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Formation Mechanism of the Micro Precipitates Causing Oxidation Induced Stacking Faults in the Czochralski Silicon Crystal.

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ABSTRACT

During the growth of macroscopically dislocation–free Czochralski silicon crystal, micro precipitates causing stacking faults in the silicon wafer during the oxidation are formed Thermal history the crystals acquire during the growth process is known to be a key factor determining the nucleation of this micro precipitates. In this article, various mechanisms suggested on the formation of microdefects in the silicon crystal are reviewed to secure the nucleation mechanism of the micro precipitates causing OSF whose pattern is normally ring or annular in CZ silicon crytal. B–defects which are known as vacancy clustering are considered to be the heterogeneous nucleation sites for the micro precipitates causing OSF in the CZ silicon crystals.

1. INTODUCTION

In the silicon crystals, stacking faults are known to be formed on the surface during the oxidation process. The nucleation sites will be scratches or some grown–in micro precipitates [1]. The micro precipitates causing the OSF nucleation is known to be formed depending on the thermal history of the crystal during pulling stage [2,3]. So far, various microdefects have been discovered in the silicon crystal, such as A–, B–, C– and D–type [2]. One of them is believed to have close relationship with the nucleation of OSF.

In the previous investigation, as can be seen in Fig. 1 and 2, it was confirmed that most OSF which are thought to be caused by the grown–in micro precipitates in CZ silicon crystal is Ring Pattern, i.e., higher density of the OSF is present near the periphery of the silicon wafers.

Fig. 1. X–ray topograph showing the presence of the ring–patternd OSF in the boron–doped silicon crystal which was oxidized at 1100℃ for 1 hr.

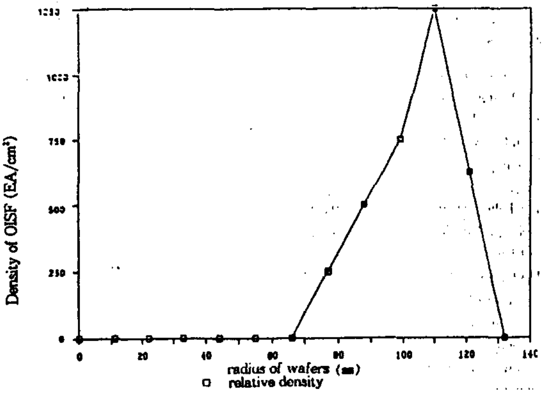

Fig. 2. Radial distribution of OSF density on the oxidized surface of silicon wafter [4].

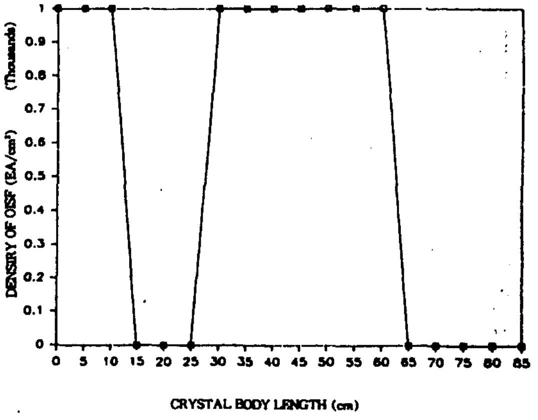

Fig. 4. Typical axial OSF density profile of the boron–doped CZ silicon crystal [4].

In the other area of the silicon wafer surface, central area or area just adjacent to the periphery of the silicon crystal, OSF is hardly observed. This Ring–Patterned OSF is found to depend upon the thermal history of the silicon crystal [4]. In phosphorous doped crystal, high density of OSF is observed to be present in the form of ring near the tail part of the crystal as can be seen in the Fig. 3. However, in the doped crystal, Ring–patterned OSF is hardly observed near the tail part of the CZ silicon crystals as can be seen in Fig. 4.

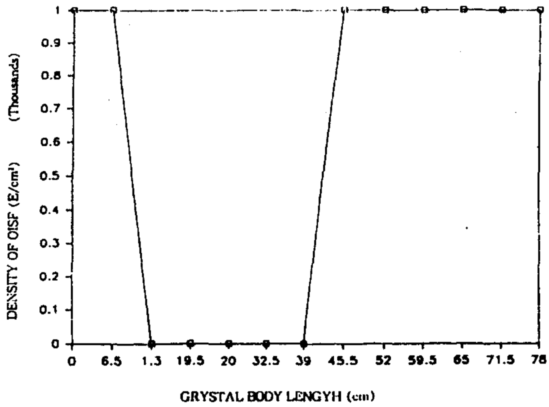

Fig. 3. Typical axial OSF density profile of the phosphorus–doped CZ silicon crystal [4].

Interestingly, it was observed that in the crystal where high density of surface OSF is present, high density of bulk OSF is present also as can be seen in Fig. 5. Various methods were known to be effective in the elimination of the OSF including TCE gas treatment [5]. However, silicon wafers having high density of surface OSF will be avoided by device makers because bulk OSF located beneath the surface might act as a source causing current leakage. For the VLSI purpose, silicon wafers having OSF density lower than 100/cm are anticipated [6]. In this article, various models of micro defects formation mechanism will be critically reviewed to find out a new mechanism describing the nucleation of the OSF.

2. MODELS OF MICRODEFECTS FORMATION MECHANISM

2.1. K.V. Ravi et al. [7]

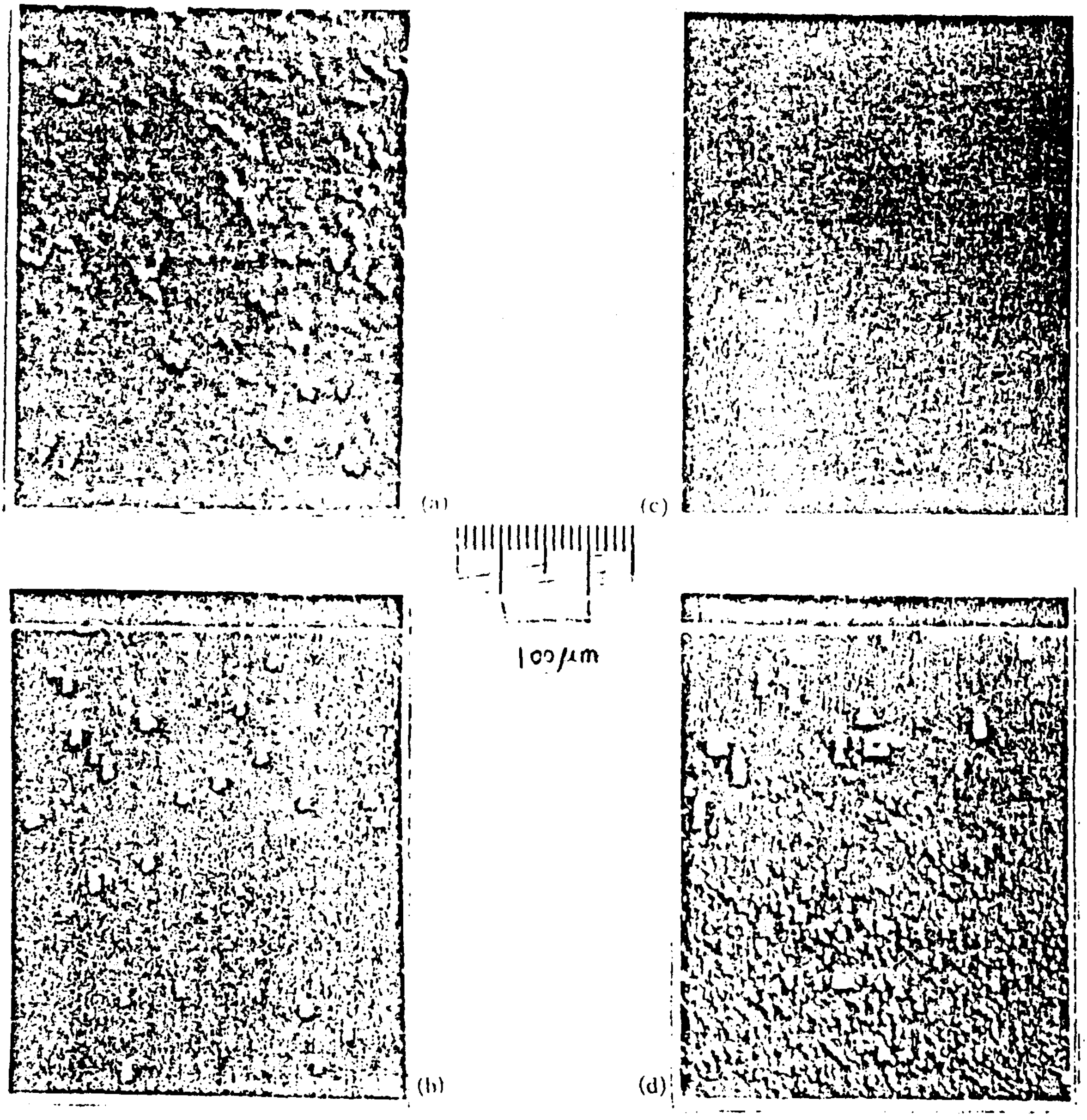

Fig. 5. Photographs showing OSF in the oxidized CZ silicon crystals doped with phosphorus. The orientation is (100). Samples are taken near the tail end of the crystal where high density of OSF is usually present. (a) On the surface of the wafer which was wet oxidized for 100 min. at 1100℃. (b) Angle lapped bulk near the surface of the wafer which was oxidized same as (a). (c) On the surface of the wafer which was wet oxidized for 100 min. at 1150℃. (d) Angle lapped bulk near the surface of the wafer which was oxidized same as (c).

It was demonstrated that fault nucleation occurs by the collapse of excess interstitials into Frank loops bounded by a/3(111)−type dislocation. The nucleation of faulted loops is governed by the local supersaturation of vacancies which promote the establishment of a local supersaturation of interstitials and hence the condensation of the interstitials into Frank loops(see Fig. 6). The excess vacancies frozen into the crystal from the melt will provide the site for the oxygen atoms to make the vacancy −oxygen complex during the oxidation process. If the concentration of oxygen exceeds the equilibrium concentration at that temperature, they will precipitate into a Frank disk.

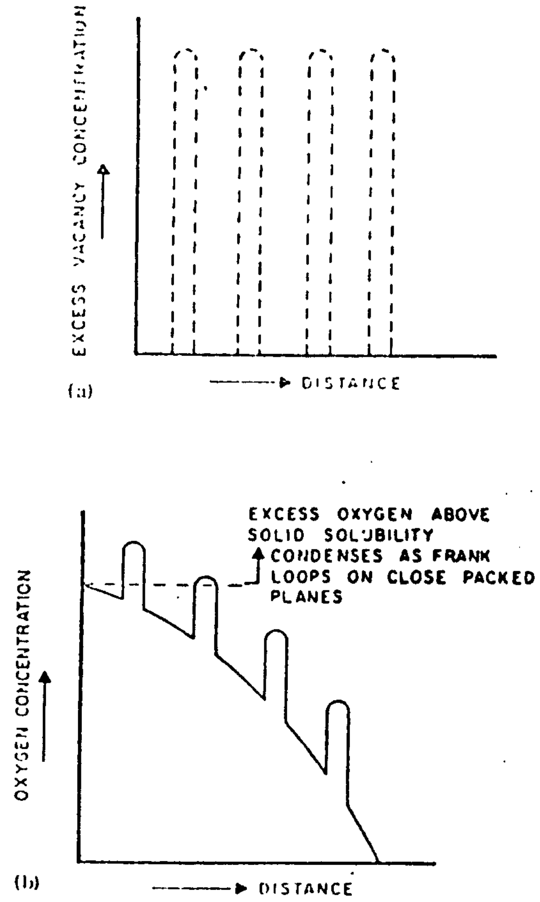

Fig. 6. Schematic of the Ravi's mechanism of heterogeneous nucleation of Frank loops. [7].

2.2. A.J.R. de KOCK et al. [8]

Employing decoration and X−ray topography, they found the fact that doping with donors and acceptors gives different result in the formation of the micro defects: Donors (Sb, concentration$>10^{17}/cm^3$) suppresses the formation of A swirl defects and doping with acceptors (concentration$>10^{17}/cm^3$) eliminates the formation of B and C swirl defects. They defined A−defect as a interstitial type dislocation loop and B−type as defect having vacancy type strain field. In their investigation, annular region full B defects is observed in the crystal doped with Sb(concentration$>8\times10^{17}/cm^3$).

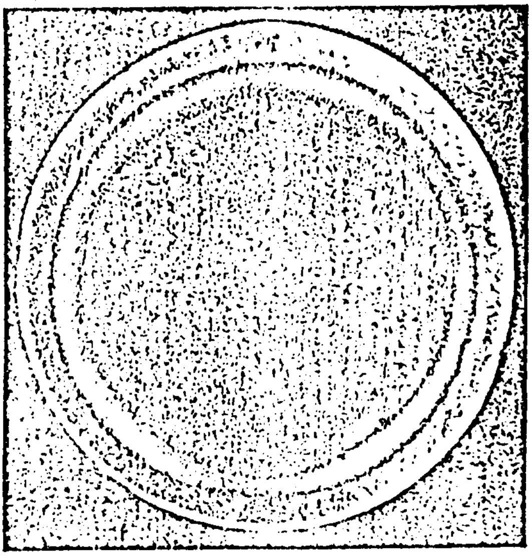

Fig. 7. Swirl defects in Sb−doped CZ silicon (Growth rate is 2mm/min, [Sb]$=8\times 10cm^3$). B defects present in an annular region [8].

(see Fig. 7). From these findings, they proposed following mechanism.

Recombination:

$$\mathrm{I}(-)+\mathrm{V}(+)=\mathrm{Si(subst.)} \qquad (1)$$

complex Foramtion:

$$\mathrm{I}(-)+\mathrm{Sb}(+)=\mathrm{Sb}-\mathrm{I} \qquad (2)$$

$$\mathrm{V}(+)+\mathrm{B}(-)=\mathrm{V}-\mathrm{B} \qquad (3)$$

In antimony doped crystals, reaction (2) prevents the condensation of self−interstitials. However reaction (1) will proceed until the interstitial is available. Consequently, the concentration of vacancies available for condensation increases. This can explain the relative high concentration of B and C defects in N−type silicon crystals. Likewise, in boron doped crystal, high concentration of a defect is observed to be present. They attributed micro defects formation to complex formation due to coulomb forces between dopants and charged thermal point defects.

2.3. T. Abe et al. [9]

Using FZ silicon crystal, they confirmed that A−defect is composed of self−interstitials and D−defect is composed of vacancies. For the generation mechanism of these two defects, they employed the stresses: conpressive stress and tensile stress in the growing crystal for A−defects and−defects respectively. They concluded that A−defects cause OSF during oxidation and D−defects can degrade the dielectric breakdown of the gate oxide. X−ray topograph after Cu decoration of a crystal with A−and D−defect is shown in Fig. 8

2.4. K.Wade et al. [10]

Wade et al. confirmed that two kind of oxide micro precipitates are present in as−grwon CZ silicon. The larger one has the diagonal length of 500 to 2600 Å and the density is 10^5 to 10^7/cm^3. They observed that their density is higher near the crystal periphery and monotonically decrease along the growth direction. The nucleation temperature is determined to be about 1000 to 1250℃. These large precipitates will provide the nucleation sites for the OSF during the oxidation. The radial and axial distribution of oxide precipitates in as−grown crystal is shown in Fig. 9.

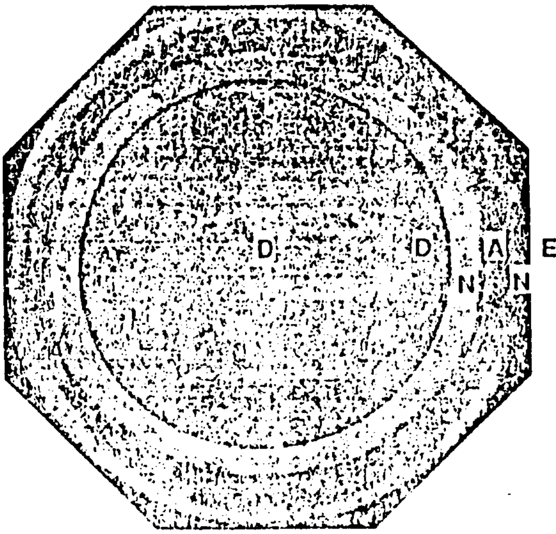

Fig. 8. X−ray topograph after Cu decoration of a crystal with A− and D−defects [9]. N in the picture represents the nutral region.

3. DISCUSSION

3.1. Possibility of A−Defect as Nucleation Centers for OSF

It is well known that the A−defects present in the as−grown silicon crystal is a perfect dislocation loop and the Burgers vector is a/2

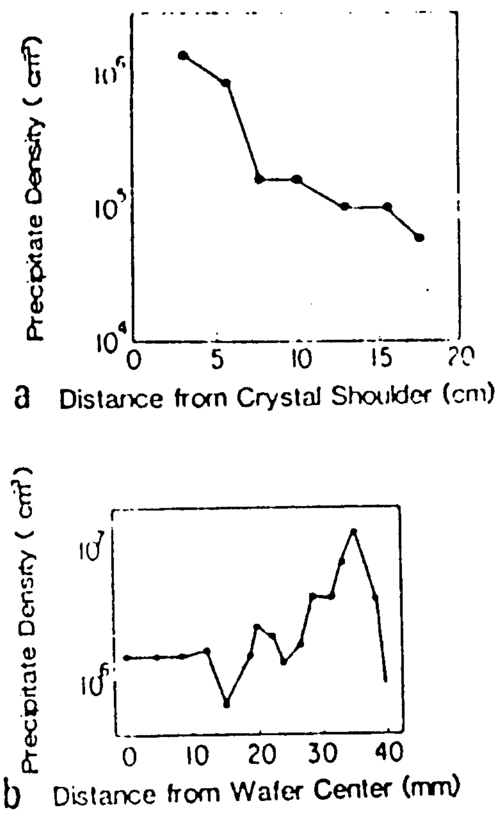

Fig. 9. Radial and axial distribution of oxide precipitates in as−grown crystal. (a) Radial distribution and (b) axial distribution [10].

(110) lying on the {111} planes, If this A defect is the nucleus of the OSF, then it needs to be decomposed into two partial a sessile Frank and a glissile Shockly by following reaction.

$$a/2(110) \Rightarrow a/3(111) + a/6(112) \tag{4}$$

Although it is possible to observe this kind of reaction taking place in other materials, it has not been observed in silicon crystal so far [11]. In addition to that, forming stacking fault through dislocation reaction as above, strong driving force will be necessary because of the stacking fault energy which is not low in silicon crystal. Thus, although T. Abe et al. depicted that A−defects can act as strong centers for the nucleation of OSF in silicon crystals, theoretically it is not easy to be happened. At this point, de Kock's idea is worth to be noted. De Kock suggested that phosphorous will suppress the formation of A−defects. In his model, density of A−defect is lower in n−doped silicon crystal than in the p−doped crystal. In reality, the OSF density is higher in the n−doped silicon crystal than in p−doped silicon crystal. Thus, in CZ silicon crystals, contrary to the idea of Abe et al., A−defects are not considered to act as strong centers for the nucleation of OSF.

3.2. Possibilty of B−Defect as Nucleation Center for OSF

As can be seen in Fig. 7, de Kock et al. confirmed the presence of B−defects in an annular region of the CZ silicon crystal. They identified that these B−defects have vacancy type strain field aronud them. As can be seen in Fig. 1, most OSF in the CZ silicon crytal is in the form of ring, which is quite similar in shape to the B−defects region in de kock's observation. Also, as depicted by do kock et al., boron suppresses the formation of these B−defects [8]. Since the density of OSF in n−doped silicon crystal is higher than in p−doped silicon crystal, possibility of b−defects to affect the nucleation of OSF in CZ silicon crystal seems to be higher than A−defects has. Furthermore, accoding to Ravi's model, vacancy can provide the site for the nucleation of OSF in combination with oxygen during oxidation. However, in Wada's investigation, some micro precipitates already present in the silicon crystal are observed. Being quite similar to the ring patterned OSF in the CZ silicon crystal, the radial density profile of the micro preciptitates in CZ silicon crystal, the radial density profile of the micro precipitates in CZ silicon crystal, the radial density profile of the micro precipitates in CZ silicon crystal has annular pattern. According to Wada, these micro precipitates are considered to be nucleated through a heterogeneous nucleation mechanism.

Combining Wada' and Ravi's ideas results in the following possible mechanism for the nucleation of the OSF in the silicon crystal. During the crystal growth process, vacancy will be clustered to form B−defects. As the temperature lowers during cooling, below about 1250'C, oxide will be formed in the center of these B−defects. In other words, these B−defects act as nucleation centers for the micro precipitates. During the oxidation treatment, these oxides will grow to generate intersititals, which will result in the stacking fault, OSF. Thus, the vacancy clusters, probably B−defects in the CZ silicon crystal strongly affect the nucleation of OSF.

3.3. Interpretation of the OSF Observation with New Model

1) At first, the denstiy of OSF in the central region is quite negligible (as in Fig. 1 and 2): During the crystal growth, the density of vacancy and interstitials will be high enough in the solid part just adjacent to the liquid solid interface. During the cooling period of the crystal, these excess point defects will be recombined to be annihilated if the cooling rate is low enough. This will occur vigorously in the central area of the silicon ingot because the cooling rate seems to be lowest there. Because of lack of excess vacancy, B−defects will not be formed so that the Wada's micro precipitates can not find heterogeneous nucleation sites during further cooling period. The absence of the OSF in the peripheral area of the silicon crystal seems to be due to the out diffusion of most point defects and oxygen which are necessary for the formation of micro precipitates.

2) In the part near the tail end of the silicon crystal doped with phosphorous, higher density of OSF is frequently observed. However, in the boron doped crystal, OSF is hardly observed in the same area (see Fig. 3 and Fig. 4): As depicted by de kock et al., boron will consume the vacancy by the reaction (3) so the B−defects will be scarcely formed just after solidification. In the phophorous doped silicon crystals, however, vacancy concentration will be high enough by the reaction (2). This high concentration of the vacancy will be clustered to be formed as B−defects which eventually cause the nucleation of the OSF in the silicon crystal.

Upon this model, two kinds of method avoiding the formation of OSF in the CZ silicon crystal are considered to be effective:

1) Cool down the crystal as slow as possible in the puller after solidification so that most vacancy can recombine with interstitials. Then oxide can not find the place to be nucleated heterogeneously.

2) Boron doping, if possible, with be helpful to avoid the OSF formation as mentioned above.

3) Lower the concentration of oxygen as low as possible so that vacany−oxygen complexes can not be grown to micro precipitates bigger than critical size.

4. CONCLUSIONS

1) B−defects, vacancy clusters, will provide heterogeneous nucleation sites for the oxide to be formed as micro precipitates, which will act as nuclei for the OSF during oxidation.

2) They will be critical cooling rate below which B−defects can not formed during the crystal growth process.

3) Slow cooling and boron doping will be beneficial to avoid the nucleation of OSF.

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