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 ~ 10^-3 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^-10^-16 atoms/cm^3 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 µs to 2 µs for < 10^3 cm^2 grains, from ~30 µs to 2 µs for ~5 x 10^3 cm^2 grains, and from ~300 µs to 2 µs for > 10^2 cm^2 grains) as the Fe content increased to 1 x 10^16 atoms/cm^3.

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/La)(C/k)V, where W is the atomic weight of the dopant, La 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 ~ 2ko, where ko is the equilibrium segregation coefficient. Because ko ~ 1 x 10^-6 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 ~2 x 10^-17 and ~1 x 10^-16 atoms/cm^3, 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 µs to 2 µs for < 10^3 cm^2 grains, from ~30 µs to 2 µs for ~5 x 10^3 cm^2 grains, and from ~300 µs to 2 µs for > 10^2 cm^2 grains) as the Fe content increased to 1 x 10^16 atoms/cm^3. The details are presented in Fig. 1. We had previously observed that grain size alone has a strong effect on lifetime[1].
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 ($10^{16}$ atoms/cm$^3$), 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 $1 \times 10^{16}$ atoms/cm$^3$. 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.

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
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-ray topography on a wafer from a <100> dislocation-free crystal pill doped with Fe at a target level of $1 \times 10^{14}$ 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.

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REFERENCES