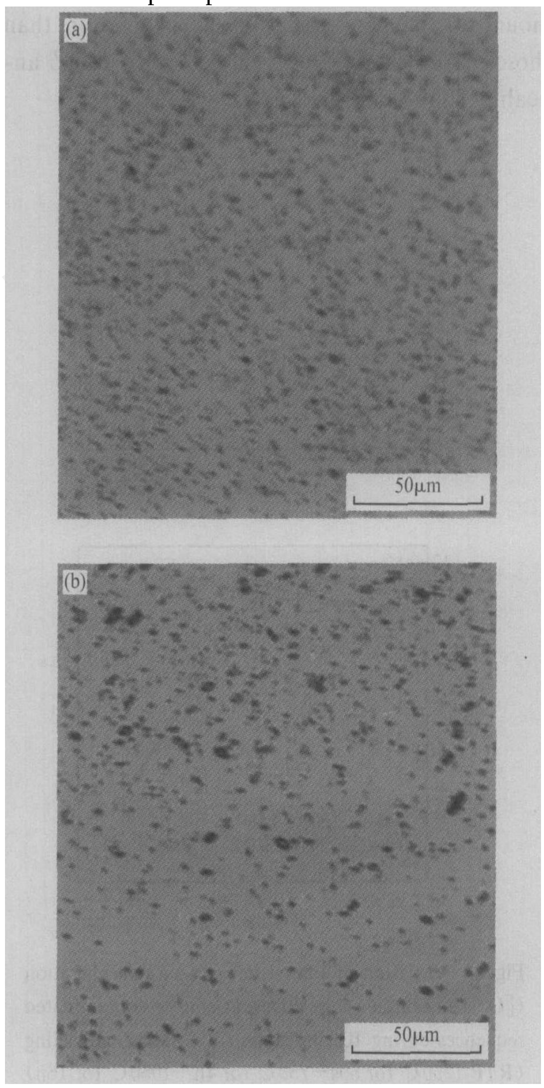

Fig. 4 Cross-sectional optical micrographs of the samples subjected to Ni annealed in groups A and B (a) MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h) + Ni contamination by RTP (1000 ℃ for 50s); (b) Ni contamination by RTP (1000 ℃ for 50s) + MDZ annealing (RTP 1250 ℃ for 50s + 750 ℃ for 4h + 1050 ℃ for 16h)

The above results indicate that in the IG process Cu and Ni have no appreciable effect on existing oxygen precipitation in CZ silicon, and can be gettered effectively, whereas initial contaminated Cu in silicon significantly enhances the subsequent oxygen precipitation in the IG process, but the effect of Ni on oxygen precipitation is small.

During the MDZ annealing, the oxygen precipitation is driven by the supersaturation of oxygen in silicon. Generally, the oxygen precipitation process includes two aspects: nucleation and growth of oxygen precipitate. During the nucleation of oxygen precipitation, a reaction between the silicon matrix and oxygen occurs as[1]

$$2Si + 2O_i \Leftrightarrow SiO_2 + y_1 I + (1 - y_1) Si_{strain} \quad (1)$$

where I represents the interstitial silicon, and Si_{strain} represents the compressed stress of oxygen precipitation on the silicon matrix. Due to the volume difference between oxygen precipitation and silicon, large stresses are generated, retarding the formation of the oxygen precipitation. Compared to carbon or vacancy absorption and generation of punching-out dislocation loops, I emission is thought to be more effective to release stress. On the basis of strain relief models, the critical size of oxygen precipitation can be written as[1]

$$r_{crit} = \frac{\Omega_{ox}\sigma}{k_B T \ln\left[\left(\frac{C_i}{C_i^{eq}}\right) \times \left(\frac{C_I^{eq}}{C_I}\right)^{1/2}\right]} \quad (2)$$

where Ω_{ox} and σ refer to the SiO_2 molecule volume and the interfacial energy density between the oxygen precipitations, C_i and C_i^{eq} are the actual and equilibrium concentrations of interstitial oxygen, respectively, and C_I^{eq} and C_I are the actual and equilibrium concentrations of interstitial silicon.

For the samples first subjected to MDZ annealing in both Cu and Ni, almost no defect existed to act as heteronucleation sites of oxygen precipitate, and the interstitial silicon atoms could not be easily absorbed, so homogeneous nucleation was the main method. According to Eq. (2), the critical size of the oxygen precipitation increases, and the density of the oxygen precipitation in silicon is low. Meanwhile, because the residual stress induced by the oxygen precipitation cannot be released easily, dislocation occurs around the oxygen precipitation. It has been found that interstitial copper and nickel do not enhance oxygen diffusion or oxygen precipitate nucleation[1]. During the next RTP annealing, the in-diffused Cu and Ni are gettered by these oxygen precipitates or their induced defects, and the effect of metals on oxygen precipitation is slight.

Copper atoms exist primarily in complexes or as interstitial copper when the annealing temperature is lower than 800 ℃. However the annealing temperatures of RTP are 1000 and 1200 ℃, higher than 800 ℃, and the copper atoms are agglomerated. Thus copper precipitation in silicon with a high density of dislocations is generated. These precipitates and dislocations could provide heteronucleation sites for the oxygen precipitation due to the much lower nucleation barrier. Furthermore, the dislocations could absorb the interstitial silicon atoms during the oxygen precipitation nucleation, thus decreasing the concentration of interstitial silicon (C_I). From Eq. (2), when the critical size of the oxygen precipitation is smaller, a high density of the oxygen precipitation appears. On the other hand, the defects generated by the copper precipitation could absorb the interstitial silicon atoms and release the strong stress induced by the oxygen precipitation, enhancing the oxygen precipitation. Therefore, copper precipitation greatly enhances the nucleation process of the oxygen precipitation and increases the final amount of the oxygen precipitation, as shown in Fig. 1.

Unlike copper, nickel atoms tend to diffuse to the surface of the silicon wafers, and only part of them precipitate in the bulk of the silicon wafers, when the annealing cooling is slow. However, the nickel precipitation fits the silicon matrix very well. They do not induce large stress in the silicon matrix, and no high density of defects is generated. Thus in these silicon wafers, there is a lack of heteronucleation sites for the oxygen precipitation, and there are no defects to absorb interstitial silicon atoms and to release the strong stress, so oxygen precipitation is not influenced by nickel. Therefore, nickel had no effect on the subsequent oxygen precipitation, and the amount of oxygen precipitation was the same in the two processes in Fig. 2.

4 Conclusion

We have investigated the impact of copper and nickel on the oxygen precipitation during the IG process in CZ silicon by means of FTIR. In CZ silicon, interstitial copper almost has no effect on the oxygen precipitation, but copper precipitation markedly enhances the oxygen precipitation; however, interstitial nickel and nickel precipitation have no effect on the oxygen precipitation. These results suggest that copper precipitate acts as heterogeneous nucleation sites for the oxygen precipitation and enhances the oxygen precipitation, whereas nickel precipitation fits well with the silicon matrix and has no effect on the oxygen precipitation nucleation.

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快速热处理工艺下直拉单晶硅中铜、镍对氧沉淀的影响*

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摘要: 研究了快速热处理工艺下直拉单晶硅中过渡族金属铜、镍对内吸杂工艺中氧沉淀形成规律的影响. 实验结果表明: 在快速热处理工艺下, 间隙铜对氧沉淀几乎没有影响, 铜沉淀却能显著地促进氧沉淀的形成; 而间隙镍或镍沉淀对氧沉淀的形成都没有影响. 基于实验结果并结合氧沉淀的形核理论, 对金属铜、镍对氧沉淀的影响机理进行了解释.

关键词: 单晶硅; 氧沉淀; Cu; Ni

PACC: 7280C; 6170; 6155F

中图分类号: TN304.1+2 **文献标识码**: A **文章编号**: 0253-4177(2006)03-0413-06

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