

# Auger recombination in silicon at *low* carrier densities

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We have discovered a simple chemical preparation method for silicon which virtually eliminates surface recombination. This has enabled us to rapidly survey wafers from many different boules in order to identify those in which bulk (defect assisted) Shockley–Read–Hall recombination happens to be unusually low. Thus, having minimized the two major sources of electron-hole recombination, we find that Auger recombination becomes dominant, even at carrier densities as low as  $3 \times 10^{15}/\text{cm}^3$ . The Auger coefficient we observe is significantly larger than the value extrapolated down from high density.

It has recently been discovered<sup>1,2</sup> that a commonplace surface preparation method for silicon results in an extraordinarily low surface recombination velocity (SRV). On Si(111), a surface with an SRV as low as 0.25 cm/s can be created.<sup>2</sup> This suggests that it would be worthwhile to reexamine the electron-hole recombination mechanisms in crystalline silicon. If both surface defects and bulk defects were absent, then only intrinsic recombination processes would occur. Such intrinsic mechanisms are radiative electron-hole recombination, a two-body process; and Auger recombination, a three-body process.

To prepare such a silicon surface is surprisingly straightforward and consists of two simple steps: (i) the oxidation of the silicon surface, (ii) the dissolution of the oxide layer by hydrofluoric acid. The oxidation step can equally well occur chemically, thermally, or as a native oxide with similarly favorable results. We have generally preferred chemical oxidation in hot sulfuric acid which is quick and convenient and seems to give slightly better results.

Since contactless measurements to be described below can be completed in less than a minute, it is an ideal survey tool which can rapidly screen sample wafers from many different boules of float zone silicon. The sample preparation does not require any high-temperature furnace processing which might degrade the bulk carrier lifetime. We have found that the bulk minority-carrier lifetime of commercial float zone silicon can be surprisingly superior to the manufacturer's specifications. It is therefore possible to select silicon boules with both very low bulk defect assisted Shockley–Read–Hall recombination and very low surface recombination leaving only the irreducible intrinsic recombination mechanisms. In other words, the elimination of surface recombination made it possible to find material in which the bulk recombination was also minimized.

The electronic measurements are made in a rapid, contactless manner with the apparatus shown in the insert of Fig. 1. For the experiment, the usual practice is to measure the electronic properties *in situ*, with the wafer immersed in hydrofluoric acid, but the apparatus is equally able to acquire data in a dry box or a vacuum chamber. The experimental setup resembles one which was introduced<sup>3</sup> to perform contactless measurements of minority-carrier lifetime in silicon wafers. A strobe lamp injects carriers into the semiconductor wafer, and their density decay is then monitored

by an inductively coupled rf bridge. In effect, the change in sheet conductivity of the wafer associated with the increased carrier concentration is the actual measured quantity. This waveform is stored on a digital oscilloscope and converted to a density from a knowledge<sup>4</sup> of the variation of carrier mobility with carrier density.

For a sufficiently small sample thickness  $L$ , the decay of excess bulk carrier density  $n_b$  is due<sup>5</sup> to the sum of a bulk contribution and a surface contribution:

$$\frac{dn_b}{dt} = -\left(\frac{1}{\tau_b} + \frac{2S}{L}\right)n_b, \quad (1)$$

where  $\tau_b$  is the bulk minority-carrier lifetime,  $S$  is the surface recombination velocity, and the factor 2 accounts for the front and back surfaces. Shockley called the reciprocal of the quantity in brackets the "filament lifetime"  $\tau$ , which in general may itself be a function of  $n_b$ . Equation (1) will be correct provided that the sample is much thinner than a diffusion length,  $L \ll \sqrt{D\tau}$  where  $D$  is the ambipolar diffusion constant. The variable absorption depth of the white strobe light source notwithstanding, the carrier density  $n_b$  will then have sufficient time to diffuse to become spatially uniform, explaining why there is no spatial dependence in Eq. (1). The "filament lifetime" was obtained by computing  $n_b/(dn_b/dt)$  numerically from the digitized waveforms.

Figure 1 is a semilog plot of the density decay from a

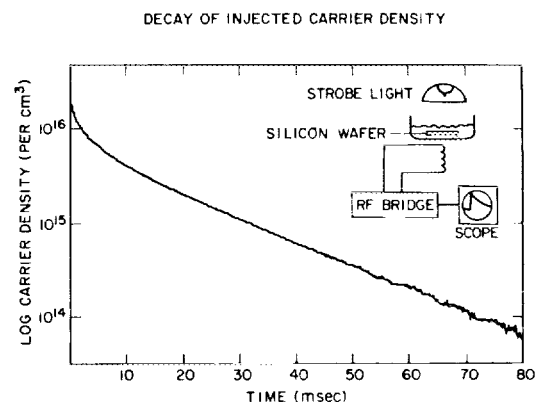


FIG. 1. Semilog plot showing how exceptionally long lived is the electron-hole plasma in our best silicon sample (<111> orientation and 250  $\mu\text{m}$  thick).

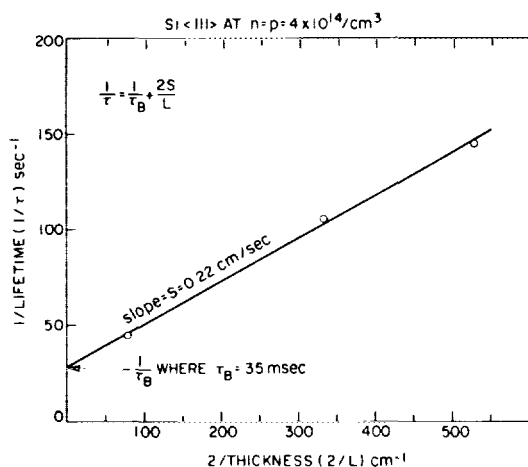


FIG. 2. On a plot of reciprocal lifetime vs reciprocal thickness, the slope gives the surface recombination velocity and the vertical intercept gives the bulk lifetime.

250- $\mu\text{m}$ -thick Si<111> wafer of a *selected* high quality boule of float zone silicon. Notice that the Auger effect with which we are concerned is evident in Fig. 1 as the fast initial decay rate at the higher injection levels. Since the reciprocal "filament lifetime" is a linear function of  $1/L$ , the reciprocal thickness, a linear graph separates the bulk contribution as the vertical intercept and the surface contribution as the slope. An example of this for a given injection level is shown in Fig. 2. In order to maintain self-consistency we found it necessary to derive the various thicknesses by etching off material from one and the same sample. The thickness ratios were accurately determined from sample weight.

The data in Figs. 1 and 2 were obtained from the boule having the longest minority-carrier lifetime that we have found after surveying about 20 different samples of float zone grade silicon. For perspective, the lifetime of 35 ms is about 20 times better than that given in the commercial specifications and about 1000 times better than that of silicon used to make integrated circuits. Having such good quality material in turn improved the accuracy of the SRV measurement and allowed us to monitor the Auger recombination at unusually low density.

An SRV of 0.25 cm/s appears to be the lowest ever reported for any semiconductor. By comparison, the SRV of the most carefully prepared<sup>6</sup> Si-SiO<sub>2</sub> interfaces is 5–10 times larger. The SRV is sometimes modeled as  $S = \sigma v_{th} N_r$ , where  $v_{th} \approx 10^7$  cm/s is a typical carrier thermal velocity,  $\sigma \approx 10^{-15}$  cm<sup>2</sup> is a typical recombination cross section, and  $N_r$  is the number of recombination centers per cm.<sup>2</sup> Under these assumptions, the surface density of electronic defects is  $2.5 \times 10^7$  cm<sup>-2</sup>, or less than 1 per 40 million surface atoms.

The dependence of SRV on the bulk injection level for two samples of differing crystallographic orientation is shown in Fig. 3. It is interesting that recombination is 50% faster on Si<100> than on Si<111>. In contrast, the Si<100>-SiO<sub>2</sub> interface has the slowest recombination and the best electronic properties. The samples were very lightly doped at about 150  $\Omega$  cm so that the doping density was negligible compared to the injected density at which the measurements in Fig. 3 were made, i.e., the measurements were made with

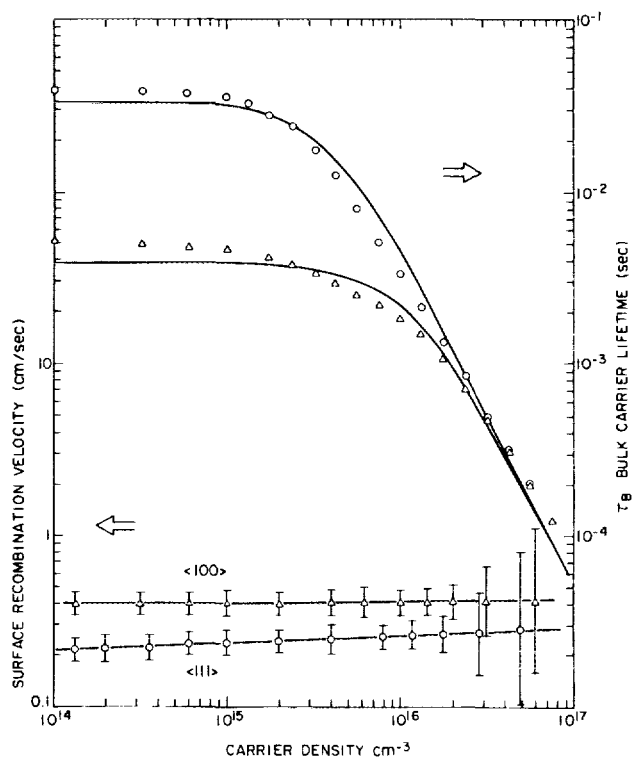


FIG. 3. Surface recombination velocity and bulk lifetime vs carrier injection level for two different boules (circles Si<111>, triangles Si<100>). The doping levels are negligible compared to the injection levels.

the samples in high level injection, where  $n_b \approx p_b$ . The injection level was calibrated by measuring the response of the rf bridge to wafers of known resistivity and correcting for the small variation of mobility with carrier density.<sup>4</sup>

There are two possible reasons for an extremely low SRV: (a) the presence of very few recombination centers on the surface, (b) the presence of a net surface charge which would bend the band to repel one type of carrier from the surface. In case (b) the band bending would be a sensitive function of the bulk carrier density and would approach flat band at higher carrier density. Under strong band bending, the SRV would be proportional to  $n_b$ . This is contrary to what is observed in Fig. 3, where SRV is virtually independent of  $n_b$ . If the small residual increase actually observed within the error bars were entirely attributed to a net surface charge, it would place an upper limit of  $10^8$  charges/cm<sup>2</sup> on such charge. This very low upper limit is due to the particular sensitivity of the band bending to small amounts of charge when the bulk density is as low as  $10^{14}$ /cm<sup>3</sup>, as in the samples from which the data of Fig. 3 were taken.

Similarly, we observed that the SRV remained low in  $n$ - or  $p$ -type material doped up to  $10^{17}$  carriers/cm<sup>3</sup>, i.e., for doping levels that would have flattened the bands for the same reason as before. Therefore, we conclude that the low SRV we observe is due to the presence of *very* few recombination centers at the surface. To the slight degree that band bending might be present, it produces a negligible effect on surface recombination.

The bulk recombination is plotted at the top of Fig. 3. The circles and triangles are from a <111> boule and a <100>

boule, respectively. This particular  $\langle 111 \rangle$  boule was the best found in our survey. The bulk lifetime may be modeled as

$$1/\tau_b = 1/\tau_{\text{SRH}} + Cn_b^2, \quad (2)$$

where  $C$  is the combined electron and hole Auger coefficient. The solid lifetime curves on Fig. 3 are plots of Eq. (2). The same Auger coefficient  $C = 2 \times 10^{-30} \text{ cm}^6/\text{s}$  fits both sets of data, but  $\tau_{\text{SRH}}$ , the crystal defect assisted Shockley–Read–Hall lifetime, was different. It is interesting to note that band-to-band radiative recombination would add a linear term  $Bn_b$  to the recombination rate in Eq. (2). Since silicon is an indirect gap semiconductor, the radiative coefficient  $B$  is<sup>7</sup> only  $2 \times 10^{-15} \text{ cm}^3/\text{s}$  and this term is frequently neglected. Because the material quality is so outstanding in this case, the band-to-band radiative recombination is larger than usual. In our best sample, the 300 K internal photoluminescence quantum efficiency peaked at 10% for an injection level  $n_b \approx 4 \times 10^{15}/\text{cm}^3$ , which is surprisingly efficient for an indirect gap semiconductor.

The Auger recombination coefficient  $C = 2 \times 10^{-30} \text{ cm}^6/\text{s}$  is significantly higher than the accepted value<sup>8</sup> extrapolated from higher density. It is probable that the Auger coefficient itself may be a decreasing function of density. Indeed the highest density data points on Fig. 3 show less Auger recombination than the fitted curve. A better fit to the actual data would be  $1.1 \times 10^{-24} n_b^{1.65}$ , but the exponent 1.65 has little theoretical justification at this time. Vaitkus and Grivitskas<sup>9</sup> predicted that the Auger coefficient would become diminished at higher density. The mechanism they invoke, the onset of carrier degeneracy, would not be expected to play a role at the very low carrier densities observed in this experiment.

Certain semiconductor devices can be influenced by Auger recombination at relatively low density. This is particularly true of solar cells, whose ultimate performance limits

are set<sup>10</sup> by Auger recombination. In this letter we have both good news and bad news to report. The good news is that it is actually possible to reduce defect-assisted bulk and surface recombination processes to such a degree that irreducible intrinsic mechanisms dominate. The bad news is that the intrinsic Auger recombination is somewhat higher than expected and will act to slightly reduce the theoretical efficiency<sup>10</sup> of solar cells.

The surfaces that we prepare are robust and relatively slow to oxidize under ambient conditions. Multiple-internal-reflection infrared spectroscopy shows<sup>2</sup> that the surface is covered by Si–H bonds. Apparently the coverage is very complete, leaving virtually no surface dangling bonds to act as recombination centers. What few strained bonds remain seem to undergo an acid-base neutralization<sup>2</sup> which reduces their number even further. More information on the surface chemical structure can be found in Ref. 2.

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