

PROPERTIES OF IRON-DOPED MULTICRYSTALLINE SILICON GROWN BY THE FLOAT-ZONE TECHNIQUE

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ABSTRACT

Multicrystalline Fe-doped Si ingots were float-zoned from high-purity feed rods. Fe was introduced by pill-doping, which gives uniform impurity content for small segregation coefficients ($k \sim 10^{-5}$ for Fe in Si). Fe concentrations were calculated from the initial weight of the Fe pill, the molten zone geometry, and the growth parameters. Values in the range of 10^{12} - 10^{16} atoms/cm³ were targeted. No additional electrically active dopants were introduced. Minority charge carrier lifetime (via YAG-laser-excited, 430-MHz ultra-high-frequency-coupled, photoconductive decay) was measured on the ingots, and wafers were cut to examine grain structure and electron-beam-induced current response of grain boundaries. Observed lifetimes decreased monotonically with increasing Fe content for similar grain sizes (from ~ 10 μ s for $< 10^{-3}$ cm² grains, from ~ 30 μ s to 2 μ s for $\sim 5 \times 10^{-3}$ cm² grains, and from ~ 300 μ s to 2 μ s for $> 10^{-2}$ cm² grains) as the Fe content increased to 1×10^{16} atoms/cm³.

INTRODUCTION

The float-zone (FZ) method for silicon crystal growth allows a high degree of control over background impurity and defect levels and is an excellent vehicle for controlled studies of deliberately introduced impurities and/or defects. In this investigation, we grew Fe-doped multicrystalline ingots by the FZ method to study Fe effects on minority charge carrier lifetime, grain structure, and electron-beam-induced current characteristics of multicrystalline silicon.

IRON-DOPED SILICON INGOT GROWTH

The 34-mm-diameter, Fe-doped ingots were grown at 4 mm/min. from high-purity polycrystalline Si feed rods in a 99.999% Ar ambient with 2.1 MHz induction heating. We used 2-cm-diameter, polycrystalline seeds that were core-drilled along the diameter of large chemical vapor deposited (CVD) polycrystalline silicon logs. This method yields an initial small multicrystalline grain size, and grains approach 1 mm in size after 3-4 cm of growth [1]. Fe was introduced by the pill-doping method[2], where a piece (or pill) of the dopant is inserted near the beginning of growth and enters the molten zone. The required mass of dopant, m , is given by $m = (W/L_A)(C/k)V$, where W is the atomic weight of the dopant, L_A is Avogadro's number, C

is the desired dopant concentration in the ingot, k is the effective segregation coefficient, and V is the volume of the floating zone. We make the assumption that $k \sim 2k_0$, where k_0 is the equilibrium segregation coefficient. Because $k_0 \sim 1 \times 10^{-5}$ for Fe in Si, the reservoir remains essentially constant and concentrations are uniform along the ingot length. Uncertainties arise in correct values for k and V , as well as in the fact that some Fe may be lost by evaporation from the zone. Nevertheless, a range of Fe concentrations, which we calculate to lie between $\sim 2 \times 10^{12}$ and $\sim 1 \times 10^{16}$ atoms/cm³, was produced using m values between 0.14 mg and 0.5 g. No additional electrically active dopants were introduced.

MINORITY CARRIER LIFETIME CHARACTERIZATION

Minority carrier lifetime (via YAG-laser-excited, 430-MHz ultra-high-frequency-coupled, photoconductive decay) was measured on the ingots. Observed lifetimes decreased monotonically with increasing Fe content for similar grain sizes (from ~ 10 μ s to 2 μ s for $< 10^{-3}$ cm² grains, from ~ 30 μ s to 2 μ s for $\sim 5 \times 10^{-3}$ cm² grains, and from ~ 300 μ s to 2 μ s for $> 10^{-2}$ cm² grains) as the Fe content increased to 1×10^{16} atoms/cm³. The details are presented in Fig. 1. We had previously observed that grain size alone has a strong effect on lifetime[1].

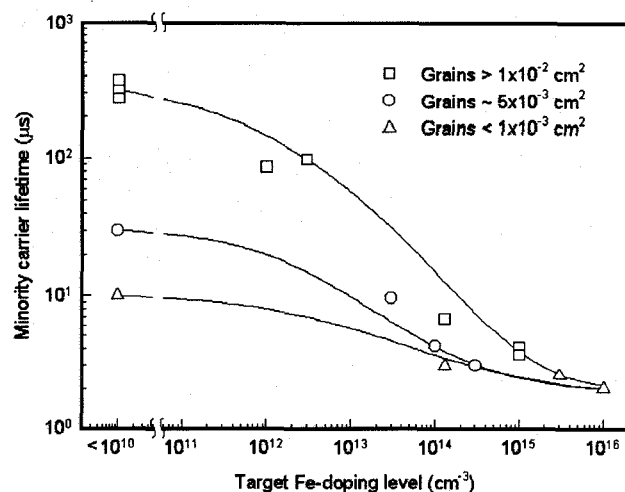


Fig. 1. Measured bulk minority carrier lifetime vs. target Fe-doping level for float-zoned multicrystalline Si ingots with various grain sizes.

GRAIN STRUCTURE AND ELECTRICAL RESPONSE

Wafers were cut to examine grain structure and electron-beam-induced current (EBIC) response of grain boundaries. In the samples with heavy Fe doping (10^{15} - 10^{16} atoms/cm³), nonuniformities in EBIC response were present. These were manifested both as large areas with reduced EBIC signals, extending over numerous grains, and as local areas of reduced response, presumably due to local agglomerations or precipitates of Fe. Fig. 2 is an EBIC photo and Fig. 3 is a scanning electron micrograph of the same area on a sample with targeted doping near 1×10^{16} atoms/cm³. We also observed that the EBIC response was reduced more near the axis of these ingots than at the periphery, perhaps indicating a coring effect in the Fe distribution.

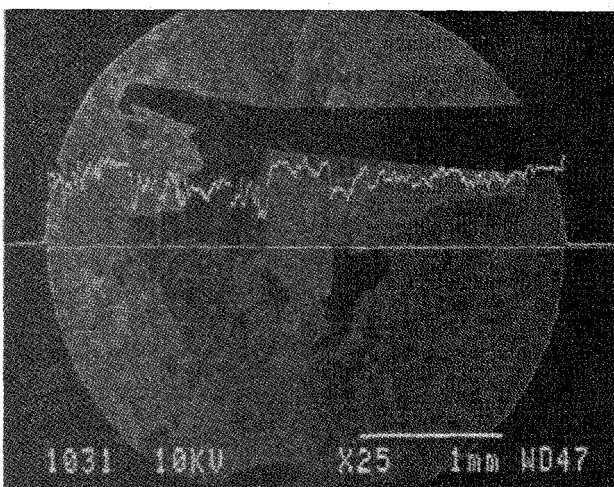


Fig. 2. EBIC photo of a wafer region from an ingot with 1×10^{16} atoms/cm³ target Fe doping concentration



Fig. 3. SEM photo of the same wafer region shown in the EBIC photo of Fig. 2.

We also saw evidence of constitutional supercooling in the heavily doped samples, with a dramatic accompanying effect on grain structure. This indicates that growth speeds of 4 mm/min., which are routine for dislocation-free, high-purity silicon float zoning, are too fast when significant amounts of Fe are present in the melt. The effect is illustrated in Figs. 4-7, where the grain structure and dislocation distributions of Secco-etched wafers from the seed end and tail end of lightly and heavily Fe-doped ingots are compared. Each photograph shows a 2.5-mm-wide region. Precipitation of Fe is particularly evident in the dislocation etch-pit clusters seen in the tail-end wafer from the heavily doped ingot.

We attempted to estimate actual Fe contents in the ingots from capacitance-voltage measurements coupled with the 0.27 eV (below the conduction band) active Fe

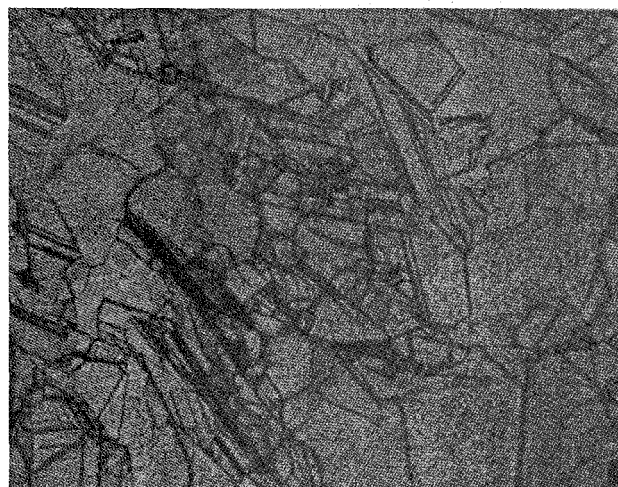


Fig. 4. Seed-end, Secco-etched wafer from an ingot with 3×10^{12} cm⁻³ target Fe doping (2.5-mm-wide region)

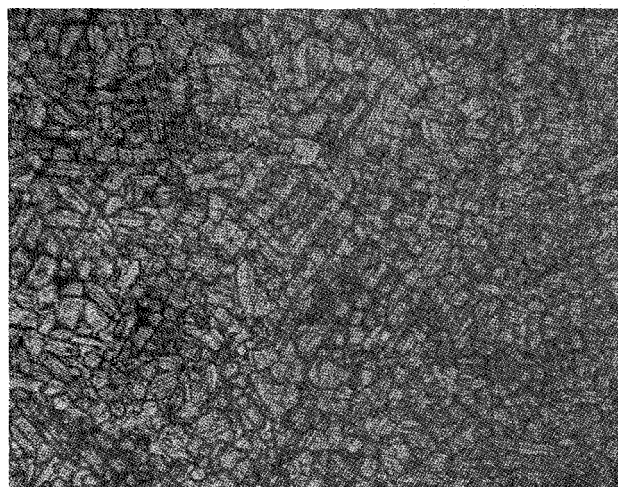


Fig. 5. Seed-end, Secco-etched wafer from an ingot with 1×10^{16} cm⁻³ target Fe doping (2.5-mm-wide region)

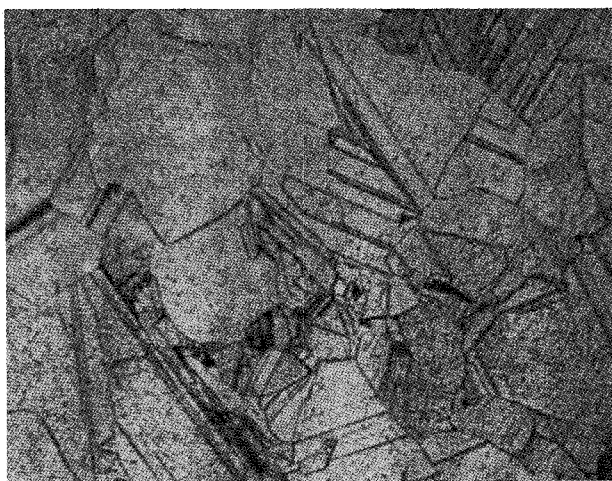


Fig. 6. Tail-end, Secco-etched wafer from an ingot with $3 \times 10^{12} \text{ cm}^{-3}$ Fe doping (2.5-mm-wide region)

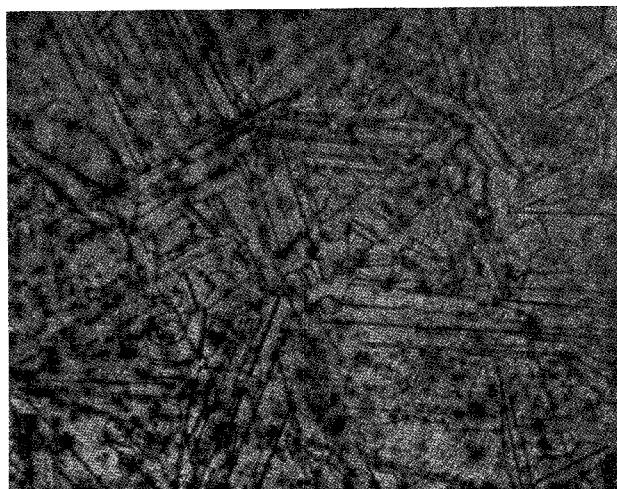


Fig. 7. Tail-end, Secco-etched wafer from an ingot with $1 \times 10^{16} \text{ cm}^{-3}$ target Fe doping (2.5-mm-wide region)

level. Generally, lower levels of Fe were indicated than the target values. Fourier-transform infrared (FTIR) spectroscopy also could not detect significant Fe in even the heavily doped samples[3].

DISCUSSION AND SUMMARY

It is difficult to quantify nonuniformities in Fe content from coring, constitutional supercooling, segregation to dislocations and grain boundaries, and formation of precipitates in the intra-grain areas (due to fast diffusivity and low solubility). The measurement of low Fe levels, even if the distribution is uniform, is also challenging, because the effects of Fe on lifetime occur at Fe levels which are below the detection limit for most analytical methods. Some of these effects might be better quantified by studies of Fe-doped single crystals. We performed x-

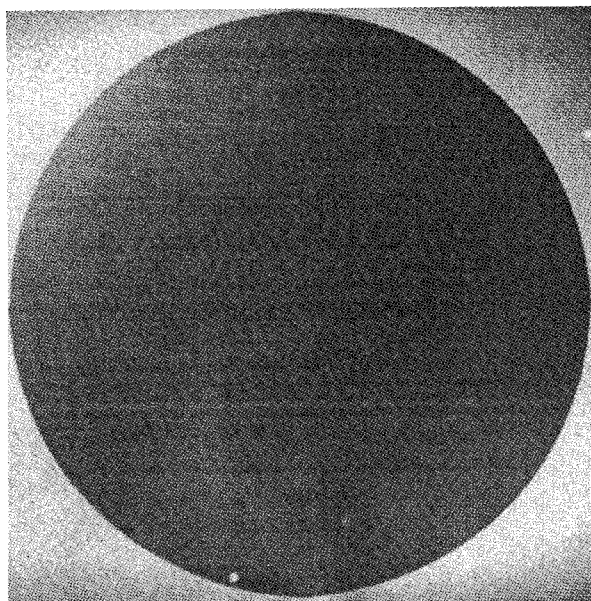


Fig. 8. (022) x-ray topograph of a 33-mm-diameter (100) wafer from a dislocation-free, float-zoned Si ingot doped with Fe during growth to a target level of $1 \times 10^{14} \text{ atoms cm}^{-3}$. The diffraction vector points to the right.

ray topography on a wafer from a $\langle 100 \rangle$ dislocation-free crystal pill doped with Fe at a target level of $1 \times 10^{14} \text{ cm}^{-3}$ and saw no evidence of Fe precipitates (Fig. 8).

We continue to explore Fe effects with other dopants, Fe effects on solar-cell efficiency, Fe-doped single crystals, and several alternative analysis methods, such as electrical resistivity measurements or photoluminescence, for determining actual Fe concentrations. Uncertainty in actual Fe concentrations is a shortcoming of the work presented here.

ACKNOWLEDGMENTS

We thank John Webb and Martha Symko for attempting FTIR spectroscopy Fe-concentration determinations on the Fe-doped samples. This work was supported by the U.S. Department of Energy under contract No. DE-AC36-83CH10093 to NREL.

REFERENCES

- [1] T. F. Ciszek, T. H. Wang, R. W. Burrows, X. Wu, J. Alleman, Y. S. Tsuo, and T. Bekkedahl, "Grain Boundary and Dislocation Effects on the PV Performance of High-Purity Silicon," *23rd IEEE PV Specialists Conf. Record, Louisville, 1993* (IEEE, New York, 1993), p. 101.
- [2] Keller and Muhlbauer, *Floating-Zone Silicon*, Marcel Dekker, Inc.: New York, 1981, pp. 79-82.
- [3] A. Thilderkvist, M. Kleverman, G. Grossman, and H. G. Grimmeiss, "Neutral Interstitial Iron Center in Silicon," *20th Int. Conf. on the Physics of Semiconductors, Thessaloniki, Greece, 1990* (World Scientific, Singapore), p. 581.