Influence of oxygen precipitation on copper precipitation in Czochralski silicon

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The influence of oxygen precipitation on copper precipitation in Czochralski silicon was investigated by means of defect etching, optical microscopy, and Fourier transform infrared spectrometer. It was found that the density, distribution, and morphology of copper precipitation can be influenced by oxygen precipitate sequence significantly. The spherelike copper precipitates uniformly distributed along the whole cross section were generated only in the specimens oxygen precipitation at the very beginning of the heating treatment. While in the specimens, copper precipitation firstly, the large star-like precipitate colonies was generated due to the repeated nucleation mechanism. Additionally, the bulk microdefects (BMDs) density of the latter was higher than the former. The influence of oxygen precipitation nuclei, which was formed during 750 °C for 8 h annealing, on copper precipitation was similar to that of oxygen precipitation, indicated that the initial density and distribution of oxygen precipitation nuclei were the main factors to decided copper precipitation. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4705421]

I. INTRODUCTION

Copper, as one of most important transition metals, has the properties of fast diffusion and noticeable solubility dependence on temperature. Copper precipitation easily occurs when cooling from high temperature. The behavior of copper precipitation in Czochralski silicon (Cz Si) has been widely researched due to its deleterious influence on semiconductor device yield and reliability. It was reported that copper precipitation in crystal silicon noticeably depended not only on doping type[1–3] and cooling rate but also on defects (such as dislocations,[4–6] grain boundaries,[7–9] and stacking faults[10,11]). However, to our knowledge, no reliable data about the impact of oxygen precipitation on copper precipitation currently existing.

Oxygen, as the most important impurity in Cz Si, is inevitably incorporated into the silicon directly from the quartz crucibles during Cz Si growth process.[12,13] During the subsequent processes of devices supersaturated oxygen atoms will agglomerate to form precipitates. Oxygen precipitates and the induced defects are essentially beneficial to internal gettering and improve the yield of integrated circuit (IC) products.[14] Oxygen precipitates also can enhance the mechanical properties of CZ silicon.[15,16]

In view of the significant impact of copper precipitation and oxygen precipitation on IC, it is important to investigate the behavior of copper precipitation and oxygen precipitation in Cz Si. In our previous work, it was found that the copper precipitation remarkably enhanced oxygen precipitation.[17] In this paper, the influence of oxygen precipitation on copper precipitation in Cz Si was investigated by means of defect etching, optical microscopy (OM), and Fourier transform infrared spectrometer (FTIR). On the basis of experiments, it was revealed that the density, distribution, and morphology of copper precipitation could be influenced by oxygen precipitate sequence significantly. And, moreover, the mechanisms underlying these phenomena had been tentatively exploited.

II. EXPERIMENT

The specimens used in this experiment were cut from a P-type Cz silicon ingot with a resistivity of about 10 Ω.cm. The specimens were cut into 2 cm × 2 cm pieces, cleaned with acetone and then chemically polished with CP4. The copper contamination was to immerse the specimen in $CuCl_2$ solution for 5 min, the Cu concentration is 0.5 mol/l which is much higher than 10^{18} cm^{-3}, the corresponding saturation concentration of Cu in silicon at around 1100 °C. The sample with some $CuCl_2$ solution was sent into a quartz tube furnace and annealed at 1100 °C for about 6 min in nitrogen atmosphere. The detailed annealing sequence and Cu contamination process were listed in Table I. After each step of annealing, the samples were usually taken out of the furnace to cool in air with a cooling rate of about 30 K/s. After finishing all the annealing process, the samples were cleaved and etched in Sirtl etchant for 5 min. Finally, OM was applied to observe the cross section of the specimens to determine the density, distribution profile, and morphology of BMDs. The oxygen concentration ($[O_i]$) was measured by FTIR at room temperature.

III. RESULTS

OM investigation reveals that in the specimen A1, the copper precipitate aggregated as a star-like configuration,

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TABLE I. Annealing sequence and copper contamination process.

Specimens	Annealing sequence I	Annealing sequence II	Annealing sequence III
A1	Cu contamination, 1100 °C/6 min		
A2	Cu contamination, 1100 °C/6 min	750 °C/8 h	1050 °C/16 h
A3	750 °C/8 h	1050 °C/16 h	Cu contamination, 1100 °C/6 min
A4	750 °C/8 h	1050 °C/16 h	
A5	750 °C/8 h	Cu contamination, 1100 °C/6 min	

as shown in Fig. 1(a). While for the specimen A2 presented in Fig. 1(b), the copper precipitation aggregated as a star-like configuration and oxygen precipitation exhibited as spherelike. However, in Fig. 2(a), the BMDs exhibited as spherelike and uniformly distributed along the cross section of the specimen A3. Moreover, Fig. 2(b) represents oxygen precipitation exhibited as spherelike and uniformly distributed along the cross section of the specimen A4. With the FTIR investigation, the $[O_i]$ of the specimens A2 and A4 were $0.526 \times 10^{18}\,\mathrm{cm}^{-3}$ and $0.710 \times 10^{18}\,\mathrm{cm}^{-3}$, respectively.

According to the results described above, it is reasonable to deduce that the oxygen precipitation and Cu contamination process sequence can influence the density, distribution and morphology of copper precipitation to a large extent: The large star-like precipitate colonies in A2 and spherelike copper precipitates uniformly distributed in A3 are strongly related to the first precipitation type, namely, copper precipitate or oxygen precipitation. Additionally, the BMDs density of the specimen A2 was higher than A3. As far as the $[O_i]$ is concerned, the copper precipitation remarkably enhanced oxygen precipitation.

Figure 3 shows the OM photograph of the BMDs distribution along the cross section in the specimen A5. Compared with Figs. 1(a), 2(a), and 3, it is reasonable to deduce that the influence of oxygen precipitation nuclei on copper precipitation was similar to that of oxygen precipitation, manifesting that the initial density and distribution of oxygen precipitation nuclei were the main factors to determine the copper precipitation mechanism.

IV. DISCUSSION

Due to the sharp dependence of the solubility of interstitial copper on temperature, these supersaturation coppers diffuse into silicon wafers at high temperature, tend to agglomerate and form copper silicides and generate a lot of interstitial silicon (Si_i) atoms during the subsequent air cooling. The reaction is presented as follows:[18]

$$xSi + 3Cu_i = Cu_3Si + (x-1)Si_i + \delta(\mathrm{stress}), \quad (1)$$

in which δ and Si_i refer to stress and interstitial silicon, respectively. According to the equilibrium phase diagrams of the binary Cu–Si system and the previous results, it was

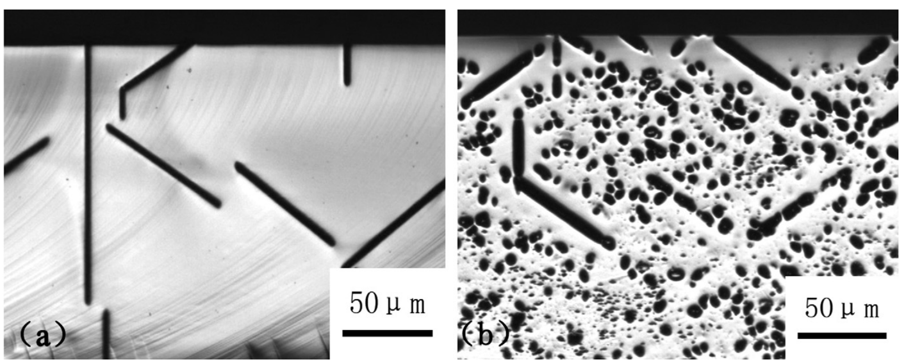

FIG. 1. OM photograph of the BMDs distribution along the cross section in the specimens A1(a) and A2(b).

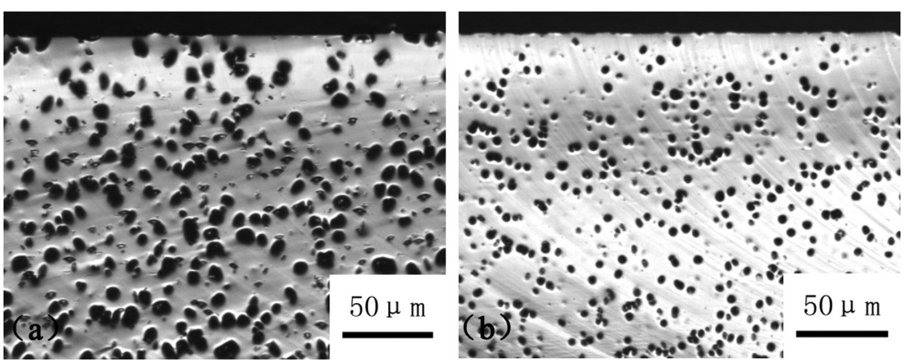

FIG. 2. OM photograph of the BMDs distribution along the cross section in the specimens A3(a) and A4(b).

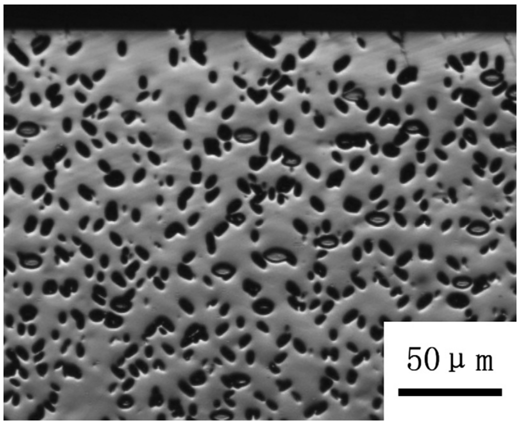

FIG. 3. OM photograph of the BMDs distribution along the cross section in the specimen A5.

assumed that η''-Cu_3Si was formed during copper precipitation. The distinct feature which affects the precipitation behavior of Cu in silicon is closely related to the lattice expansion. The η''-Cu_3Si has a large molecular volume of 0.046 nm^3, approximately 2.3 times as large as that of the silicon, 0.02 nm^3.[19–21] It means once a copper precipitate formed, 1.3 Si_i atom will be emitted to release the compress stress generated around the copper precipitates in the silicon matrix.[22] As mentioned above, it can also be inferred that the nucleation barrier of copper precipitation includes strong compress strain between copper precipitates and silicon matrix due to volume expansion, and electrostatic repulsion between the positively charged copper precipitates and the ionized interstitial copper, and the drive force is the supersaturation of interstitial copper, respectively.

Oxygen is inevitably incorporated into the silicon directly from the quartz crucibles during Cz Si growth process. Considering that the oxygen is incorporated at about 1400 °C, it is easy to understand that the interstitial oxygen is supersaturated in silicon bulk at temperature characteristic of device processing, generally lower than 1200 °C. When specimens are annealed at high temperatures, oxygen atoms diffuse comparably quickly so that oxygen precipitation takes place by the driving force of the supersaturation of oxygen concentration.[23] Generally, the oxygen precipitation process includes two aspects: nucleation and growth of oxygen precipitates. During nucleation of oxygen precipitates, a reaction between the silicon matrix and oxygen occurs as follows:[24]

$$(1+\gamma)\mathrm{Si} + \mathrm{yO_i} + \beta\mathrm{V} = \mathrm{SiO_y} + \gamma\mathrm{Si_i} + \varphi(\mathrm{stress}), \qquad (2)$$

where β, γ, and φ refer to the number of absorbed vacancy, the number of injected self-interstitial, and the relaxed strain, respectively. It should be pointed out that the above equation is bi-directional. During the annealing at a given temperature, the forward reaction leading to the formation of oxygen precipitates is based on the nuclei larger than a temperature-dependent critical size (r_c): While the size of precipitates is smaller than r_c; the backward reaction occurs, resulting in the dissolution of oxygen precipitates. Because the volume of oxygen precipitates (SiO_y) is larger than that of matrix, the strain around the precipitates will arise, which can be partially relieved by absorption of β vacancies or by injection of γ self-interstitials. Additionally, the stress arising from the precipitates impacts not only the precipitate shape but also the r_c for the formation of oxygen precipitates.

As mentioned above, a lot of Si_i atoms would be generated once copper precipitation occurs. If these saturated Si_i atoms could not be annihilated completely, they would form dislocation loops near the generated precipitates, which can serve as the potential nucleation sites for new copper precipitates. This process is also defined as the repeated nucleation process, the copper precipitate colonies repeat their growth on the dislocation loops which formed near the generated precipitate. As shown in Fig. 1(a), when the copper precipitated, a lot of Si_i atoms emitted, leading to the formation of dislocation loops near the generated precipitates, which provided the nucleation sites for new copper precipitates. So the copper precipitation nucleation repeated, leading to the generation of large star-like precipitate colonies.

In the specimen A2, the copper precipitated firstly, the mechanism was similar to specimen A1, so the copper precipitation aggregated as a star-like configuration. A high density dislocations generated by copper precipitation in the specimen A2 could provide heteronucleation sites for the subsequent oxygen precipitates due to much lower nucleation barrier. Furthermore, these dislocations could absorb the Si_i atoms during the oxygen precipitate nucleation, which is beneficial to the formation of oxygen precipitates, as described in Eq. (2).[17] As mentioned above, the copper precipitation remarkably enhanced oxygen precipitation. It means that the density of oxygen precipitate in specimen A2 was higher than specimen A4.

About specimen A3, the oxygen precipitation at the very beginning of the heating treatment, the spherelike BMDs uniformly distributed along the whole cross section as shown in Fig. 2(a). The main reason has been ascribed to the heterogeneous nucleation process of copper precipitation: On the one hand, the large stress around the oxygen precipitation generated, which is beneficial to decrease the nucleation potential barrier, thus the copper precipitation was more prone to nucleate around them; on the other hand, the oxygen precipitation induced secondary defects, dislocation, or stacking fault, which would offer the heteronucleation sites to copper precipitation. Considering the oxygen precipitation mechanism, the oxygen precipitates generated in the bulk of silicon matrix uniformly distribute along the whole cross section during the annealing, 750 °C/8 h + 1050 °C/16 h (Fig. 2(b)). Cu impurity introduced into the bulk of a wafer will not immediately form precipitates but will diffuse back to the surface or trap by the oxygen precipitate. Finally, the copper precipitation complexes generated in the bulk of the samples underwent the annealing at 1100 °C for 6 min and cooling in air, which is sufficient for the copper impurity precipitate. Combing with the analysis mentioned above, it is reasonable to conclude that the copper precipitation also exhibited as spherelike and uniformly distributed along the cross section, which was similar to the distribution of oxygen precipitates (see Fig. 2(b)). And the density of oxygen precipitate in specimen A3 was similar to specimen A4. Then, in comparison with specimens A2 and A3, the density of BMDs in specimen A2 was higher than specimen A3.

For specimen A5, the tendency is nearly the same as specimen A3. It was well-known that 750 °C was the optimum temperature for the oxide precipitates to nucleate. The nuclei of oxygen precipitation also would offer the heteronucleation sites for copper precipitation, so the influence on copper precipitation was similar to oxygen precipitation.

V. CONCLUSION

In this paper, the influence of oxygen precipitation on copper precipitation in Cz Si was studied. By means of defect etching, OM and FTIR, it was found that the large star-like precipitate colonies in the specimen A2 and spherelike copper precipitates uniformly distributed in the specimen A3, were strongly related to the first precipitation type, namely, copper precipitate or oxygen precipitation. Additionally, the BMDs density of the specimen A2 was higher than A3. The influence of oxygen precipitation nuclei, which was formed during 750 °C for 8 h annealing, on copper precipitation was similar to that of oxygen precipitation.

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