Copper precipitation in large-diameter Czochralski silicon

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The behavior of the copper precipitation in the large-diameter Czochralski silicon (Cz–Si) annealed at 1100 °C followed by air cooling or slow cooling was studied by means of scanning infrared microscopy (SIRM), optical microscopy, and surface photovoltage. For the air-cooled specimen, a high density of copper-precipitate colonies with strong contrast could be easily found in the A-defect zone, while in the D-defect zone of the same specimen almost no colonies could be observed through SIRM. However, optical images showed that the higher density of the etching pits induced by the copper-precipitate colonies occurred in the D-defect zone, which indicates that the copper-precipitate colonies in the D-defect zone was below the detection limitation of SIRM. This suggestion was confirmed by minority-carrier diffusion-length mapping, which revealed that the diffusion length of the minority carriers in the D-defect zone was noticeably lower than that in the A-defect zone. As for the slow-cooled specimen, big star-like colonies formed both in the D-defect zone and A-defect zone, but the diffusion length of the minority carriers in the D-defect zone was also lower than that in the A-defect zone. On the basis of experiments, it is suggested that the as-grown vacancies or their related defects in the D-defect zone enhance the nucleation of copper precipitation either under air cooling or under slow cooling, resulting in the lower diffusion length of minority carriers. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1875740]

I. INTRODUCTION

With the development of microelectronic industry, copper may replace aluminum as the main interconnection material, but the cases of copper contamination and its deleteriousness to devises have to be considered. As one of the common transitional metals, copper has the properties of fast diffusion and noticeable solubility dependence on temperature in silicon. Thus, copper precipitation easily occurs in silicon-based devices or materials contaminated with copper after high temperature annealing. It has been considered that copper precipitates may be more deleterious than interstitial copper in silicon because deep band-like-defect states form in the band gap.[1]

In the past decades, the behavior of copper precipitation in silicon has been researched intensively.[2–4] It has been reported that copper precipitation in silicon depends on many factors, including cooling rate,[5–7] doping type,[8,9] doping concentration,[10] dislocations,[11,12] and grain boundaries.[13,14] However, up to now, few papers have been published about the influence of point defects on copper precipitation in silicon.[15] In our recent letter,[15] we have reported that intrinsic point defects have a great effect on copper precipitation in large-diameter Czochrolski (Cz)–Si under air cooling. Nevertheless, there are still many open questions. Whether intrinsic point defects affect copper precipitation in silicon under

slow cooling or not is unknown. How copper precipitates formed in different defect zones influence on their recombination of minority carriers is also unknown.

In this article, we applied scanning infrared microscopy (SIRM) and optical microscopy (OM) to reveal the distribution of copper-precipitate colonies formed in different defect zones, and used surface photovoltage (SPV) to scan the diffusion length of minority carriers in the same specimens. It was found that intrinsic point defects noticeably influenced on copper precipitation not only under air cooling (about 30 K/s) but also under slow cooling (about 0.3 K/s).

II. EXPERIMENT

The specimens used in this experiment were cut from *P*-type, ⟨100⟩-orientation, 8 in. Cz–Si ingot grown in Ar atmosphere. Both the A-defect zone and the D-defect zone, identified by thermal oxidation and selective etching, existed in each specimen. Prior to anneal, the specimens were chemical polished with CP4, cleaned with the Radio Corporation of America process, etched with about 5% HF solution to remove surface oxide and dipped into 0.5 mol/ℓ $CuCl_2$ solution. Then, these specimens were annealed at 1100 °C for 6 min in nitrogen atmosphere followed by air cooling (about 30 K/s) or slow cooling (about 0.3 K/s). Following that, these specimens were chemical polished with CP4 and mechanically polished on both sides. A thickness of about 100 μm on each side was removed.

Copper-precipitate colonies were observed by SIRM with a detection limit of about 60 nm for precipitates.[16] OM combined with Secco etching was applied to determine the

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density and distribution of etching pits induced by copper-precipitate colonies. The diffusion length of minority carriers was measured with SPV.

III. RESULTS

A. Copper precipitation under air cooling

As a convenient and nondestructive tool, SIRM could be used to observe different kinds of precipitates in silicon.[17] Figure 1 shows the SIRM images of the copper-precipitate colonies in the different defect zones of the large-diameter Cz–Si specimen annealed at 1100 °C for 6 min followed by air cooling. From Fig. 1(a), it can be found that the dot copper-precipitate colonies with a density of about 10^8 cm^{-3} formed in the A-defect zone. The largest contrast of those colonies is about 70%, which indicates that the huge stress generated during copper precipitation had not been released. However, almost no copper-precipitate colonies could be observed in the D-defect zone, as shown in Fig. 1(b). It means that copper-precipitate colonies in this zone was too small to be observed with SIRM or no copper-precipitate colonies formed at all. The *P*-band between the A-defect zone and the D-defect zone is also an interesting zone, in which oxide particles generally form during crystal growth.[18] Those as-grown oxide particles as heteronucleation sites may enhance copper precipitation. However, as shown in Fig. 1(c), the density of copper-precipitate colonies in this zone is only about 5×10^6 cm^{-3} and the contrast of those colonies is just about 8%. Both the density and contrast of the observed-colonies in the *P* band are between those in the A-defect zone and in the D-defect zone. This seems to indicate that as-grown oxide particles have no obvious influence on copper precipitation.

OM combined with Secco etching and SPV were carried out to study copper precipitation in the same specimen. A high density of etching pits induced by copper-precipitate colonies was found to exist both in the A-defect zone and the D-defect zone. The density distribution of the etching pits is shown in Fig. 2. It can be observed from Fig. 2 that the density of the etching pits in the D-defect zone is much higher than that in the A-defect zone, indicating a high density of copper-precipitate colonies which were below the detect limit of SIRM formed indeed in the D defect. This observation is consistent with the measure results of SPV, as seen in Fig. 3. The average diffusion length of the minority carriers in the D-defect zone is about 13 μm, while in the A-defect zone the average diffusion length is about 35 μm. Noticeable difference of the diffusion length between these two defect zones implies again that the vacancy-type defects in the D-defect zone enhance the nucleation of copper precipitates but hinder their growth, leading to the formation of the higher density but small size of copper-precipitate colonies.

B. Copper precipitation under slow cooling

It is well accepted that cooling rate has a great influence on copper precipitation. Copper precipitation in the specimen annealed at 1100 °C followed by slow cooling was also studied. Figure 4 displays the typical SIRM image of a
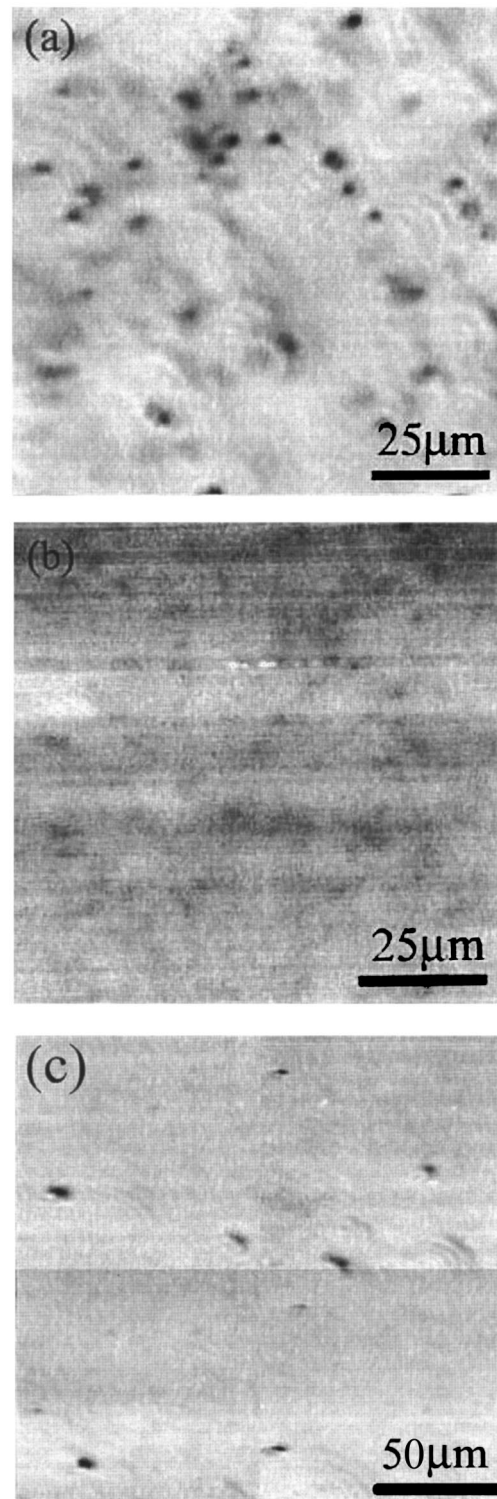

FIG. 1. SIRM images of the copper-precipitate colonies in the large diameter Cz–Si annealed at 1100 °C for 6 min followed by air cooling: (a) in the A-defect zone, (b) in the D-defect zone, and (c) near the boundary between the A-defect zone and the D-defect zone.

copper-precipitate colony formed in the large-diameter Cz–Si under slow cooling. Due to high local stress, large star-like colonies with strong contrast can be easily observed in the whole specimen in spite of different kinds of the as-grown point defects. However, the contrast of the colonies in the D-defect zone is far lower than that of the colonies
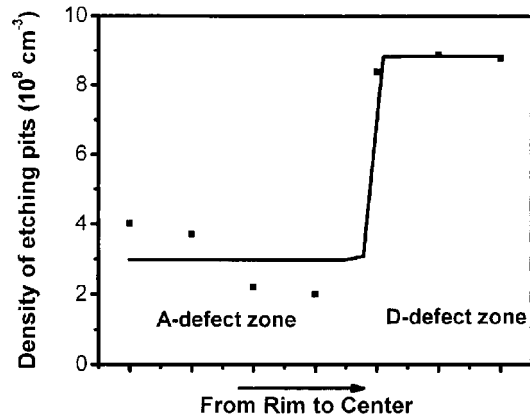
FIG. 2. Density distribution of the Secco etching pits along the radius from rim to center in the large diameter Cz−Si annealed at 1100 °C for 6 min followed by air cooling.

FIG. 4. SIRM image of the copper-precipitate colony in the large diameter Cz−Si annealed at 1100 °C for 6 min followed by slow cooling both in the A-defect zone and the D-defect zone.

formed in the A-defect zone, indicating that under the condition of slow cooling the as-grown vacancies in the D-defect zone can also release part of the stress generated during copper precipitation. Another difference of the colonies formed in the two defect zones is the colony density measured by SIRM. In the D-defect zone, the colony density is about 1.5×10^6 cm^{-3}, while it is about 1×10^6 cm^{-3} in the A-defect zone. In addition, SPV was applied to map the minority carrier diffusion length from the A-defect zone to the D-defect zone in this specimen and the result is shown in Fig. 5. The average diffusion length of the minority carriers in the A-defect zone is about 130 μm, much higher than that in the D-defect zone. These results imply that intrinsic defects also affect copper precipitation despite slow cooling.

IV. DISCUSSION

Due to the quick diffusion and sharp solubility dependence on temperature, the supersaturated copper atoms precipitated during cooling following the annealing at 1100 °C and formed copper silicides. Generally, this kind of silicides was considered as η''-Cu$_3$Si.[3,4] Because of the great volume difference between η''-Cu^{3}Si and silicon matrix, a lot of interstitial silicon atoms and the large compress stress as the

main barrier for copper precipitation were generated during precipitation. As a result, those precipitates could be easily observed by SIRM, as seen in Figs. 1 and 4. When the specimen cooled in air, a high density of the dot precipitate colonies formed (Fig. 1). However, if the cooling rate was small, large star-like precipitate colonies were generated (Fig. 4). The mechanism of the influence of cooling rate on copper precipitation in Cz−Si has been reported by Nes.[19,20] With the reaction going on, the supersaturated interstitial silicon atoms formed dislocation loops near the initial precipitates, which became the nucleation sites for copper precipitation. Thus, each colony in Fig. 1 or in Fig. 4 is composed of many tiny precipitates and the density of colonies depends on the density of the initial precipitates.

According to the model put forward by Falster and Voronkov,[18] vacancy-oxygen complexes (V$_2$O) and voids are considered as the main intrinsic defects to exist in the D-defect zone. These vacancy-related defects may offer the heteronucleation sites so as to enhance copper precipitation. Generally, the density of voids in the large-diameter Czo-
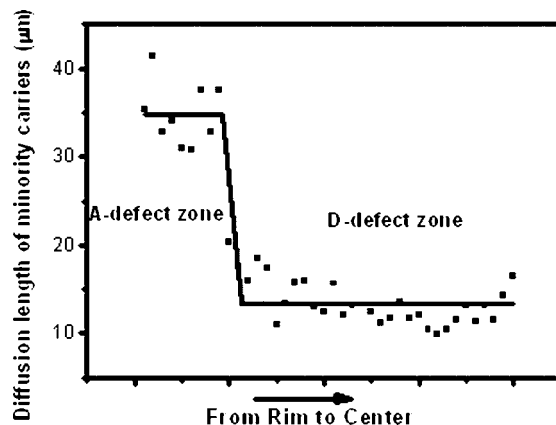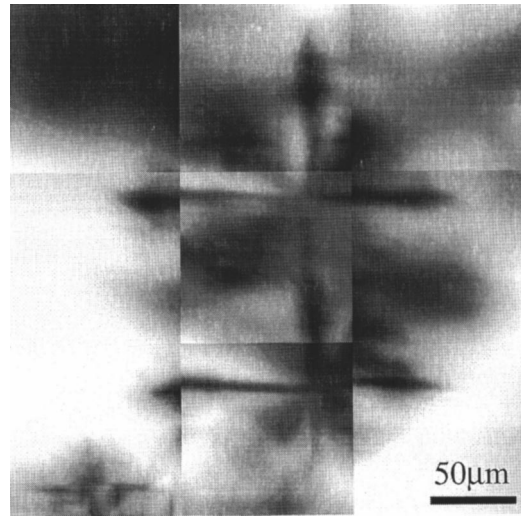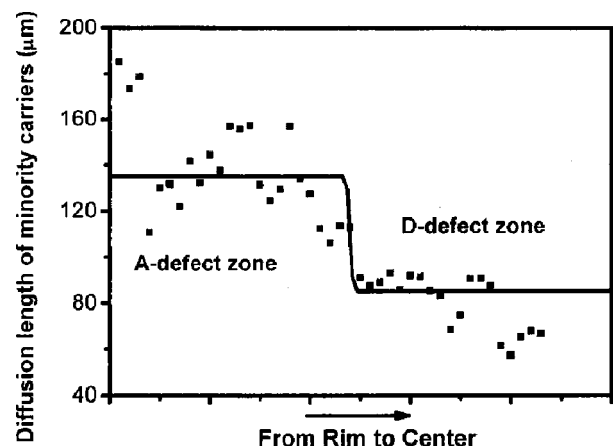

FIG. 3. Diffusion length distribution of the minority carriers along the radius from rim to center in the large diameter Cz−Si annealed at 1100 °C for 6 min followed by air cooling.

FIG. 5. Diffusion length distribution of the minority carriers along the radius from rim to center in the large diameter Cz−Si annealed at 1100 °C for 6 min followed by slow cooling.

chralski silicon is only about 10^6 cm^{-3}, which is much lower than the density of copper precipitates, so that they are not the main nucleation sites of copper precipitates in the air-cooled specimen. However, vacancy-oxygen complexes (V_2O) and part of voids may be dissolved to generate vacancy by the annealing at 1100 °C.[18,21] During the nucleation of copper precipitates, the vacancies may react with the interstitial silicon atoms generated by copper precipitation to release the stress between copper precipitates and silicon matrix, and thus enhance the nucleation of copper precipitates in spite of different cooling rates. Consequently, the density of the initial precipitates in the D-defect zone is higher than that in the A-defect zone where interstitial-silicon-related defects exist predominately, as seen in Fig. 2. Moreover, the sizes of the copper precipitate colonies in the D-defect zone, especially in the air-cooled specimen, is smaller, so that they are below the limitation of SIRM and cannot be observed by SIRM [Fig. 1(b)]. Although internal gettering processes based on oxygen precipitation have been widely applied in microelectronic industry, the as-grown oxygen precipitates in the *P* band could not grow up to induce dislocation or other defects as the effective gettering sites during the annealing at 1100 °C only for 6 min, resulting in almost no influence on copper precipitation [Fig. 1(c)]. In addition, some of the stress generated by copper precipitation has been released in the D-defect zone despite different cooling rates, resulting in the low contrast of colonies in the D-defect zone.

The electrical properties of the silicon contaminated with copper have been widely investigated by many groups although the recombination mechanism of copper precipitates is still unclear.[4] It has been reported that the band-like states induced by copper precipitates appear in the band gap, resulting in that copper precipitates become the effective killers for minority carriers in silicon.[1] Furthermore, it is believed that the position and width of the band depend on cooling rate. According to the Shockley–Read–Hall statistics, it can be deduced that the square of the minority carrier diffusion length is inverse ratio to the density of recombination sites. No matter what kind of cooling rate, the density of the colonies in the D-defect zone is always much higher than that in the A-defect zone. Consequently, the minority carrier diffusion length in the D-defect zone is lower (Figs. 3 and 5).

V. CONCLUSION

In this article, the copper precipitation in the large-diameter Cz−Si annealed at 1100 °C followed by air cooling or slow cooling was investigated. It was found that a high density of the copper precipitate colonies with less contrast formed in the D-defect zone in spite of different cooling rates, resulting in the lower diffusion length of minority carriers. The as-grown oxygen precipitates in the *P* band were found to have no influence on the copper precipitation. On the basis of experimental facts, it was suggested that the as-grown vacancy-related defects in the D-defect zone annihilated the interstitial silicon atoms and released some of the compress stress generated by copper precipitation at the beginning of the nucleation. As a result, the initial nucleation sites in the D-defect zone were increased, leading to the lower diffusion length despite different cooling ways.

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