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# PHYSICAL MECHANISMS OF RECOMBINATION PROCESSES IN SEMICONDUCTOR MATERIALS

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**Abstract**

Recombination of electron–hole pairs sets the carrier lifetime and, through it, the efficiency of solar cells, light-emitting diodes, lasers and bipolar devices. This article reviews the physical mechanisms of recombination in semiconductors: radiative band-to-band recombination, trap-assisted Shockley–Read–Hall (SRH) recombination, Auger recombination and recombination at surfaces and interfaces. For each mechanism the rate expression, the limiting lifetimes at low and high injection, the dependence on doping, temperature and band structure, and the practical ways of suppressing it are given. The mechanisms are then combined in a transparent calculation for crystalline silicon at 300 K, using representative coefficients and a mid-gap defect with a 1 ms SRH lifetime. In this model the radiative and Auger lifetimes become equal at a doping density of about $1.7\times10^{16}$ $cm^{-3}$, Auger recombination overtakes the SRH channel at about $6.0\times10^{16}$ $cm^{-3}$, and at $10^{19}$ $cm^{-3}$ the total low-injection lifetime falls to about 0.0357 μs. A surface recombination velocity above roughly 100 cm/s limits the effective lifetime of a 200 μm wafer to below 100 μs. The calculation is illustrative: it uses simplified constants and does not reproduce the full parametrizations used in device simulation.

**Keywords**: Recombination, carrier lifetime, Shockley–Read–Hall statistics, radiative recombination, Auger recombination, surface recombination velocity, silicon.

## Introduction

Under illumination or electrical injection, a semiconductor contains more electrons and holes than it does in thermal equilibrium. The excess carriers disappear through recombination, in which an electron from the conduction band fills a vacancy (hole) in the valence band and the released energy is carried away by a photon, by lattice vibrations or by another carrier. How fast this happens determines how long a carrier

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lives, how far it diffuses, and how much of the injected or photogenerated charge reaches the contacts or is converted into light.

The study of recombination developed together with the first transistors. In 1952 Shockley and Read analysed recombination through localized states as a statistical problem and obtained the dependence of the carrier lifetime on the initial conductivity and on the injection level (1, pp. 835–842); Hall published an independent analysis of recombination through traps in germanium in the same year (2, p. 387). Two years later van Roosbroeck and Shockley derived the radiative recombination rate from the optical absorption by the principle of detailed balance (3, pp. 1558–1560), and in 1959 Beattie and Landsberg calculated the lifetime when the only process is the Auger effect between bands (4, pp. 16–29).

The same physics decides practical limits. If only radiative recombination remains, the efficiency of a single-junction solar cell reaches the detailed-balance limit (5, pp. 510–519). In light-emitting diodes the opposite is wanted: radiative recombination must dominate, yet at high current density Auger processes reduce the efficiency ("droop") (6, Art. 177406). In silicon photovoltaics, defects and surfaces matter first and the intrinsic Auger limit matters last, and this ordering depends on the doping and injection level.

The aim of this article is to present the physical mechanisms of recombination in a unified way and to show quantitatively how they compete. The objectives are (1) to define the quantities and the classification of recombination processes; (2) to give the rate expressions and limiting lifetimes for radiative, SRH, Auger and surface recombination; (3) to combine them in a simple, fully specified calculation for silicon and to identify the regimes in which each mechanism dominates; and (4) to summarize what the model can and cannot say about devices.

## FUNDAMENTALS

### 2.1. Carrier densities and the mass-action law

In thermal equilibrium, the electron and hole densities $n_0$ and $p_0$ obey the mass-action law $n_0 p_0 = n_i^2$, where $n_i$ is the intrinsic carrier density. Generation of excess pairs adds $\Delta n$ electrons and $\Delta p = \Delta n$ holes (charge neutrality and no trapping are assumed), so that $n = n_0 + \Delta n$ and $p = p_0 + \Delta n$. Low injection means $\Delta n \ll n_0$ (for an n-type sample), and high injection means $\Delta n \gg n_0$. Out of equilibrium the product $np$ exceeds $n_i^2$, and

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every recombination rate below contains the factor $(np - n_i^2)$, which vanishes in equilibrium, where generation and recombination balance exactly.

Net recombination rate and lifetime

The net recombination rate $U$ ($cm^{-3}s^{-1}$) is the difference between recombination and thermal generation. For a uniform sample without trapping, the decay of the excess density is governed by

$$d\Delta n/dt = G - U(\Delta n), \quad (1)$$

and the (effective) carrier lifetime is defined as

$$\tau = \Delta n / U. \quad (2)$$

Several independent channels act in parallel, so their rates add and the lifetimes combine as $1/\tau = \Sigma\, 1/\tau_j$; the fastest channel dominates. A lifetime defined by equation (2) generally depends on $\Delta n$, which is why measurements are reported as lifetime–injection curves (7, pp. 160–170).

### 2.3. Classification of processes

Recombination processes are classified by what happens to the released energy and by where the pair meets (Fig. 1). In *radiative* recombination a photon is emitted. In *SRH* recombination a defect level in the band gap captures first one carrier and then the other, and the energy is given to the lattice as phonons. In *Auger* recombination the energy is transferred to a third carrier, which is excited high into its band and then relaxes thermally. *Surface* recombination is the SRH process at the interface, where a continuum of states exists. Radiative recombination is unavoidable and therefore sets an upper limit on lifetime, whereas SRH and surface recombination can in principle be reduced by material quality and passivation; Auger recombination is intrinsic but strongly depends on carrier density.

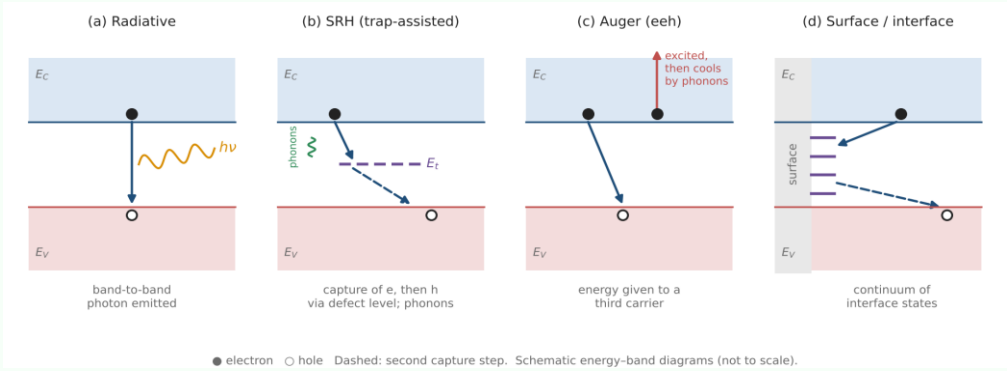



**Fig. 1.** Recombination mechanisms: (a) radiative, (b) Shockley–Read–Hall, (c) Auger (electron–electron–hole), (d) surface/interface

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## RADIATIVE RECOMBINATION

In radiative recombination an electron and a hole annihilate and a photon with energy close to the band gap is emitted. Since the reverse process is the absorption of a photon, the rates are linked by detailed balance. Van Roosbroeck and Shockley used this to calculate the spectral rate of spontaneous emission from the measured absorption coefficient $\alpha(E)$ (3, pp. 1558–1560). In a commonly used form, the spontaneous emission rate per unit volume and photon energy is

$$r_{sp}(E) = (n_r^2 E^2 / \pi^2 \hbar^3 c^2) \cdot \alpha(E) / [\exp((E - \Delta\mu)/k_B T) - 1], \quad (3)$$

where $n_r$ is the refractive index and $\Delta\mu$ is the splitting of the quasi-Fermi levels. For non-degenerate carriers the integral over energy is proportional to $np$, and the net rate is written

$$U_{rad} = B(np - n_i^2), \quad (4)$$

with the radiative coefficient $B$. The lifetime follows from equation (2): in low injection for an n-type sample $\tau_{rad} = 1/(BN_D)$, and in high injection $\tau_{rad} = 1/(B\Delta n)$. The lifetime therefore falls as carriers are added, but only linearly in the carrier density.

The size of $B$ depends on the band structure. In direct-gap materials, such as GaAs, the transition conserves momentum, and values of the order of $10^{-10}$ $cm^3 s^{-1}$ are typically quoted. Silicon has an indirect gap: the transition also requires a phonon, which lowers $B$ by about five orders of magnitude ($4.73\times10^{-15}$ $cm^3 s^{-1}$ at 300 K in the value used below). Trupke et al. determined $B$ for intrinsic silicon between 77 and 300 K and found that it decreases strongly with increasing temperature (8, pp. 4930–4937). In thick samples, emitted photons can be reabsorbed (photon recycling), so the observable lifetime exceeds the one obtained from $B$ alone; Niewelt et al. found that this reabsorption must be taken into account for a precise description of radiative recombination in silicon (9, Art. 111467).

Radiative recombination is the process that light-emitting devices exploit, and it is also the ultimate loss in a solar cell: when it is the only recombination mechanism, the efficiency of a single p–n junction reaches the detailed-balance limit (5, pp. 510–519).

## SHOCKLEY–READ–HALL RECOMBINATION

Defects, impurities and dislocations introduce localized energy levels in the band gap. A level at energy $E_t$ with density $N_t$ can capture an electron from the conduction band and then a hole from the valence band, so that a pair recombines in two steps.

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Shockley and Read derived the statistics of this process for a single level (1, pp. 835–842), and Hall obtained the corresponding result independently (2, p. 387). In steady state the net recombination rate is

$$U_{SRH} = (np - n_i^2) / [\tau_{p0}(n + n_1) + \tau_{n0}(p + p_1)], \quad (5)$$

where $\tau_{n0} = 1/(\sigma_n v_{th} N_t)$ and $\tau_{p0} = 1/(\sigma_p v_{th} N_t)$ are the capture time constants ($\sigma$ are capture cross-sections and $v_{th}$ is the thermal velocity), and $n_1 = n_i \exp((E_t - E_i)/k_B T)$ and $p_1 = n_i \exp((E_i - E_t)/k_B T)$ are the densities for which the Fermi level coincides with the trap level.

Three consequences follow from equation (5). First, in low injection in n-type material with a level not too far from mid-gap, $\tau_{SRH} \to \tau_{p0}$: the minority carrier (hole) capture limits the lifetime, and it does not depend on doping or injection. Second, in high injection $\tau_{SRH} \to \tau_{n0} + \tau_{p0}$, so the lifetime saturates at a larger value; a lifetime that rises with injection therefore points to an SRH-limited bulk, and the ratio of the two limits carries information about the capture cross-section ratio. Third, the efficiency of a trap depends exponentially on its position: levels close to mid-gap are the most effective recombination centres, because $n_1$ and $p_1$ become large for levels near a band edge, and such shallow levels act as traps that hold carriers temporarily rather than as recombination centres.

The simple form of equation (5) assumes a single level, equal densities of free and trapped carriers neglected, and no trapping of excess carriers. Macdonald and Cuevas compared the simplified model with a more general solution of the continuity equations that includes trapping, and derived an upper limit on the recombination centre density for which the simplified model remains accurate (10, pp. 075203-1–7). Temperature-dependent and injection-dependent lifetime curves are therefore interpreted with SRH statistics only within this range of validity. SRH recombination is reduced by high-purity growth, gettering of metallic impurities and avoidance of extended defects (7, pp. 160–170).

## AUGER RECOMBINATION

In Auger recombination, the energy released when an electron recombines with a hole is transferred to a third carrier instead of being emitted as a photon. In the *eeh* process two electrons and a hole take part: one electron recombines with the hole and the other is excited high into the conduction band, from where it relaxes to the band edge by emitting phonons; in the *ehh* process the energy is transferred to a hole. Beattie and

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Landsberg calculated the lifetime when the Auger effect between bands is the only recombination mechanism (4, pp. 16–29). Because three carriers are involved, the rate scales with the cube of the carrier density:

$$U_{\text{Auger}} = (C_n n + C_p p)(np - n_i^2). \quad (6)$$

In low injection in n-type material, $\tau_{\text{Auger}} = 1/(C_n N_D^2)$, and in high injection $\tau_{\text{Auger}} = 1/((C_n + C_p)\Delta n^2)$, i.e. the lifetime falls quadratically with the carrier density. This steep dependence explains why Auger recombination is negligible in lightly doped, weakly excited material and dominates in heavily doped regions of devices, emitters of solar cells and at high injection.

For silicon, a precise description requires coefficients that depend on the doping and injection level, because Coulomb interaction between the carriers enhances the rate. Richter et al. performed a systematic study of injection-dependent recombination over a broad range of dopant concentrations in well-passivated wafers and obtained an Auger rate that is lower than previously thought (11, Art. 165202); a recent reassessment based on twelve sets of high-quality samples refined the intrinsic recombination further (9, Art. 111467). The calculation below uses constant coefficients and is therefore only illustrative.

In wide-gap, direct-gap nitrides, direct Auger processes were expected to be weak because of the large band gap. First-principles calculations showed that indirect Auger processes, assisted by electron–phonon coupling and alloy scattering, can account for the efficiency loss at high carrier densities in InGaN light-emitting diodes (12, pp. 161107-1–3). Experimentally, high-energy electrons were detected from a cesiated InGaN/GaN diode under injection, appearing together with the drop of electroluminescence efficiency and correlated linearly with the “droop current”, which was taken as evidence that droop originates from Auger processes (6, Art. 177406).

## 6. SURFACE AND INTERFACE RECOMBINATION

At a surface the periodic crystal potential ends and dangling bonds, defects and impurities create a continuum of states in the band gap. Recombination through them is described by the same statistics as in Section 4, but it is characterized by a flux rather than a volume rate. The surface recombination velocity $S$ is defined by the boundary condition $D\partial\Delta n/\partial x = S\Delta n|_{\text{surface}}$, where $D$ is the diffusion coefficient of minority carriers. It depends on the density of interface states and on the carrier

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densities at the surface: measurements at thermally grown Si–$SiO_2$ interfaces show that the surface recombination current depends on both the electron and hole densities at the interface (13, pp. 245–247).

For a wafer of thickness $W$ with equal surface recombination velocity $S$ on both sides, a commonly used approximation for the surface-limited lifetime is

$$\tau_s = W/(2S) + (1/D)(W/\pi)^2, \quad (7)$$

and the effective lifetime is obtained from $1/\tau_{eff} = 1/\tau_b + 1/\tau_s$. The first term describes recombination at the surface and the second the time needed for carriers to diffuse to it, so the surface only controls the lifetime when $S$ is large enough that the diffusion term can be neglected. Schroder notes that surface recombination plays an important role in today's high-purity silicon and will matter more as bulk impurity densities fall (7, pp. 160–170).

The range of $S$ is very wide and depends on treatment. Very low values can be achieved by chemical passivation: on Si(111) prepared by a specific chemical treatment, Yablonovitch et al. reported a surface recombination velocity of only 0.25 cm/s, the lowest reported for any semiconductor at that time (14, pp. 249–252). Practical passivation uses dielectric layers (thermal oxide, nitride, aluminium oxide) that reduce the density of interface states (chemical passivation) and, with fixed charge, repel one carrier type from the surface (field-effect passivation), and surface diffusions (back- and front-surface fields) act in the same way.

## COMPETITION OF MECHANISMS: A CALCULATION FOR SILICON

### Model

To show how the mechanisms compete, the lifetimes were calculated for n-type crystalline silicon at 300 K from equations (4)–(6), with the parameters of Table 1, as functions of the injection level and of the doping density, and then combined by summing the rates. The coefficients are representative values for illustration, and they are not the injection- and doping-dependent parametrization of Richter et al. (11, Art. 165202). The code was checked against the analytical limits (Table 1, last row).

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**Table 1.** Parameters and checks of the calculation

| Quantity | Value |
|---|---|
| Intrinsic carrier density $n_i$ | $10^{10}$ cm$^{-3}$ (representative) |
| Radiative coefficient $B$ | $4.73\times10^{-15}$ cm$^3$s$^{-1}$ |
| Auger coefficients $C_n$, $C_p$ | $2.8\times10^{-31}$, $9.9\times10^{-32}$ cm$^6$s$^{-1}$ (constant, simplified) |
| SRH defect | mid-gap ($E_t = E_i$); $\tau_{n0} = \tau_{p0} = 1$ ms |
| Wafer and diffusion coefficient (surface term) | $W = 200$ μm; $D = 12$ cm$^2$s$^{-1}$ |
| Check: SRH, low / high injection | 1.000 ms (expected $\tau_{p0} = 1$ ms) / 2.98 ms (expected 3 ms for $\tau_{n0} = 2$ ms, $\tau_{p0} = 1$ ms) |
| Check: radiative, Auger (low and high injection) | agree with $1/(BN_D)$ and $1/(C_nN_D^2)$ to better than 0.01%, and with $1/((C_n+C_p)\Delta n^2)$ to better than 0.02% |

### 7.2. Dependence on injection and doping

Figure 2a shows the lifetimes for $N_D = 10^{16}$ cm$^{-3}$. At low injection the total lifetime is controlled by the SRH channel (about 1 ms), as radiative and Auger lifetimes are longer by one to two orders of magnitude. As the injection approaches the doping density, the Auger lifetime starts to fall with $\Delta n^{-2}$, and above about $10^{17}$ cm$^{-3}$ it is the shortest of the three and determines the total. The radiative lifetime falls only as $\Delta n^{-1}$ and stays longer than the Auger lifetime in high injection. The rise of the SRH lifetime from $\tau_{p0}$ to $\tau_{n0} + \tau_{p0}$ is visible in the same panel.

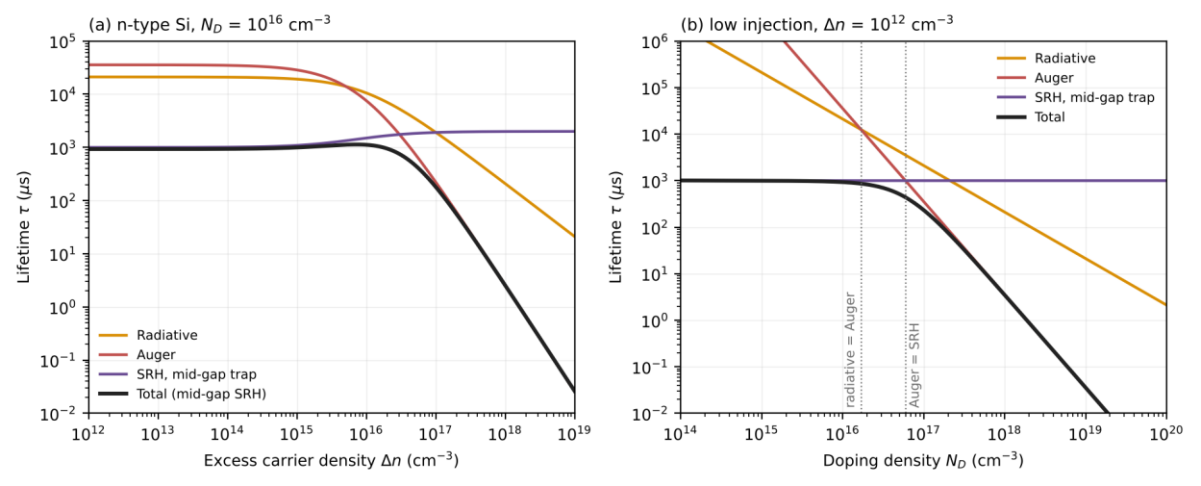



**Fig. 2.** Calculated lifetimes in n-type silicon at 300 K: (a) as a function of excess carrier density, $N_D = 10^{16}$ cm$^{-3}$; (b) as a function of doping density at low injection

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Figure 2b and Table 2 show the dependence on doping at low injection. The radiative lifetime falls as $1/N_D$ and the Auger lifetime as $1/N_D^2$. In this model they are equal at $N_D = B/C_n \approx 1.7\times10^{16}$ cm$^{-3}$, and for higher doping Auger recombination is the faster intrinsic process. A 1 ms SRH channel is overtaken by Auger recombination at $N_D = (1/C_n\tau_{SRH})^{1/2} \approx 6.0\times10^{16}$ cm$^{-3}$. In silicon with a better bulk (longer $\tau_{SRH}$) this crossover moves to lower doping. At $10^{19}$ cm$^{-3}$ the total lifetime is only about 0.0357 µs, entirely due to Auger recombination.

**Table 2.** Calculated low-injection lifetimes in n-type silicon (µs), $\Delta n = 10^{12}$ cm$^{-3}$

| $N_D$, cm$^{-3}$ | Radiative | Auger | SRH | Intrinsic (rad.+Auger) | Total |
|---|---|---|---|---|---|
| **$10^{15}$** | $2.11\times10^{5}$ | $3.56\times10^{6}$ | 1000 | $1.99\times10^{5}$ | 996 |
| **$10^{16}$** | $2.11\times10^{4}$ | $3.57\times10^{4}$ | 1000 | $1.33\times10^{4}$ | 930 |
| **$10^{17}$** | 2110 | 357 | 1000 | 306 | 234 |
| **$10^{18}$** | 211 | 3.57 | 1000 | 3.51 | 3.5 |
| **$10^{19}$** | 21.1 | 0.0357 | 1000 | 0.0357 | 0.0357 |

### 7.3. Role of the surface

The effect of the surface was calculated from equation (7) for a 200 µm wafer with $N_D = 10^{15}$ cm$^{-3}$, whose bulk lifetime in the model is 996 µs (Table 3). At $S = 1$ cm/s the surface term ($1.00\times10^{4}$ µs) is longer than the bulk lifetime and reduces the effective lifetime only by about 9%; at $S = 10$ cm/s it halves it (500 µs); and at $S \geq 100$ cm/s the effective lifetime is practically set by the surface (93.7 µs at 100 cm/s and 13.2 µs at 1000 cm/s). A good bulk lifetime therefore cannot be exploited without surface passivation.

**Table 3.** Surface-limited and effective lifetimes (µs) of a 200 µm wafer, $N_D = 10^{15}$ cm$^{-3}$

| $S$, cm/s | $\tau_s$, eq. (7) | $\tau_b$ | $\tau_{eff}$ |
|---|---|---|---|
| **1** | $1.00\times10^{4}$ | 996 | 906 |
| **10** | 1000 | 996 | 500 |
| **100** | 103 | 996 | 93.7 |
| **1000** | 13.4 | 996 | 13.2 |
| **10000** | 4.38 | 996 | 4.36 |

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## 8. DISCUSSION

### 8.1. Summary of the mechanisms

Table 4 summarizes the mechanisms. The ordering in the calculation (SRH and surface first, Auger at high doping or injection, radiative as the floor in lightly doped silicon) agrees with the qualitative picture in the literature, in which defects and surfaces limit most real samples while Auger recombination sets the intrinsic limit at high carrier density (11, Art. 165202).

**Table 4.** Comparison of recombination mechanisms

| Mechanism | Rate | Lifetime (n-type) | Main dependences | Control |
|---|---|---|---|---|
| **Radiative** | $B(np - n_i^2)$ | low: $1/(BN_D)$; high: $1/(B\Delta n)$ | band structure (direct/indirect), temperature, photon recycling | unavoidable; maximize in LEDs |
| **SRH** | $(np - n_i^2) / [\tau_{p0}(n+n_1) + \tau_{n0}(p+p_1)]$ | low: $\tau_{p0}$; high: $\tau_{n0}+\tau_{p0}$ | defect density, level position, cross-sections | purity, gettering, defect engineering |
| **Auger** | $(C_n n+C_p p)(np - n_i^2)$ | low: $1/(C_n N_D^2)$; high: $1/((C_n+C_p)\Delta n^2)$ | carrier density (cubic), band structure, Coulomb enhancement | limit doping and injection; design of active region |
| **Surface** | $S\Delta n$ | $W/(2S) + (W/\pi)^2/D$ | interface state density, surface charge | passivation, surface fields |

### 8.2. Implications for devices

For solar cells made from silicon, the calculation shows why bulk lifetime and surface passivation have to be improved together, and why the intrinsic Auger limit becomes relevant only when both are good and carrier densities are high, for example in heavily doped emitters. For light-emitting diodes and lasers, the goal is the opposite: nonradiative SRH and surface channels must be minimized, and the cubic dependence of the Auger rate means that efficiency eventually decreases at high current density even in a perfect crystal, which is the origin of droop discussed in Section 5 (6, Art. 177406). For materials with an indirect gap, such as silicon, the small radiative coefficient makes efficient light emission difficult, since nonradiative channels easily outcompete it.

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### 8.3. Limitations

The calculation is deliberately simple. It uses one mid-gap trap with equal capture constants, constant Auger coefficients without Coulomb enhancement, no photon recycling, no band-gap narrowing at high doping and a bulk-averaged surface term, and it neglects trapping, temperature dependence and real defect distributions. Real lifetimes of silicon wafers also depend on the quality of the samples and on measurement artefacts, for which more complete parametrizations are needed (9, Art. 111467). The results should therefore be read as showing regimes and scalings, and absolute values should be taken from measurements or from published parametrizations. The extension to other materials requires their own coefficients.

## CONCLUSION

Recombination in semiconductors proceeds through four main channels: radiative recombination, which is fixed by the band structure and sets the lifetime floor in lightly doped, defect-free material; SRH recombination through defect levels, which is most effective for levels near mid-gap and controls the lifetime of most real samples at low injection; Auger recombination, whose cubic dependence on carrier density makes it dominant at high doping or injection; and surface recombination, which is characterized by the velocity $S$ and requires passivation. In a calculation for n-type silicon at 300 K with representative constants, radiative and Auger lifetimes became equal at about $1.7\times10^{16}$ $cm^{-3}$, Auger recombination overtook a 1 ms SRH channel at about $6.0\times10^{16}$ $cm^{-3}$, and a surface velocity of 100 cm/s or more limited the lifetime of a 200 µm wafer to below 100 µs. A natural continuation is to replace the constant coefficients with injection- and doping-dependent parametrizations, to add several defect levels and temperature, and to compare the model with measured lifetime curves.

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