

Solid-Source Doping of Float-Zoned Silicon with B, N, O, and C

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Solid-Source Doping of Float-Zoned Silicon with B, N, O, and C

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Abstract

We report on a solid-source method to introduce dopants or controlled impurities directly into the melt zone during float-zone growth of single- or multicrystalline ingots. Unlike the Czochralski (CZ) growth situation, float zoning allows control over the levels of some impurities (O, C) that cannot be avoided in CZ growth or ingot casting. But aside from impurity studies, the method turns out to be very practical for routine p-type doping in semicontinuous growth processes such as float-zoning, electromagnetic casting, or melt-replenished ribbon growth. Equations governing dopant incorporation, dopant withdrawal, and N co-doping are presented and experimentally verified. Doping uniformity, and doping initiation and withdrawal time constants are also reported. The method uses nontoxic source materials and is flexible with quick turnaround times for changing doping levels. Boron p-type doping with nitrogen co-doping is particularly attractive for silicon lattice strengthening against process-induced dislocation motion and also allows greater freedom from incorporation of Si self-interstitial cluster or A and B swirl-type defects and “D”-type microdefects than nitrogen-free p-type material.

Introduction

Float-zoned (FZ) silicon crystals (or other continuous, melt-replenished Si materials such as electromagnetically cast ingots, melt-replenished ribbons, or rapidly solidified continuous ribbons on a substrate) are doped by different methods depending on the dopant’s segregation coefficient. If $k \ll 1$ (e.g., Ga dopant or N impurity in Si), it is best to place all dopant at the starting end of the feed rod or growth process. If $k \approx 1$ (e.g., B dopant or O impurity in Si), it is best to add the impurity uniformly and continuously as growth progresses. The choices for continuous dopant addition have traditionally been to either predope the feedstock uniformly (this sometimes involves long scheduling times and is somewhat inflexible) or to dope from the gas phase (e.g., with diborane during growth). Diborane is exceptionally toxic and requires stringent safety measures. Figure 1 summarizes doping strategies and introduces our solid-source method. Its applicability to high k (~ 1 , e.g., B, O), low k ($\sim 10^{-4}$, e.g., N), and intermediate k ($\sim 10^{-2}$, e.g., C) materials is discussed and characterized in the subsequent sections.

Experimental Procedure

For single crystals, a $\langle 100 \rangle$ seed orientation was used and the initial growth was necked to produce dislocation-free crystals. The feedstock was undoped polycrystalline silicon rods with resistivity $> 5,000 \Omega\text{-cm}$. The growth experiments were carried out in argon. The zone melting was done with an induction coil operating at 2 MHz. A usual growth rate was $0.33 \text{ cm} \cdot \text{min}^{-1}$, with a rotation rate of 10-15 rpm.

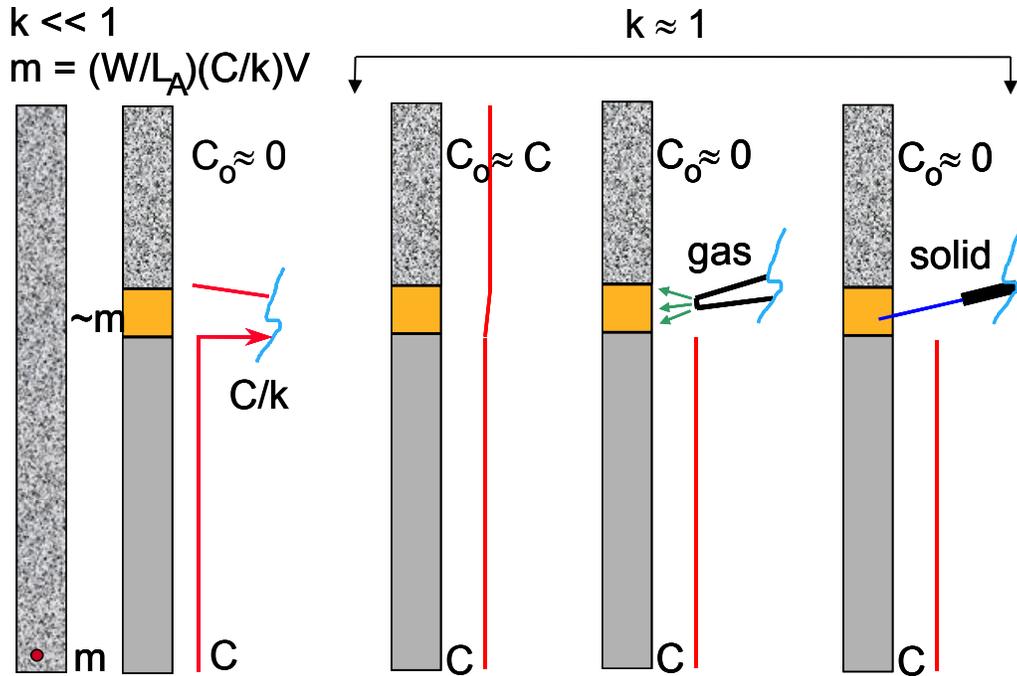


Fig. 1. Schematic representation of FZ doping strategies for $k \ll 1$ (pill doping with mass m at origin: $W =$ atomic weight, $L_A =$ Avogadro's No., $C =$ desired concentration, $k =$ effective segregation coefficient, $V =$ melt volume); and for $k \approx 1$ (predoped feed, gas doping, and the solid-source method discussed in more detail in this manuscript).

Thin, long slivers of high-purity pyrolytic boron nitride were cut, cleaned in a mixed acid etch ($3\text{CH}_3\text{COOH} : 1\text{HF} : 2\text{HNO}_3$), and mounted on a translatable rod, which allowed the sliver tip to be inserted into the molten zone. This was the solid source for boron and nitrogen doping. High-purity fused quartz rods were used for O doping, and vitreous carbon slivers were used for C doping. The immersion was done manually with the sliver or rod attached to a metal rod passing through an "O"-ring-sealed connector in the chamber wall. The source was inserted radially, beneath the RF coil. Figure 2 is a photograph showing the doping arrangement for the particular case of O, N, and B co-doping a $\langle 100 \rangle$ dislocation-free FZ silicon crystal. Here, a $0.8 \Omega\text{-cm}$ B-doped crystal containing $N_B \approx 2 \times 10^{16} \text{ atoms} \cdot \text{cm}^{-3}$ and $N_O \approx 8 \times 10^{16} \text{ atoms} \cdot \text{cm}^{-3}$ was produced with a

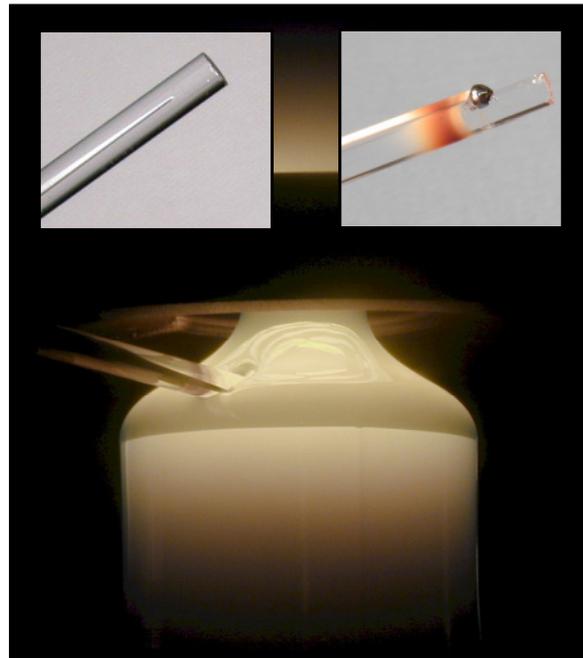


Fig. 2. B, N, and O co-doping a FZ crystal. The insets show the BN and SiO_2 solid sources before growth (left) and after growth (right).

gradually changing mid- 10^{15} atoms·cm⁻³ level for N_N (N is concentration and the subscript refers to the species). A 0.3-cm-diameter high-purity fused quartz rod was immersed 0.6 cm into the melt zone in conjunction with a thin BN sliver immersed 0.2 cm.

Our dopant incorporation model equation is

$$C_o = 4AD/\pi d^2 v, \quad (1)$$

where C_o is the uniform dopant concentration entering the melt zone (atoms·cm⁻³), A is the surface area (cm²) of the immersed solid source, D is the dissolution rate (atoms·cm⁻²·min⁻¹) of the source's doping component in molten silicon, d is the crystal diameter (cm), and v is the crystal growth rate (cm·min⁻¹). A one-time determination of D with the other parameters known allows eq. (1) to be used to calculate the A required for a desired N.

Results

Table I gives the D values that we have determined for the solid sources mentioned earlier, in units atoms·cm⁻²·min⁻¹. They depend on specific experimental conditions and are subject to error from imprecise knowledge of A. The estimated accuracy of the D values is about 10% for 3.4-cm-diameter float-zoned crystal growth. It is best to determine the values within the set of experimental conditions that will be used in a particular growth configuration.

Table I. D Values for B, N, O, and C

Dopant	B	N	O	C
D	3.7×10 ¹⁹	3.7×10 ¹⁹	2.3×10 ¹⁷	9.7×10 ¹⁸

Some of the main features of solid-source B doping from a pyrolytic BN source can be deduced from Fig. 3. A 3.4-cm-diameter, dislocation-free, <100> FZ crystal was grown at 0.32 cm·min⁻¹ from a 3.4-cm-diameter feed rod that had a resistivity of 5,000 Ω·cm or greater. After 7.5 cm of undoped growth, a 0.01-cm x 0.015-cm cross-section pyrolytic BN sliver was inserted about 0.15 cm into the melt zone. After 4.3 cm of additional growth, the immersion depth was increased to about 0.4 cm for another 4 cm of growth. Then the doping sliver was withdrawn. The resultant longitudinal resistivity profile of the crystal (as measured by a linear 4-point probe on a flat surface ground along the length of the crystal) is shown. The time constant for reaching uniform (0.22 Ω·cm or 9 × 10¹⁶ atoms·cm⁻³) B doping, starting from undoped growth, is about 3.2 min. The time constant for changing from one uniform B doping level (0.22 Ω·cm) to another (0.12 Ω·cm or 2.1 × 10¹⁷ atoms·cm⁻³) is about 2.4 min. The resistivity uniformity is about ± 9% in each segment. The profile after withdrawal of the BN (at 16.9 cm) fits an equation of the type

$$\rho = \rho_o e^{(k_B/L)z}, \quad (2)$$

as expected, with a fit standard error of 0.05 (and a coefficient of determination, r², of 0.9995) for k_B/L = 0.795. Here ρ is resistivity, ρ_o is the resistivity at the point of dopant withdrawal, L is the effective zone length (cm), and z is the position after withdrawal (cm). The fitted value of k_B/L is consistent with k_B = 0.9 and L = 1.13 cm. L is the length the zone would be if all of the melt was in a right circular cylinder of diameter d. Radial resistivity profiles for a 5.2-cm-diameter, dislocation-free, <100> crystal doped to 1.3 Ω·cm are shown in Fig. 3 for positions 2 and 8 cm after dopant insertion. At 8 cm, the doping uniformity is ±0.03 Ω·cm or 2%.

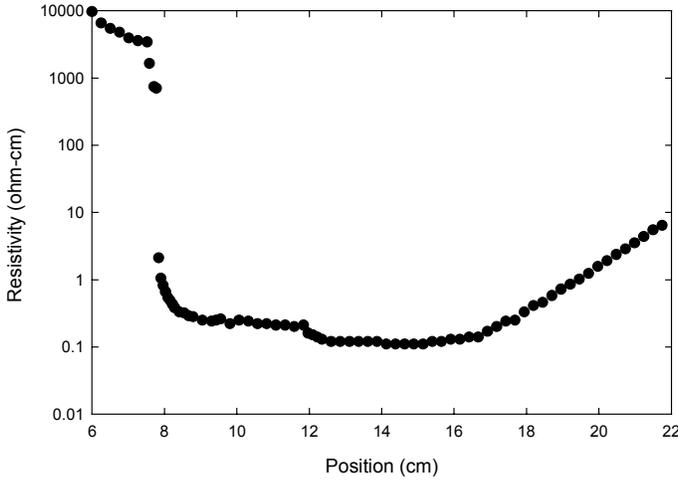


Fig. 3. Doping profile for insertion, change of immersed depth, and withdrawal of BN source.

Pfann's zoning equation:

$$N_N(z) = C_o[1-(1-k_N)e^{-k_N z/L}] = N_B[1-(1-k_N)e^{-k_N z/L}] = (4AD/\pi d^2 v)[1-(1-k_N)e^{-k_N z/L}]. \quad (3)$$

One-meter-long crystals can be grown with $\rho \geq 0.3 \Omega\text{-cm}$ without exceeding the N solubility limit of $4.5 \times 10^{15} \text{ atoms} \cdot \text{cm}^{-3}$. N is essentially electrically inactive as an n-type dopant. Nitrogen below the solubility limit is beneficial. It provides mechanical strengthening analogous to the way O does for CZ crystals, but at 100x lower concentration levels. It also allows swirl-defect-free growth at a larger range of growth rates than is the case for N-free crystals.

C doping is also governed by an equation analogous to eq. (3). Figure 5 shows that a nearly linear $N_C(z)$ distribution can be obtained by solid-source doping with a vitreous C sliver.

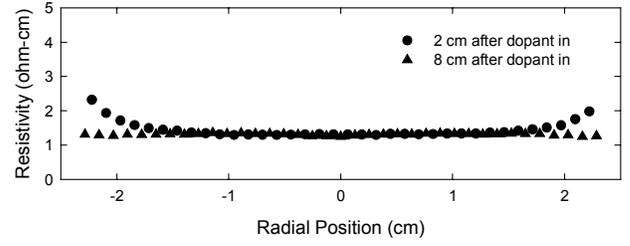


Fig. 4. Radial resistivity profiles for two locations along a 5.2-cm-dia. BN-doped crystal.

Of course, both nitrogen and boron enter the growing crystal during solid-source BN doping. Although k_B is about 0.9, a much lower value of $k_N = 7 \times 10^{-4}$ is characteristic of N in liquid silicon. The distribution of nitrogen along a BN-doped crystal, $N_N(z)$, can be obtained from

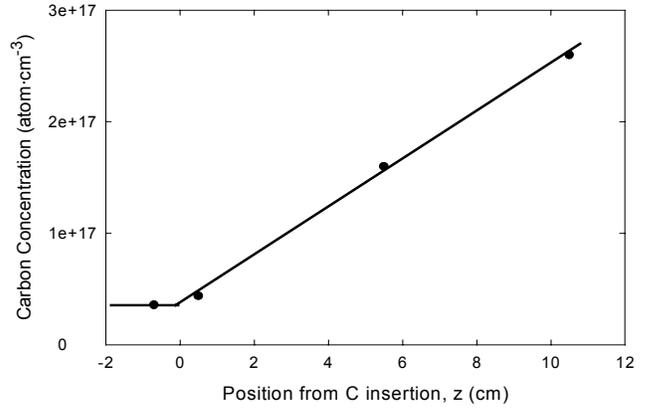


Fig. 5. Solid-source C doping

Summary and Discussion

A solid-source doping method for boron doping from a pyrolytic BN source has been described. It is applicable for B doping concentrations $\leq 6 \times 10^{16} \text{ atoms} \cdot \text{cm}^{-3}$, corresponding to $\rho \geq 0.3 \Omega\text{-cm}$ in meter-long crystals. Nitrogen incorporation below the solubility limit is desirable in FZ crystals for mechanical strengthening and point-defect control. This doping method has the benefit of nitrogen incorporation and allows B doping from a nontoxic source compared to diborane gas that is usually used for doping. Solid-source O and C doping were also described. Co-doping with B, N, and O was demonstrated. Equations for dopant intake into the melt, dopant withdrawal, and dopant distribution along the crystal were developed and experimentally verified.

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