CHARACTERIZATION OF SWIRL DEFECTS IN FLOATING-ZONE SILICON CRYSTALS

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The swirl defects in dislocation-free silicon crystals grown in argon atmosphere by the floating-zone method have been analysed by transmission electron microscopy. The 2 types of swirl defects consist of: (a) perfect dislocation loops for the type A swirl defect and (b) coherent or semicoherent precipitates for the type B swirl defects. Since both vacancy and interstitial dislocation loops are observed in the type A swirl defects it is concluded that their formation cannot adequately be described by previously developed nucleation models which were based on vacancy condensation only. It is possible that the aggregation of silicon self-interstitials has to be taken into account. It is also concluded from the observation of precipitates in the type B swirl defects that impurities may play an important role in determining the nature of the swirl defects.

1. Introduction

A striated distribution of microdefects usually designated as “swirls” is a most common defect structure in high purity float zone dislocation free silicon crystals. Several investigations on device failures [1–3] in silicon semiconductor devices have correlated swirl defects with device failure and shown that these defects may become electrically active during processing of silicon wafers. Thus, with the present needs for improved yields and device performances it appears important to understand their nature and origin in order to eventually define the conditions for growing swirl free silicon crystals [1,4].

In a recent detailed investigation [1,4] it has been shown through etch pit experiments and X-ray transmission topographic observations that 2 types of swirl defects are present in the swirl pattern. The “A Type” defects are found in the central region of the crystal with a maximum concentration halfway from the crystal axis. The “B Type” defects are distributed throughout the crystal. The long range strain field of both types of swirl defects is presumably small since they do not produce visible contrast features in the standard X-ray transmission topographs. An often used technique to reveal these defects is X-ray topography combined with a decoration technique in which a metallic element (copper or lithium) is diffused into the crystal. The required diffusion temperature for copper is about 950°C and for lithium ≥400°C. The X-ray topographs of copper decorated crystals indicate that both A and B defects produce visible features on the X-ray topographs, whereas in the lithium-decorated crystals only the A defects are revealed [1,4]. The observations not only indicated that the 2 defect types are structurally different but also revealed their distribution. The major drawback of these decoration techniques is that the original defect is transformed by the presence of the metallic impurity atmosphere and the formation of precipitates on the swirl defects. Further, on the X-ray topographs, the decorated defects give rise to a strain contrast which does not reveal the nature of the defects. Consequently, the ambiguities introduced by this technique make it difficult to propose a model for the defect formation. Recently these difficulties were overcome by use of transmission electron microscopy [5,6] (hereafter designated as TEM). In these studies only the A type defect has been detected and associated with dislocation loops. In the present paper a TEM analysis of both A and B type swirl defects is given. The character of these defects is established.

2. Experimental

Dislocation free pedestal pulled (111) silicon crystals were used for the present experiments. These crystals were the same as those used by one of the authors in a detailed investigation of swirl defects [1]. The crystals were grown in argon atmosphere with a pulling rate of 3 mm/min and a rotation rate of 30 rpm. These growth conditions produce an A type defect concentration of \( \approx 10^6 \text{ cm}^{-3} \), while the B defect concentration amounts to \( 10^7 \text{ cm}^{-3} \). No intentional doping of the crystal was done and the crystal resistivity was \( \approx 1000 \text{ \Omega cm} \). The oxygen concentration in these crystals was lower than \( 3 \times 10^{15} \text{ cm}^{-3} \) as was established by infrared-absorption spectroscopy. From precision lattice parameter measurements and annealing studies the carbon concentration was found [7] to be between 2 and \( 4 \times 10^{16} \text{ cm}^{-3} \). Metallic impurities were not detected by mass spectroscopy indicating their concentration to be a few ppb or less. However, from neutron activation analysis measurements the copper and gold concentration were respectively found to be: \( 10^{14} \leq C_{\text{Cu}} \leq 3 \times 10^{14} \text{ atoms/cm}^3 \) and \( C_{\text{Au}} < 10^{12} \text{ atoms/cm}^3 \). The minority carrier lifetime of the material studied was 200 to 250 μsec.

Wafers (0.012 cm thick) with (111) and (112) surfaces were prepared from the crystal by standard cutting and lapping techniques. The surface of the wafers was Syton polished to remove 0.0025 cm from the surfaces and chemically polished with a nonpreferential etch to remove any damage left by the Syton polishing. A short etching (15 to 30 sec) in a Siril etch solution at 15 °C was used to delineate the swirl defects. This procedure has been shown [8] to adequately reveal the presence of a defect below the surface without removing it. Small discs (3 mm in diameter)...

Fig. 1. (A) Optical micrograph of a Siril etched (111) surface. Part of the swirl pattern is visible and the 2 types of swirl defects are denoted by A and B. (B) TEM micrograph (bright field) of a type A swirl defect corresponding to the etch features shown in A of fig. 1A. (C) and (D) TEM micrographs (bright field) of type B₁ and B₂ swirl defects corresponding to the etch features shown in B of fig. 1A.
in the swirl defect region of the crystal were then punched by ultrasonic cutting. The discs were thinned to a final thickness of 1.5 to 2 μm by chemical etching in a nonpreferential etch solution. The swirl defects near the surfaces of the TEM samples are then located by optical microscopy and an electron microscope grid is glued to the sample to record their exact position. The samples were examined in a transmission electron microscope operated at 200 keV. The copper grid on the specimen surface which appeared opaque on the microscope screen was used to relocate rapidly the swirl defects recorded in the optical micrographs. Standard 2 beam dynamical diffraction conditions and quasi-kinematical conditions [9] were used to image the defects. In addition, stereo-electron micrographs were taken to ascertain the geometry of the defects.

3. Results

Three types of swirl defects were observed by TEM underneath the etch features although only 2 different types of etch features are revealed on the optical micrographs of the etched surface. Fig. 1 shows an optical micrograph of the Sirtl etched surface along with TEM micrographs of the 3 types of crystallographic defects observed in the samples. The large etch hillocks (A) in fig. 1A correspond to the defect shown in fig. 1B and the smaller hillocks (B) in fig. 1A correspond to the defects shown in figs. 1C and 1D. These 3 types of defects which have been differentiated on the basis of their size differences and crystallographic nature are designated hereafter as type A, B₁ and B₂ defects.

3.1. Type A swirl defect

The type A swirl defect consists of a large dislocation loop (size 1 to 3 μm) or of a cluster of dislocation loops which are preferentially elongated along the ⟨110⟩ directions. In general, these dislocation loops are lying on ⟨111⟩ planes. Three examples of “A” defects are shown in fig. 2. In addition, the dislocations forming the loops are decorated by coherent or semi-coherent precipitates which give rise to a large strain contrast under 2 beam dynamical imaging conditions (see fig. 2). The Burgers vector analysis of the dislocation loops was complicated by the presence of these
Fig. 3. TEM micrographs (bright field) of a type A swirl defect imaged under various 2 beam Bragg diffraction conditions. The image plane is (111) in figs. 3A and 3B; (011) in figs. 3G and 3H; (110) in figs. 3C and 3D; and (101) in figs. 3E and 3F. The Bragg deviation parameter is positive for all the micrographs.
precipitates, however, undecorated parts of the dislocation loop were analyzed and the Burgers vector of the loops identified as \( b = \frac{1}{2}a \langle 111 \rangle \) inclined at 35° 26' with respect to the dislocation loop planes. All the dislocation loops analyzed were found to be perfect loops. The intrinsic or extrinsic character of the loops was determined by the Burgers vector method of Maher et al. [10]. The series of micrographs (printed emulsion side down) in fig. 3 allows the determination of the loop character; the Bragg deviation parameter, \( s \), for each of these micrographs was set positive. From stereomicrograph pairs, this A defect is found to contain 3 dislocation loops labeled \( L_1 \), \( L_2 \) and \( L_3 \) (fig. 3A). The unit vectors \( n \) normal to the loop plane for defects \( L_1 \), \( L_2 \) and \( L_3 \) are found to be respectively, 111, 111 and 111. The dislocation loop \( L_1 \) becomes invisible for the Bragg reflection \( g = \pm \langle 220 \rangle \) (see figs. 3C and 3D), thus its Burgers vector is \( b = \pm \frac{1}{2}a \langle 110 \rangle \). From the micrographs 3A and 3B the sign of \((g \cdot b) \cdot s \) is obtained as positive for \( g = \langle 022 \rangle \) thus, \( b = \frac{1}{2}a \langle 110 \rangle \) and the loop \( L_1 \) is of vacancy type since \( n \cdot b \) is negative. The micrographs in figs. 3E and 3F indicate that for \( g = \pm \langle 040 \rangle \) only the precipitates are visible on the image and that no inside or outside contrast is observed for the dislocation loop \( L_2 \). Thus, the Burgers vector of this loop is \( b = \pm \frac{1}{2}a \langle 101 \rangle \). From the micrograph in figs. 3G and 3H the sign of \((g \cdot b) \cdot s \) is found positive for \( g = \langle 400 \rangle \). Thus, \( b = \frac{1}{2}a \langle 101 \rangle \) and

Fig. 4. TEM micrographs (bright field) of a type B₁ swirl defect imaged under various 2 beams Bragg diffraction conditions. The image plane is (111).
the loop $L_2$ is of interstitial type since $\mathbf{u} \cdot \mathbf{b} > 0$. A similar analysis for loop $L_3$ shows that its Burgers vector is $\mathbf{b} = \frac{1}{2} \mathbf{a} [101]$ and that it also is an interstitial loop. The decorating precipitates on the dislocations have an anisotropic strain field as is noticed in figs. 3A and 3C. Their strain contrast is minimum for the Bragg reflection $g = \pm [022]$ indicating that the main component of their strain field is along a $(110)$ or $(111)$ direction.

### 3.2. Type $B_1$ swirl defect

The $B_1$ swirl defects shown in fig. 4 are formed by semicoherent or coherent precipitates. The shapes of these precipitates observed under dark field weak beam imaging conditions (fig. 4D) are variable and their sizes range from 600 Å to 800 Å. All these precipitates exhibit an anisotropic strain field; as seen in fig. 4C the main component of this strain field is along a $(110)$ or $(111)$ direction. The intrinsic or extrinsic character of these defects could not be determined.

### 3.3. Type $B_2$ swirl defect

The $B_2$ swirl defects shown in fig. 5 consist of small (500 to 700 Å) semicoherent or coherent precipitates. The line of no contrast in the precipitate images for all Bragg reflections shown in fig. 5 is perpendicular to the Bragg vector; thus, these defects have a spherical strain field. The extrinsic character of these defects was obtained for a defect close to the surface using the Ashby—Brown analysis [11]. Assuming that the matrix was elastically isotropic, the $B_2$ swirl defects are found to have an extrinsic character. The density of $B_2$ defects was found to be smaller than the $B_1$ defect density by an order of magnitude (15 $B_1$ and $B_2$ defects were analyzed).

### 4. Discussion

The origin of the swirl defects has been the subject of several investigations [1,12,13]. Based on various experimental observations it was concluded that they should be composed of vacancy aggregates [1,13].

A more detailed model of the swirl defect formation [14] was based on the observation that the 2 types of swirl defects appeared at different temper-
atures. The B type defects were found to form during the crystal growth at temperature close to the melting point (1420 °C); they were thought to consist of vacancy clusters with a spherical strain field formed by vacancy condensation on vacancy-oxygen complexes. On the other hand, the larger A type defects which appeared at lower temperatures (≤ 1050 °C) were attributed to large vacancy loops originating from the collapse of B type defects.

The results described in section 3 do not appear to confirm this simple model. The existence of both vacancy and interstitial dislocation loops (of the A type defects analyzed were of interstitial type and 1 of vacancy type) and precipitates in these crystals suggest that the defect formation process is indeed more complex. It is presently difficult to single out a mechanism which would explain the formation of both vacancy and interstitial swirl defects. Thus, this discussion has been limited to a survey of possible mechanisms which could account for the experimental observations.

The existence of vacancy type swirl defects which was established in this work and other investigations [6] can be accounted for by the model of De Kock [1]. The A type defects analyzed by Bernewitz et al. [5] and Grienauer et al. [6] were reported to consist of large dislocation loops (> 3 μm); surrounded by smaller vacancy loops (100 – 300 Å). However, these authors did not report on the character of the largest dislocation loops which composed most of the A type defects thus leaving open many questions as to their nature.

The above-mentioned model does not account for the formation of the observed extrinsic loops. Two different mechanisms for their formation are considered. The present results show that impurity precipitation at both A and B type defects takes place. It is well known that extrinsic loops can be generated from a precipitate by a loop punching mechanism. The impurity analysis of the crystal investigated shows that the main residual impurities are carbon (2 – 4 × 10^{16} cm^{-3}), oxygen (≤ 3 × 10^{15} cm^{-3}) and copper (∼ 10^{14} cm^{-3}). If precipitation of oxygen or carbon on, e.g., the B-clusters takes place at temperatures around 1050 °C this process would allow for the emission of interstitial-type dislocation loops from the precipitates to relieve local stresses caused by the difference in thermal expansion coefficient between the precipitate and silicon. The loops, after unfaulting, may grow to large dimensions by climb and glide due to thermally induced stresses in the crystal, thus producing the extrinsic A type defects. Regarding the concentration of copper present and its solubility in silicon, precipitation of this impurity at temperatures around 1050 °C can be excluded. However, copper precipitation at much lower temperatures on the A and B type defects is likely to occur and thus could explain their decorated appearance.

Recent silicon growth experiments [15] have shown that fast diffusing point defects (10^{-5} < D (1100 °C) < 10^{-4} cm^2/sec) are involved in the formation of both extrinsic and intrinsic A defects. The diffusion coefficients of oxygen and carbon at 1100 °C are about 10^{-10} and 10^{-11} cm^2/sec, respectively. Therefore, oxygen or carbon precipitation alone cannot account for the formation of the interstitial loops.

At present it is still not well established whether at temperatures near the melting point the concentration of Si self-interstitials is negligible compared to that of vacancies. Seeger and Swanson [16] developed their extended interstitial and vacancy defect model to account for the high entropy and activation energy for self-diffusion in silicon. Although they do not obtain quantitative values for the defect concentrations, they propose that the interstitial defect is predominant at high temperatures. Furthermore, calculations of Bennemann [17] indicate that the formation energy of a self-interstitial in the diamond lattice is lower than that of a vacancy. Finally, Si self-interstitials are considered to be very mobile [18]. Therefore, it is possible that Si self-interstitials are involved in the formation of the extrinsic dislocation loops.

The present results have produced evidence that both vacancies and interstitials as well as impurities are involved in the swirl defect formation. Furthermore, these results and those of previous investigations [1,4] raise a number of questions which will have to be answered before the swirl defect formation process is understood. Among these are:

(a) The nature of the B defects in their undecorated state.
(b) The identification of the impurity elements which decorate the A and B defects during the crystal growth.
(c) An explanation for the nonreactivity of lithium with the B defects during a decoration treatment.
(d) The role of the growth rate and impurities on the final defect configuration and dimensions. In particular, recent observations [15] have shown that the growth rate influences the final defect size to a point where the largest ones which form under slow growth rates are revealed by X-ray topographic techniques. These latter results suggest that the observations reported in the present investigation are pertinent only to crystals grown at a moderate growth rate (3 mm/min).

5. Conclusion

The swirl defects in dislocation-free silicon crystals grown in argon atmosphere by the floating-zone method have been identified by TEM. They are: (a) perfect dislocation loops (type A defects) with a size of 1 μm to 3 μm. The loop plane is in general (111) and their Burgers vector is $b = \frac{1}{2} a <110>$ inclined at 35° 26' with the loop plane. Both vacancy and interstitial loops are observed in the type A swirl defects. (b) Semicoherent or coherent precipitates with an anisotropic strain field (type B₁ defects) or spherical strain field (type B₂ defects). The B precipitate sizes range from 600 Å to 800 Å. The present results have produced evidence that both vacancies and interstitials as well as impurities are involved in the swirl defect formation and that previously developed nucleation models which considered vacancy condensation only cannot adequately describe the swirl formation process.

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References

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