Quantitative Analysis of Microsegregation in the Faceted and Non-Faceted Czochralski Silicon Crystal Growth

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The microsegregation behaviour of antimony in the faceted and non-faceted Czochralski silicon crystal growth was analyzed quantitatively. Using small melt heights and no rotation, dopant striations of various small spacings were eliminated. Interface demarcation and spreading resistance measurements were used for the segregation analysis. The dopant concentration and its fluctuation during the faceted growth were both higher than during non-faceted growth. On the other hand, fluctuations of the microscopic growth rate were about the same in magnitude and periodicity in the two growth regions.

The interface demarcation technique in conjunction with spreading resistance measurement has been applied successfully for the quantitative analysis of dopant segregation on a microscale as a function of growth conditions in the crystal growth of germanium [1, 2]. However, if dopant striations of comparable spacings as those of the interface demarcations or time markers are present, the time markers cannot be readily identified. The resolution for interface demarcartion in silicon (about 5 μm) is not as high as in InSb or Ge. Dopant striations of various small spacings (henceforth called random striations) which have been attributed to turbulent convections in the melt [3 – 5] are invariably present in conventional Czochralski grown silicon crystals. Thus, quantitative analyses of the dopant segregation behaviour in the conventional Czochralski grown silicon crystals are difficult. Only in special Czochralski silicon crystal growth conditions the random striations have been eliminated by introducing a severe thermal asymmetry in the melt in conjunction with crystal rotation, and interface demarcation technique has been applied for the segregation analysis [6].

The present investigation is concerned with the dopant segregation behavior in Czochralski silicon crystals grown mostly without random striations. This growth condition was achieved by providing a low thermal gradient in the melt in conjunction with the use of a small melt height. Interface demarcation and spreading resistance measurements were employed to investigate the relationship between the microscopic growth rate and microsegregation behavior. In particular, the effects of faceting and non-faceting at the growth interface on the segregation behavior were investigated.

A resistance-heated Czochralski puller was used. The heater was a cylindrical cup-shaped graphite, which was slotted at three peripheral positions parallel to the cylinder axis for a three phase a.c. power supply. It was provided with three lips at the upper end, which were supported by water-cooled current leads. A cylindrical heat shield of 0.025 cm thick molybdenum sheet surrounded the side and the lower closed end of the heater. A graphite crucible holder was positioned directly on the bottom of the heater. A fused silica crucible (3.8×3.0 cm I.D.) was used with a 40 g silicon charge. The melt height at the start of crystal growth was 2.2 cm, and the initial aspect ratio defined as crucible diameter over melt height was 1.36. ⟨111⟩ silicon crystals, typically 0.4 – 1.2 cm in diameter and 10 – 16 cm long, were grown from heavily Sb-doped melts ($4.6 \times 10^{20}\ \mathrm{cm}^{-3}$). The crucible was not rotated. The crystals were grown also without rotation in most crystal segments being analyzed.

Electrical contacts to implement interface demarcation by current pulsing were made to the seed crystal through the electrically isolated pull shaft; to the melt by a Mo-wire (0.6 mm in diameter) inserted in a quartz capillary immersed in the melt. Current pulses (20 A) of 50 msec duration were transmitted across the solid-liquid growth interface at a repetition rate of 0.5 sec during the crystal growth.

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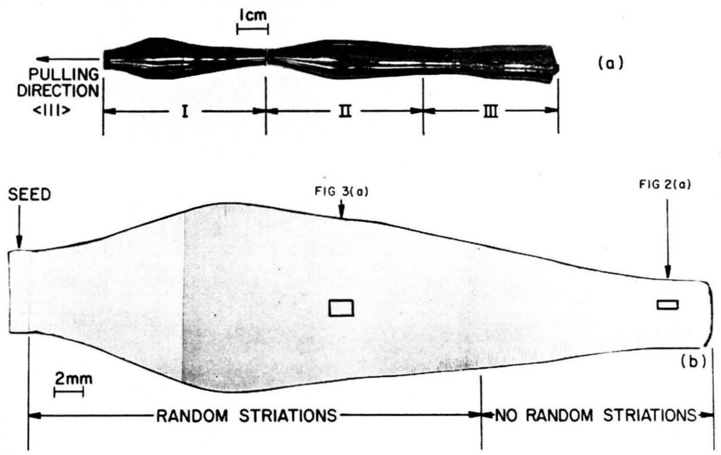

Fig. 1. Optical macrograph of (a) the silicon crystal being investigated (only the first Part I is used for the present segregation analysis), (b) a longitudinal section of the Part I after etching. The rectangled crystal segments are analyzed for the segregation behavior (see Fig. 2(a) and 3(a).

The growth and segregation analysis was made with longitudinal crystal sections cut along the growth axis. The specimens were Syton polished and Sirtl etched for 1 min to delineate the time markers and any other dopant striations. The dopant segregation profile was determined by the two-point-probe (100 μm spacing) spreading resistance measurement at 5 μm intervals. The two-point-probe was positioned parallel to the growth interface as delineated by the time markers. The reproducibility of the spreading resistance measurement for the evaluation of the microscopic dopant concentration has been established to be better than ±1% [1]. The microscopic growth rates were measured with an accuracy of about ±5%.

The silicon crystal being investigated is seen in the photomacrograph of Figure 1(a). The first grown crystal section, Part I, especially its last half segment, was analyzed for the microsegregation reported in the present communication. Due to the high doping level with antimony, morphological instabilities of the growth solid-liquid interface were observed in the crystal Parts II and III, which have been reported in a separate communication [7]. Figure 1(b) is a photomacrograph of the longitudinal section of the crystal Part I after etching. In the initial segment of the Part I corresponding up to 15% use of the original melt amount, a large number of random striations were observed. The aspect ratios of the melt (diameter over height) at seeding and at 15% depletion of the melt were 1.36 and 1.63, respectively. In the subsequently grown segment of the Part I (last one third of the length), random striations were not present as seen in Figure 2(a).

Microsegregation in Faceted and Non-Faceted Growth

The microsegregation behavior of antimony in the faceted and non-faceted regions was analyzed in the crystal segments grown without random striations. Figure 2(a) shows a typical crystal segment where random striations are not present. Time markers introduced by the current pulsing at 0.5 sec intervals are delineated here unambiguously. Neither crystal nor crucible were rotated. The growth interface was planar during crystal growth of this segment, and it became faceted with the (111) plane perpendicular to the ⟨111⟩ growth orientation across the whole interface. The transition from non-faceted to the faceted growth is clearly delineated after etching as seen in Figure 2(a).

The compositional profile (C_s) and the microscopic growth rate (V) prior to and during faceted growth are presented in Figure 2(b). The microscopic growth rates were measured from the spacing of the rate striations introduced at 0.5 sec intervals. Although random striations are not observed, we find fluctuations both in the microscopic growth rate and the dopant concentration. This behavior is caused, probably, by some electromagnetic stirring. The three phase a.c. power supply (60 Hz) being used could have induced a rotational shear flow by electromagnetic coupling into the melt. On the other hand, possibility of the onset of some oscillatory

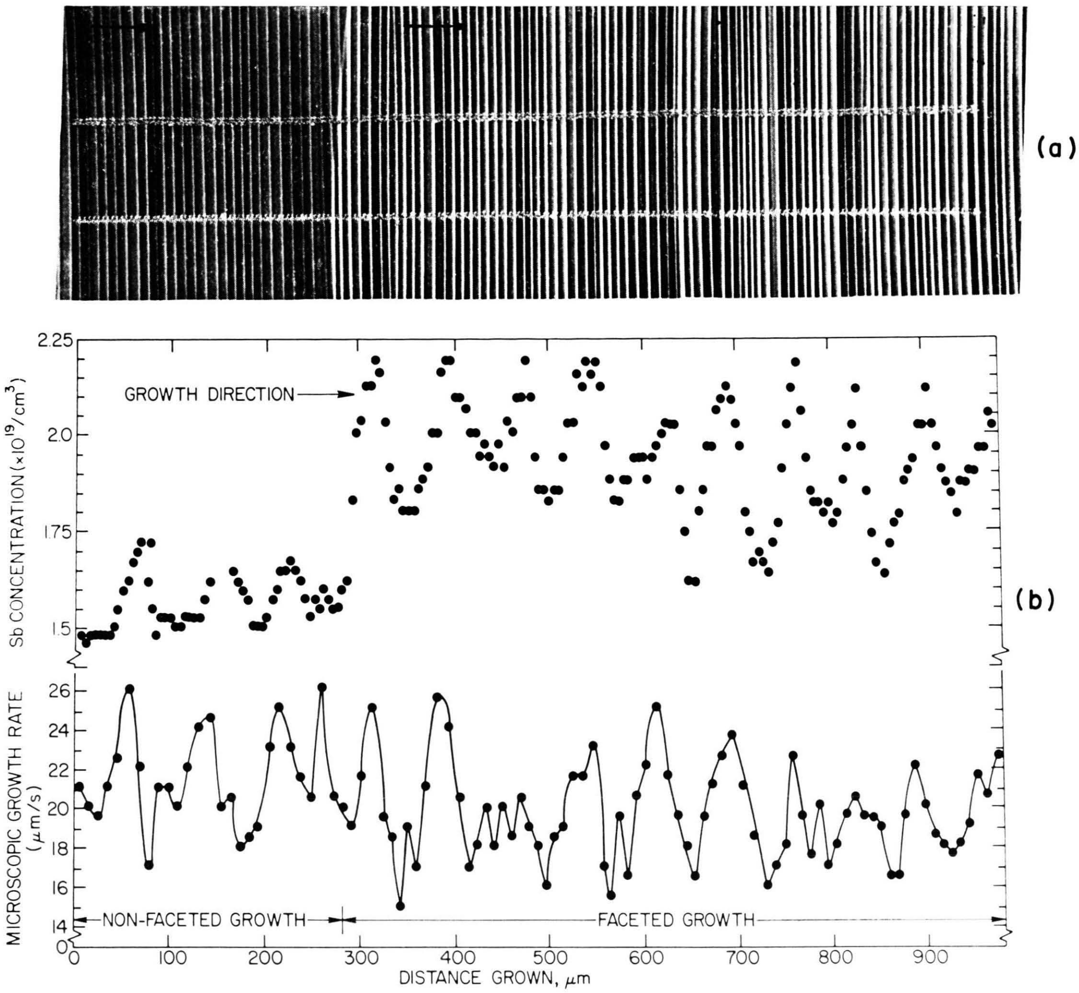

Fig. 2. Microsegregation analysis of the faceted and nonfaceted silicon crystal growth: (a) optical micrograph of the etched crystal segment (the vertical striations are the time markers of 0.5 sec), (b) dopant concentration and microscopic growth rate as a function of the crystal length.

thermal convection [5] may not be excluded. We have observed rotation of a small particle of SiO_2 floating on the melt surface, which were dropped there when the crystal was detached from the melt. The period of the rotation was about 4 sec, which is approximately the same period of the temporal fluctuations of V and C_s (see Figure 2(b)). Thus, some fluid flow was present in the melt which modulated C_s and V, although origin of the flow is not understood exactly at the present time.

A comparison of the curves of C_s and V in Fig. 2(b) shows that fluctuations in V are of similar magnitude both in the faceted and in the immediately preceding non-faceted growth. However, the fluctuations in C_s are significantly higher in the faceted growth than in the preceding non-faceted growth. This behavior is different from the previously reported results [8] on the faceted growth and segregation behavior under crystal rotation in a thermally asymmetric melt. The fluctuations of V in the facet were reported to be significantly smaller than in the simultaneously grown adjacent off-facet region, while the fluctuations in C_s were equal in magnitude and of the same periodicity in the two growth regions.

The measured effective segregation coefficients (k_{eff}) in the faceted and non-faceted growth are 0.033 and 0.028, respectively. The values of k_{eff}

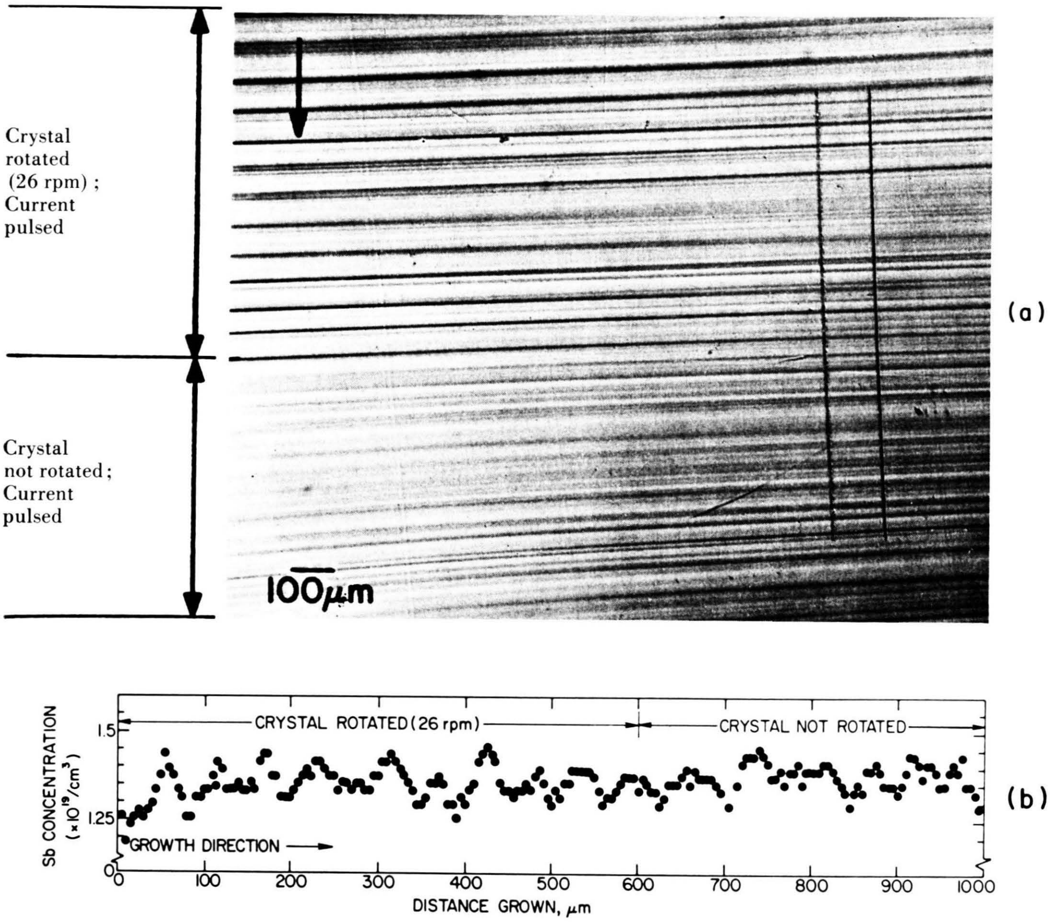

Fig. 3. Segregation analysis of crystal growth with a large number of random striations: (a) optical micrograph of the etched crystal segment; the upper region without rotation, (b) dopant concentration as a function of the crystal length. Note that no time markers are resolved although current pulsing was applied during the growth.

evaluated in the present investigation are close to the equilibrium segregation coefficient of 0.023 [9]. The fluctuations in C_s are about $\pm 15\%$ in the former and about $\pm 6\%$ in the latter case.

Macrosegregation Analysis in Non-Faceted Section with Random Striations

The dopant segregation in the non-faceted region with random striations will be discussed briefly. In the initial segment of the crystal corresponding up to about 15% of the starting melt, random striations were observed as mentioned previously. A non-faceted crystal segment with random striations is seen in Figure 3(a). The upper and lower segment in the figure was grown with crystal rotation at 26 r.p.m. and without crystal rotation, respectively. The growth interface was not faceted. The crucible was stationary. Although current pulses (20 A/ 50 msec/0.5 sec repetition rate) were applied in both cases, time markers are not delineated unambiguously in the crystal section grown with random striations. The microscopic growth rates cannot be measured, and thus quantitative analysis of segregation as a function of growth rate is not possible in the crystal segment grown with random striations.

The spreading resistance measurements at 5 μm intervals, however, give some interesting results on the segregation behavior in the presence of the random striations. We find that the segregation

Table 1. Experimental Parameters and Summary of the Microsegregation Analysis.

Symbols	Crystal Segments Investigated	
	Figure 2 (a)	Figure 3 (a)
Fraction solidified, g	0.2	0.15
Aspect ratio of the melt (Diameter over height)	1.70	1.60
Bulk conc. of Sb in melt, C_l (cm^{-3})	5.72×10^{20}	5.41×10^{20}
Average conc. of Sb in crystal, C_S (cm^{-3})		
Non-faceted growth	1.6×10^{19}	1.35×10^{19}
Faceted growth	1.9×10^{19}	
Fluctuation in C_S, $\Delta C_S/C_S$ (%)		
Non-faceted growth	± 6	± 4
Faceted growth	± 15	
Effective seg. coeff., k_{eff}		
Non-faceted growth	0.028	0.025
Faceted growth	0.333	

behavior is not affected significantly, whether the crystal is rotated or not (see Figure 3 b). The effective segregation coefficient and the fluctuation in C_s are 0.025 and $\pm 4\%$, respectively.

In summary, the microsegregation behavior in faceted and non-faceted Czochralski silicon crystal growth was analyzed quantitatively. The dopant concentration and its fluctuation during faceted growth were higher compared to those in non-faceted growth. On the other hand, the fluctuation of the microscopic growth rate was about the same both in magnitude and periodicity in the two growth regions.

The effective segregation coefficients (k_{eff}) were 0.033 and 0.028 in the faceted and non-faceted growth regions, respectively. The fluctuations of the dopant concentration in the crystal ($\Delta C_s/C_s$) were about $\pm 15\%$ and $\pm 6\%$ for the former and latter growth regions, respectively. On the other hand, k_{eff} and $\Delta C_s/C_s$ in the crystal section with random striations were 0.025 and $\pm 4\%$, respectively.

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