Very efficient light emission from bulk crystalline silicon

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Due to its indirect bandstructure, bulk crystalline silicon is generally regarded as a poor light emitter. In contrast to this common perception, we report here on surprisingly large external photoluminescence quantum efficiencies of textured bulk crystalline silicon wafers of up to 10.2% at $T=130$ K and of 6.1% at room temperature. Using a theoretical model to calculate the escape probability for internally generated photons, we can conclude from these experimental figures that the radiative recombination probability or internal luminescence quantum efficiency exceeds 20% at room temperature. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1572473]

One of the most promising and challenging tasks in the development of microelectronic structures today is the combination of optical and electrical functions on a silicon chip.[1,2] The availability of efficient silicon-based light emitters suitable for integration into microelectronic chips is a prerequisite for such developments. In the past, the research on silicon-based light emission has been concentrated mainly on alternative approaches like porous silicon,[3] nanocrystalline silicon,[4,5] Si/SiO_2 superlattices,[6] or rare-earth-doped silicon[7] because bulk crystalline silicon itself has generally been regarded as an inherently poor light emitter. In fact, low luminescence quantum efficiencies of bulk crystalline silicon, which are attributed to the fact that phonons are necessarily involved in optical band–band transitions in indirect semiconductors, seem to be widely accepted as a fundamental reality[2,8] and are mentioned in hundreds of publications related to silicon and to silicon-based light emission. However, surprisingly high external electroluminescence quantum efficiencies (EQE) of bulk crystalline silicon light-emitting devices of up to 0.6% at room temperature and up to 0.9% at $T=180$ K, reported recently,[9] show that fairly large luminescence quantum efficiencies can be achieved with highest-purity bulk float-zone silicon. The most crucial aspects of such high external luminescence quantum efficiencies from silicon are the surface texture and an efficient surface passivation, which were achieved in Ref. 9 and in this study by surface processing techniques developed for high-efficiency silicon solar cells.[10]

Here, we investigate the external photoluminescence quantum efficiency (PL-EQE) of a variety of commercially available float-zone silicon wafers. The PL-EQE was measured using a 780 nm/50 mW laser diode to excite the sample. A calibrated thermoelectrically cooled germanium diode, placed typically 12 cm away from the sample, was used as detector. The PL signal was measured in lock-in technique. Due to very long effective carrier lifetimes, the modulation frequency of the exciting laser had to be very low, typically 2 Hz. At very large light intensities, where dc measurements could be carried out accurately, we find very good agreement between the results from the lock-in measurements and the dc measurements. The EQE was determined by a comparison of the PL signal emitted by the sample with the reflection from a calibrated 99% reflecting diffuse white reference. Lambertian cosine distributions for both the PL signal from the sample and for the reflection from the white surface are assumed in the calculation of the EQE by this method. Both were confirmed experimentally within 5% accuracy. The front and the rear surface emission from the wafers were added to give the total luminescence intensity. The relative error in the experimental EQE values determined with our setup is estimated as 15%. For low-temperature measurements, the samples were mounted in a closed-cycle liquid-helium cryostat. Because absolute measurements of the EQE were not possible in that case, the relative variation of the signal as a function of temperature was used to calculate the EQE from the room-temperature values.

The investigated silicon wafers were textured with an inverted pyramid structure, passivated with thermally grown oxides, and annealed with aluminum (Alnealed). The inverted pyramids have a base width of 10 μm. They are formed on a photolithographically masked 100 surface by anisotropic etching in a KOH solution, which exposes the 111 surfaces.[10] Texturing of the surfaces strongly enhances the escape probability for internally generated photons, ideally by a factor twice the refractive index squared ($\approx$26 for silicon with a refractive index $n\approx3.6$ in the wavelength range around $\lambda=1150$ nm, where luminescence is emitted). The surface passivation results in reduced surface recombination and, consequently, in a higher effective lifetime, i.e., in a higher internal radiative recombination probability. A further improvement of the surface passivation was achieved by charging the oxides on both sides of the wafers using a static discharge. The charge on the oxides was found to be stable for several days and could be changed reversibly.

An external PL-EQE of 4.6% was measured at room temperature on a 4×4.5 cm^2 sample that was cut out of a 4 inch 500 μm thick 30 Ω cm *n*-type wafer manufactured by Wacker. The EQE varies with the incident light intensity and peaks at an incident light intensity around 50 mW/cm^2 (Fig. 1). A similar dependence of the EQE of silicon light-emitting diodes (LEDs) on the electric current density through the device has been reported and discussed in Ref. 9. A slightly

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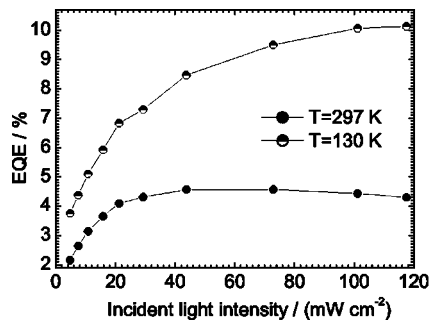

FIG. 1. PL-EQE of a textured 500 μm thick 30 Ω cm *n*-type silicon sample as a function of the incident light intensity at room temperature (full circles) and at $T=130$ K (half circles). The low-temperature values were obtained by scaling the room-temperature data by the relative change of the integral PL intensity as a function of temperature.

higher efficiency of 5.3% was measured on the same position of the entire wafer before the sample was cut out, which demonstrates that the enhanced edge recombination affects the EQE of the cut out sample despite the fact that the illuminated area is more than 1 cm away from the edges. We also observe that higher efficiencies are measured if the incident laser illuminates a larger area (10×4 mm^2 for the measurements shown in Fig. 1) rather than being focused. This is explained by the fact that with focused illumination, a larger fraction of carriers diffuse away from the illuminated area into nonexcited regions with a nonoptimal injection level.

The theoretical upper limit for the EQE of a given sample is the internal radiative recombination probability, which is the EQE divided by the escape probability for internally generated photons. For a sample with given thickness and surface texture the latter can be calcualted theoretically as the ratio between the emitted photon flux and the total internal radiative recombination rate per unit area. We calculated the total rate of internal radiative recombination according to the generalized Planck's law,[11,12] using the absorption coefficient for band-to-band transitions taken from literature.[13] The emitted photon flux was calculated according to a generalized form of Kirchhoff's law[14] using an approximate analytical relation between the absorptance of textured silicon samples and the absorption coefficient.[15] According to these calculations (details can be found in Ref. 16), only a fraction of 29% of internally generated photons can escape a 500 μm thick textured silicon wafer, in principle, even under the idealistic assumption of negligible free carrier absorption. The radiative recombination probability (or internal luminescence quantum efficiency) for a given electron–hole pair must, therefore, be more than three times larger than the experimentally determined EQE. Taking into account that the light trapping properties of the inverted pyramid texture are inferior to the properties of an ideal Lambertian surface[17] and including the effect of free carrier absorption, we can conclude from the experimentally determined EQE of 5.3% that the internal radiative recombination probability exceeds 20% at room temperature.

The escape probability can be strongly increased by a reduction of the thickness. An EQE of 6.1% was measured at room temperature on a 1 Ω cm *p*-type silicon wafer purchased from Wacker that was etched down to a thickness of

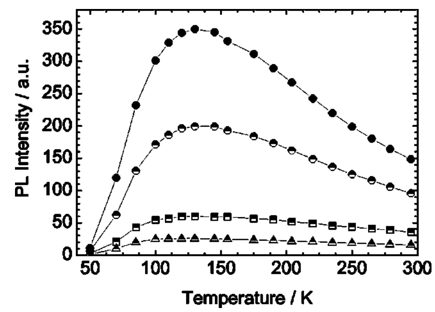

FIG. 2. Temperature dependence of the PL intensity of the 30 Ω cm *n*-type wafer for different light intensities (from top to bottom in mW cm^{-2}: 117, 72.9, 29.3, and 15.8).

100 μm and subsequently textured and passivated. A similar dependence of the EQE on the incident light intensity as shown in Fig. 1 was observed. On a 450 μm thick wafer of the same type, a significantly lower EQE of "only" 3.4% was measured despite a larger effective lifetime. The reduced lifetime in the thin wafer, which is due to the larger relative impact of the residual surface recombination, was thus overcompensated for by a higher escape probability for internally generated photons.

Another way to enhance the escape probability is the reduction of the temperature. At reduced temperatures, the absorption coefficient of silicon for band-to-band transitions decreases strongly in the spectral range 1000–1250 nm where significant luminescence is emitted from bulk silicon.[18] Consequently, reabsorption of internally generated photons on their way to the surface by band-to-band transitions becomes less probable. The temperature dependence of the integral PL signal of the 500 μm thick 30 Ω cm *n*-type wafer is shown in Fig. 2 for different illumination intensities. Starting at room temperature, the PL signal increases with decreasing temperature until a maximum of the EQE is reached around $T=130$ K. As the relative increase of the PL signal is stronger at large incident light intensities, the maximum of the EQE shifts toward higher light intensities as the temperature is reduced (Fig. 1). An external luminescence efficiency of 10.2% is found for the 30 Ω cm *n*-type wafer at $T=130$ K.

The PL signal was also measured as a function of the modulation frequency of the exciting laser diode. Figure 3 shows how the first Fourier component of the modulated PL

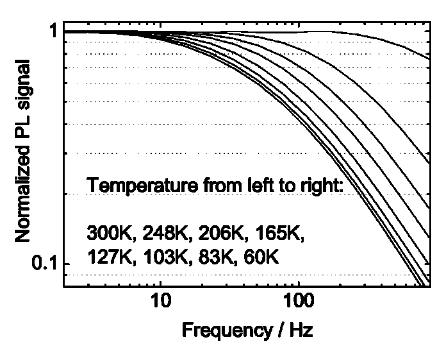

FIG. 3. Normalized PL signal measured with a lock-in amplifier with sinusoidally modulated laser intensity as a function of the modulation frequency for different temperatures. The peak light intensity was 117 mW cm^{-2} for these measurements. The shift of the curves toward higher frequencies indicates that the carrier effective lifetime decreases as the temperature is reduced.

signal, that is detected by the lock-in amplifier, decreases with increasing modulation frequency. Measurements of the frequency response were taken at different temperatures. At reduced temperatures, the curves, which are normalized at low frequencies, shift toward higher frequencies, which indicates a decreasing carrier effective lifetime with decreasing temperature. This effective lifetime results from a combination of bulk and surface recombination. According to these data, the lifetime decreases gradually with decreasing temperature at temperatures $100\,\mathrm{K} < T < 300\,\mathrm{K}$ then steeply at lower temperature. The enhanced PL intensity at $T = 130\,\mathrm{K}$, despite a lower lifetime compared to room temperature, is explained by the enhanced escape probability and by the increasing radiative recombination coefficient of silicon at low temperatures.[19] The steep decrease of the lifetime, i.e., of the EQE, at temperatures below 100 K, is explained by an enhanced surface recombination at low temperatures.

One of the key requirements for the use of silicon LEDs in microelectronics is the possibility to modulate the light signal at high frequencies. The PL response of the $30\,\Omega\,\mathrm{cm}$ *n*-type sample as a function of the modulation frequency shown in Fig. 3 demonstrates that, due to the long effective lifetime, modulation frequencies higher than a few hundred Hz are not compatible with highly efficient silicon PL. This is because a lower lifetime that would allow higher modulation frequencies would certainly be associated with a lower luminescence efficiency. However, high modulation frequencies may yet be achieved, because for very large effective lifetimes, the upper limit of the modulation frequency is determined by the injection and extraction times for the charge carriers rather than by the effective carrier lifetimes.

Surprisingly large values of the EQE up to 6.1% and an internal radiative recombination probability larger than 20% at room temperature demonstrate that contrary to a widely accepted perception, silicon can be a very efficient light emitter if the surface recombination is reduced by an efficient surface passivation and if the escape of photons from this high refractive index semiconductor is facilitated by texturing the surface. We would like to stress that after our surface processing the EQE of a large number of commercially available float-zone *n*- and *p*-type silicon wafers with different resistivities was found to be on the order of a few percent. This shows that our findings are generally valid for highest-quality silicon. More importantly, our results demonstrate that rather than relying on alternative approaches for integrated optical functions on a silicon chip, the base material of microelectronic chips, bulk crystalline silicon, might be used in the future for such developments.

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