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MINORITY-CARRIER LIFETIME DEGRADATION IN SILICON CO-DOPED WITH IRON AND GALLIUM

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ABSTRACT

The effect of Fe-Ga pair defects on minority-carrier lifetime τ in high-purity, dislocation-free float-zoned Si is presented, and their properties are documented by deep-level transient spectroscopy and annealing studies. The typical τ of Fe-Ga co-doped crystals (0.4 µs) was dramatically lower than τ of crystals doped with similar amounts of either Fe alone (12 µs) or Ga alone (1,400 µs), contrary to the τ behavior at low injection of Fe-B pair defects. Thermal dissociation of Fe-Ga pairs increased τ, confirming a stronger carrier-recombination activity at Fe-Ga pairs than at interstitial Fe. Defect energies (relative to the valance band) equal to 0.10 and 0.21 eV were observed for Fe-Ga co-doped samples, and the corresponding hole-capture cross sections (at T = ∞) were 3 x 10^{-16} and 6 x 10^{-15} cm^2. An estimation of the binding energies resulted in much lower values than expected (0.09eV and 0.15 eV, respectively).

INTRODUCTION

We report a bulk minority-carrier lifetime killing effect observed in silicon that is deliberately co-doped with Fe and Ga during growth by a high-purity float-zoning (FZ) method. Fe-Ga pairing appears to be similar to Fe-B pairing in creating recombination sites in the material. The Fe-B pair-defect metastability has been studied quite thoroughly [1,2], and deep-level transient spectroscopy has been used to investigate a number of Fe-dopant pairs in silicon, including Fe-Ga [3]. Features of the present work include growth by the FZ method with minimal extraneous impurities, in-situ iron doping during crystal growth, bulk τ measurements on the grown Fe-Ga material, a study of the lifetime degradation effects of the Fe-Ga pair defect, refinement of defect-energy values, and an estimation of defect-binding energies.

Ga is an important alternative p-type dopant to B for growth configurations that are continuous in nature, such as float zoning, electromagnetic semicontinuous casting, or zone crystallization of sheet silicon. It easily produces uniform doping in such configurations, and is compatible with high lifetime silicon growth [4]. Fe is a common impurity in Si, so the study of Fe-Ga defects is relevant.

CRYSTAL GROWTH AND FE-GA DOPING

Crystal growth was conducted by the FZ method from high-purity polycrystalline-Si feed rods using 2.1-MHz induction heating. Prepassing in a high vacuum with final-pass crystal growth in 99.9995% argon was used to assure freedom from extraneous impurities. The crystal diameters were about 34 mm, the growth rate was typically 4 mm/min, and rotation rates on the order of 10 rpm were employed. A series of dislocation-free <100> single crystals were generated by necking the initial growth from the seed.

Fe-, Ga-, or co-doping of the two, was introduced by the pill-doping method. A fragment (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 crystal, k is the effective segregation coefficient, and V is the volume of the floating zone. We make the assumption that $k \sim 2k_o$, where $k_o \sim 1 \times 10^{-5}$ for Fe in Si and ~ 8 x 10^{-3} for Ga in Si. Because of the low k_o values, the dopant reservoir in the molten zone remains essentially constant during growth and concentrations are uniform along the crystal length. A range of Fe concentrations, which we calculate to lie between ~5 x 10^{11} and ~1 x 10^{16} atoms/cm^3, was produced using m values between 0.06 mg and 0.5 g. Ga concentrations between 2 x 10^{15} and 1 X 10^{16} atoms/cm^3 result from Ga mass values between 0.3 and 1.3 mg. Details of seeding, doping, growth, and the effects of Fe (alone) on lifetime may be found in our prior work [5].

CRYSTAL CHARACTERIZATION

Minority-Carrier Bulk Lifetime

Minority-carrier lifetime τ was measured on 1-cm x 1-cm x 3-cm bars cut from the as-grown crystals, which had been at room-temperature for more than a month between growth and measurement. A low injection (<3x10^{12} carriers·cm^{-3}), YAG- or 940-nm diode-laser excited, ASTM F28-75 DC photoconductive decay (PCD) method was used. We had previously studied the effect of Ga doping [4] and Fe doping [5] on bulk lifetime, and the measured values of the control samples in the present study with only Ga doping (see row one in Table

1) or only Fe doping (see row two in Table 1) were consistent with earlier observations. The co-doped samples (rows 3–5) had lifetime values up to a factor of 20 lower than those with only Fe doping, even though very high lifetimes are obtained in Ga-doped material with no Fe, indicating a dramatic lifetime-killing effect for Fe-Ga co-doping. A Fe-Ga defect-pair phenomenon, with different properties from those of the much-studied Fe-B pair defect, appears to be responsible for the lifetime-killing effect. Fig. 1 shows the measured voltage decay vs time, which is used to determine τ, for one sample (70515). The voltage decay is observed to be closely exponential.

Table1. Minority-Carrier Lifetime of Dislocation-free <100> FZ Single Crystals Doped With Fe and Ga

Crystal	Resistivity (Ω-cm)	Ga (cm^{-3})	Fe Target (cm^{-3})	Lifetime (μs)
41121 a	3.5	3.8×10^{15}	0	> 1400
51129-1	24,000	0	1.2×10^{14}	12
70515	6	2.2×10^{15}	4.8×10^{11}	2.2
51212-la	4.1	3.3×10^{15}	1.3×10^{14}	0.40
51212-lb	1.4	1×10^{16}	1.3×10^{14}	0.34

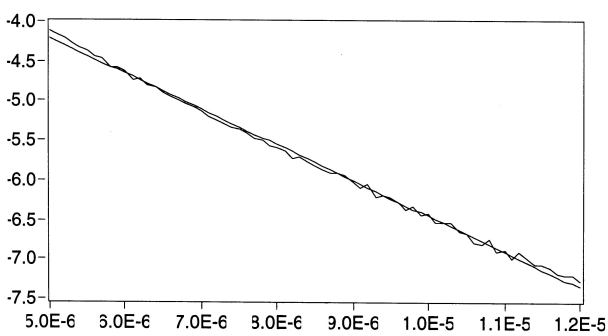

Fig. 1. Logarithm of voltage plotted vs. time in seconds for PCD lifetime measurement on sample 70515. The straight line is the best semilogarithmic fit to the data.

Deep-Level Transient Spectroscopy

Deep-level transient spectroscopy (DLTS) was conducted on co-doped samples 51212-1b (1×10^{16} cm^{-3} Ga and 1.3×10^{14} cm^{-3} Fe) and 70515 (2.2×10^{15} cm^{-3} Ga and 4.8×10^{11} cm^{-3} Fe) to examine the energy-band defect levels of the pairing defect. The samples were RCA-cleaned, etched with a polishing etch (~5 μm), and Al Schottky diodes were fabricated using lithography. Ag was evaporated on the entire 1/4 of the wafers for a back ohmic contact. The sample was cooled under -5 V reverse bias (ensuring detection of both metastable configurations of the Fe-Ga pair) and DLTS was performed. The results for the more heavily Fe-doped

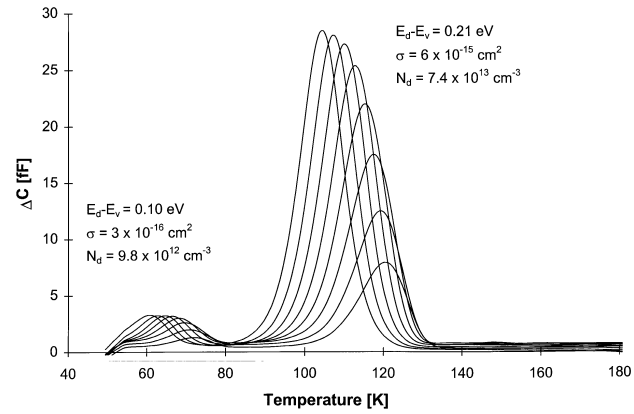

Fig. 2. High energy resolution DLTS spectra for a dislocation-free FZ silicon sample co-doped with 1×10^{16} cm^{-3} Ga and 1.3×10^{14} cm^{-3} Fe.

sample 51212-lb (see Fig. 2) indicate defect energies (relative to the valance band) equal to 0.10 and 0.21 eV, defect concentrations of 9.8×10^{12} and 7.4×10^{13} cm^{-3}, and hole- capture cross sections (at $T = \infty$) equal to 3×10^{-16} and 6×10^{-15} cm^2, respectively. DLTS spectra for the less heavily Fe-doped sample 70515 (not shown) indicate a similar ratio between the concentrations of the two levels. According to Chantre and Kimerling [3], these two levels are attributable to two metastable configurations of Fe-Ga pairs in both of their charge states, + and 0. The E_v +0.1 eV peak is also close in energy to one for Fe-B. But the associated concentration is too high to represent residual B in the high-purity FZ process and the capture cross section is too low relative to the earlier reported value of 4×10^{-15} cm^{-2} [6].

Annealing Experiments

To confirm that the lower lifetimes in co-doped samples are indeed due to Fe-Ga pair defects, we performed two types of low-temperature (50–250°C) annealing experiments for durations of 10 min to 2 h, depending on the temperature used. The first annealing study consisted of heating the sample to a prescribed sequence of temperatures and measuring τ at those temperatures. At high Fe concentrations (~10^{14} cm^{-3}), Fe-precipitation effects are evident (see Table 2). The lifetime of the sample with only Fe doping at ~10^{14} cm^{-3} decreases with increasing annealing temperature, presumably due to dissolution of Fe precipitates. Annealing studies on the co-doped sample with similar Fe concentration show a competing effect between an increase of τ with increasing annealing temperature, as expected if Fe-Ga pairs are dissociating at high temperatures, and the decrease of τ with increasing annealing temperatures due to precipitate dissolution. Pair dissociation is still dominant at 10^{14} cm^{-3} Fe concentration when the sample is heated. We examined a (100) wafer from the 10^{14} cm^{-3} Fe-doped crystal by (022) Mo $K_{\alpha 1}$ x-ray topography and did not observe

Table 2. Lifetime at Various Temperatures for 1.2 x 10^{14} cm^{-3} Fe-doped Silicon and 1.3 x 10^{14} cm^{-3} Fe/3.3 x 10^{15} cm^{-3} Ga Co-doped Silicon Single Crystals

Crystal Number	Ga (cm^{-3})	Fe Target (cm^{-3})	Temperature (^{o}C)	Lifetime (µs)
51120-1	0	1.2 x 10^{14}	25	12
			150	1.4
			200	1.0
			250	0.69
51212-1a	3.3 x 10^{15}	1.3 x 10^{14}	25	0.40
			100	0.85
			150	0.99

precipitate strain fields, but they may be present below the resolution of this technique.

From the lifetime data, with the assumption that the electron capture cross section of interstitial Fe in p-type silicon is 1.5x10^{-15} cm^2 [7], the concentration of interstitial Fe is about 1x10^{13} cm^{-3} after annealing at 150°C for Fe-Ga doped sample (51212-1a), and 1x10^{12} cm^{-3} at room temperature for the only Fe-doped sample (51120-1).

The second annealing experiment was done by heating a sample with low-levels of Fe, but co-doped with Ga (70515 in Table 1) to different prescribed temperatures and quenching it to room-temperature in water after holding it for approximately 10 min at each of the temperatures. Lifetime was measured immediately after the quenching. Because of the low target Fe doping (4.8x10^{11} cm^{-3}), the Fe-precipitation effect is expected to be minimal. Fig. 3 shows the resultant lifetime values. Dissociation of Fe-Ga pairs at higher temperature leads to higher lifetime, confirming that interstitial Fe has less recombination activity than the Fe-Ga defects. The interstitial Fe concentration after a 210°C anneal and quench is estimated to be about 1.9x10^{12} cm^{-3}.

Because Fe-Ga defects exhibit configurational bistability, it was impossible from the annealing experiment alone to derive the binding energies E^b of Fe-Ga. However, the DLTS measurements discussed above indicate a roughly 0.1 concentration ratio between the two levels. Therefore,

$$\frac{N_{0.1eV}}{N_{0.21eV}} = \exp\left(\frac{E^b_{0.1eV} - E^b_{0.21eV}}{kT}\right) = 0.1 \qquad (1)$$

where N is defect concentration. The difference between the two binding energies should be around 0.06 eV. Assuming that the minority carrier (electron) capture cross section ratio is inverted from that of the majority carrier (0.05), then we may obtain the binding energies of the two defects from an Arrhenius plot (Fig. 3) of the following expression in which C is a constant:

. (2)

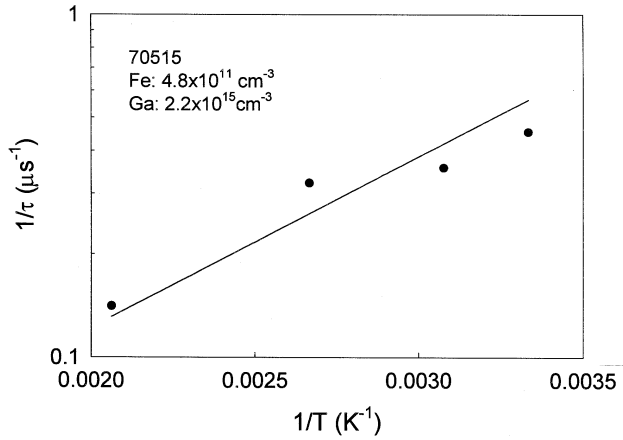

Fig. 3. Lifetime vs. annealing temperature as an Ahrrenius plot for crystal 70515 (Fe: 4.8 x 10^{11} cm^{-3}, Ga: 2.2 x 10^{15} cm^{-3}).

$$\frac{1}{t} = C\exp\left(\frac{E^b_{0.1eV}}{kT}\right) + 0.05C\exp\left(\frac{E^b_{0.21eV} + 0.06}{kT}\right)$$

The resulting binding energies are 0.09 eV and 0.15 eV for the defects at energy levels E_v + 0.1 eV and E_v + 0.21 eV, respectively. Error estimation is not possible due to large uncertainties in the electron-capture cross sections. These binding energy values are surprisingly low, if compared with calculations done with a simple model of two electrostatically bound point charges, which would be about 0.5 eV and 0.6 eV [3]. On the other hand, the ease of formation of these defects at or near room temperature is consistent with the low binding energies we obtained.

DISCUSSION AND CONCLUSIONS

Fe-Ga pair defects cause significant degradation of τ and presumably of photovoltaic properties as well, particularly at Fe concentrations near or above 10^{13} cm^{-3}. In all of our co-doped samples, Ga concentrations exceeded Fe concentrations, so that the Fe concentrations determined the extent of pairing. Characteristics of the pair defects have been determined. The binding energies of the two metastable defects are estimated, from annealing studies and DLTS measurements, to be 0.09 eV and 0.15 eV, respectively. Because there is considerable uncertainty in the proper value to use for the ratio of minority-carrier (electron)-capture cross sections, there is also much uncertainty in our values for the binding energies. We assumed the ratio to be inverted from that of the hole-capture cross sections which we know from the DLTS data to be 0.05. If we instead assume that the ratios are the same, the resultant binding energies would be lower yet (0.04 eV and 0.10 eV respectively). From high-energy-resolution DLTS measurements, we found that the energy levels of the two metastable pair defects are 0.1 eV and 0.21 eV above the valence band, and the hole-capture cross sections are 3x10^{-16} cm^2 and 6 x 10^{-15} cm^2, respectively.

Unlike Fe-B pair defects, Fe-Ga pairs exhibit a stronger lifetime-killing effect than interstitial Fe even at low-injection conditions. The lifetime of minority carriers is lower by up to a factor of 20 in Fe/Ga co-doped silicon than the value for Fe doping alone. Typical lifetime values are in the range 0.3 µs–2.5 µs. In the case of Fe-B defects, although SPV measurements (low injection) show lower recombination activity for Fe-B than for interstitial Fe [8], higher injection [9] showed the opposite trend, possibly due to majority-carrier participation in the acceptor Fe-B at Ec-0.55 eV [1]. In the case of Fe-Ga, both the E_v + 0.1 eV and the E_v + 0.21 eV levels are donors, so they both act as minority-carrier recombination centers. The electron-capture cross section (1.5×10^{-15} cm^2) [7] for interstitial Fe is expected to be smaller than those for E_v + 0.1 eV and at E_v + 0.21 eV combined.

We have so far not devised an adequate method to directly measure the Fe content in our Fe-doped crystals. However, indirect determinations via lifetime and DLTS of the defect concentrations agree reasonably well with our calculated doping levels.

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