Impact of Carrier Profile and Rear-Side Reflection on Photoluminescence Spectra in Planar Crystalline Silicon Wafers at Different Temperatures

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Abstract—The increasing use of spectral photoluminescence as an advanced and accurate diagnostic tool motivates a comprehensive assessment of the effects of some important optical and electrical properties on the photoluminescence spectra from crystalline silicon wafers. In this paper, we present both modeling results and measurements to elucidate the effects of the internal reflectance at the planar wafer surfaces, as well as the carrier profile varying across the sample thickness due to an increased rear-surface recombination velocity, as a function of temperature. These results suggest that the accuracy of existing spectral PL techniques may be improved by using higher temperatures due to the increased effect of the carrier profile at higher temperatures. They also show that changes in the photoluminescence spectrum shape caused by the addition of a rear-side specular reflector offset those caused by changes in the carrier profile due to increased rear surface recombination, and therefore, considerable care needs to be taken when changing the rear-side optics. Finally, the possible impact of variations in the rear-side reflectance on the band–band absorption coefficient and radiative recombination coefficient, which have previously been determined using the spectral photoluminescence technique, is assessed and demonstrated to be insignificant in practice.

Index Terms—Absorption, charge carrier density, photovoltaic cells, photoluminescence (PL), radiative recombination, silicon.

I. INTRODUCTION

RECENTLY, there has been increasing interest in using spectral photoluminescence (PL) as the basis of accurate new characterization techniques for crystalline silicon photovoltaics. Würfel et al. [1] first developed an approach to extract the minoritcarrier minority diffusion length from PL spectra. Later works derived from this approach have been applied for both silicon wafers [2]–[4] and bricks [5]–[7] to separate the effects of bulk and surface recombination at room temperature. In addition, Schinke et al. [8] modeled PL spectra for different surface morphologies, and Barugkin et al. [9] employed spectral PL measurements to quantify the light trapping for various plasmonic structures. Besides these characterization techniques, spectral PL has also been employed to determine very precise values of fundamental parameters in silicon, such as the band–band absorption coefficient $\alpha_{BB}$ [10]–[12] and the radiative recombination coefficient $B$ [11], [13], [14], at different temperatures. These two parameters, in turn, are very important inputs in modeling the PL spectra.

In order to ensure precision and accuracy, special care should be taken regarding the potential effects of the optical and electrical properties of a silicon sample when using spectral PL as a diagnostic tool. In particular, the internal reflectance and the shape of the excess carrier profile inside samples can play critical roles in many potential applications of spectral PL. In practice, the effects of changes in the optical properties and the carrier profiles often occur simultaneously, meaning their impacts are combined, and the resulting spectra may be misinterpreted.

In this paper, we will first examine the independent impacts of the internal reflection and the carrier profile on the PL spectrum shape, as a function of temperature, and via both modeling and measurement for planar wafers. We will demonstrate that the accuracy of spectrally resolved diagnostic PL methods [2]–[7] can potentially be enhanced at increased temperatures due to the more significant impact of the carrier profile at higher temperatures. After that, the combined effects of the reflection and the carrier profile will be demonstrated. Finally, we will reassess their potential impacts on the determination of $\alpha_{BB}$ and $B$, which have been reestablished recently using the spectral PL technique [12], [14].

II. BACKGROUND

The spontaneous generation rate of photons per volume and energy interval due to band–band transitions in an excited nondegenerate semiconductor is described by the generalized Planck law [15], [16]:

$$dr_{sp} = C(h\omega)^2 \alpha_{BB} \exp\left(-\frac{h\omega}{kT}\right) \exp\left(\frac{\Delta\eta}{kT}\right) d(h\omega)$$

(1)

with $C$ a physical constant, $k$ Boltzmann’s constant, $T$ the absolute temperature of the sample, and $\Delta\eta$ the difference between the quasi-Fermi levels of electrons and holes under illumination.

The total PL signal emitted outside a planar silicon sample, which is excited by monochromatic light, per energy interval is approximated by [17]:

$$PL = \left[ \int_0^d \frac{dr_{sp}}{4n_s^2} \exp(-\alpha_{BB} x) dx \right] \times A$$

(2)

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where

\[ A = \frac{[1 - R_f]}{1 - R_f R_0 e^{-2\alpha_{BB}d}} \]

and \( R_f \) and \( R_0 \) are the internal reflectances at normal incident angle upon the front and back surfaces, since the spectra measured here are captured nearly perpendicularly to the sample surfaces, \( d \) is the sample thickness, and \( n_{si} \) is the silicon refractive index. We also have the relationship [18]

\[ \exp \left( \frac{\Delta \eta}{kT} \right) = \frac{np}{n_i^2} \approx \frac{(N_{A/D} + \Delta n) \Delta n}{n_i^2} \]

where \( n \) and \( p \) are the electron and hole concentrations, \( N_{A/D} \) is the background doping concentration, \( \Delta n \) is the excess carrier density, and \( n_i \) is the intrinsic carrier density.

Substituting (1) and (4) into (2), we have the following formula for the PL flux emitted outside the planar sample at a given energy:

\[ PL = C(\hbar \omega)^2 \alpha_{BB} \exp \left( -\frac{\hbar \omega}{kT} \right) \times \left[ \int_0^d [(N_{A/D} + \Delta n) \Delta n \exp(-\alpha_{BB}x)] \, dx \right] \times A \times d(\hbar \omega). \]

Again, \( C \) is a prefactor whose value is constant with photon energy.

An underlying assumption in (2), (3), and (5) is that the reabsorption of the generated photons is dominated by the band–band transitions. This assumption has been shown to be valid at room temperature when the free carrier density is less than \( 2 \times 10^{17} \, \text{cm}^{-3} \) by Trupke et al. [19]. Here, we did not observe any change in the spectrum shape when we decreased the average laser intensity from 80 to 8 suns at 363 K. Thus, we conclude that the free carrier absorption does not affect the spectrum shape in the experiments reported here, in which an average intensity of 23 suns is used.

### III. EXPERIMENTAL DETAILS

The experimental setup to capture the PL spectra is largely the same as described in detail in [12]. In this paper, the laser employed has a wavelength of 532 nm, and on-sample average power of 160 mW. The laser spot diameter, corresponding to the width of a Gaussian intensity distribution at half maximum, is about 3 mm. The average intensity is around 23 suns. The sample temperature was controlled with a Janis VNF-100 liquid nitrogen cryostat in which the sample and sample stage were immersed in temperature-controlled nitrogen vapor. The local sample temperature under illumination was found to increase less than 0.5 K using a thermocouple attached behind the illuminated spot for 30 min.

The investigated silicon sample is a high-quality phosphorous-doped n-type float zone wafer with a resistivity of 6 Ω·cm, corresponding to a background doping of around \( 8 \times 10^{14} \, \text{cm}^{-3} \). Both sides were chemically polished to achieve planar surfaces, and the final thickness was 280 μm. This sample was then divided into two different samples, each of which was processed in a different way to create a different carrier profile.

The first sample was processed to achieve a homogeneous carrier profile through the entire thickness. Both surfaces of this sample were passivated with a 10-nm layer of \( \text{Al}_2\text{O}_3 \) deposited by plasma-assisted atomic layer deposition. It was then annealed at 450 °C in forming a gas consisting of argon and hydrogen for 30 min to activate the surface passivation. The effective lifetime of minority carriers was found to be around 3.3 ms at an injection level of \( 8 \times 10^{14} \, \text{cm}^{-3} \), using the quasi-steady-state photoconductance technique [20]. The second sample was processed to achieve an inhomogeneous carrier profile, which reduces toward the rear surface. This sample went through the same passivation process as the first sample, and then its passivation layer on the rear was removed by fuming this surface with hydrofluoric acid for 3 min. The effective lifetime in this case was about 6 μs at the same injection level. The carrier profile of the first sample was considered to be uniform throughout the thickness, whereas that of the second one was estimated with the formula \( \Delta n(x) = \Delta n(0) \times (1 - x/d) \), in which \( x \) is the distance from the front surface.

The very thin layer (10 nm) of \( \text{Al}_2\text{O}_3 \) was used for both samples in order to maintain the same optical conditions at the front and rear surfaces, since this film is thin enough to have no impact on reflection or absorption in the wavelength range of interest. Using a thicker passivation layer, or depositing a metal film on the rear to achieve a high surface recombination velocity (SRV), would create a significant difference in the optical properties between the front and rear surfaces of the second sample. This difference may have a significant impact on the spectra via rear-side internal reflection, and can mask the impact of the different carrier profiles, as shown below. The impact of the rear reflection itself and its masking effect on the carrier profile will be demonstrated in detail in Sections IV and VI, respectively.

### IV. IMPACT OF INTERNAL REFLECTION ON PHOTOLUMINESCENCE SPECTRUM SHAPE

First, we examine the impact of the internal reflection on the PL spectrum shape at different temperatures. To avoid being confounded with the effect of the carrier profile, we used the first sample whose carrier profiles are symmetrical at all temperatures. We modeled the spectra from this sample for two cases. The optically symmetric case has two sides passivated with 10-nm layers of \( \text{Al}_2\text{O}_3 \); hence, the reflectances on both sides are the same. The optically asymmetric case also has two sides passivated with \( \text{Al}_2\text{O}_3 \), but a specular reflector was attached on the rear side, creating a near unity reflection on this surface. The internal reflectance of the silicon/\( \text{Al}_2\text{O}_3 \)/air interface was modeled using the optical simulator OPAL developed by McIn-tosh and Baker-Finch [21], [22], and was approximately 30% for the wavelengths of interest. The specular reflector was a planar silicon wafer deposited with a 100-nm layer of silver. Its reflectance spectrum was both modeled and measured and was found to be around 95% for the wavelengths of interest. Here, we did not deposit silver directly on the \( \text{Al}_2\text{O}_3 \) layer to make
Fig. 1. Comparison of modeled (lines) and measured (symbols) normalized PL spectra between the optically symmetric (blue lines and blue circles) and optically asymmetric (red-dashed lines and red squares) cases at various temperatures. Both cases have two sides passivated with 10-nm layers of Al₂O₃, but the latter has the rear specular reflector to achieve almost unity rear reflectance. The enhanced rear reflectance increases the signal at longer wavelengths but barely affects the signal at 990 nm. This corresponds to a lowering of the normalized spectra on the shorter wavelength side.

Fig. 2. Comparison of modeled (lines) and measured (symbols) normalized PL spectra between the uniform (blue lines and blue circles) and nonuniform (red-dashed lines and red squares) carrier profile cases at various temperatures.

V. IMPACT OF CARRIER PROFILE ON PHOTOLUMINESCENCE SPECTRUM SHAPE

Next, we investigate the impact of the carrier profile on the PL spectrum shape at different temperatures. Fig. 2 compares the modeled and measured normalized spectra at various temperatures between the uniform (the first sample with both surfaces well passivated) and nonuniform (the second sample whose front surface was well passivated and rear surface was a bare silicon/air interface) carrier profile cases. The low-wavelength sides of the normalized spectra in the latter case are higher than those in the former case. Moreover, this deviation is more obvious at shorter wavelengths and higher temperatures. Once again, this is because \( \alpha_{BB} \) is larger at shorter wavelengths and, hence, the generated photons are more strongly reabsorbed in transit toward the front surface. Therefore, the more carriers near the front surface (relatively speaking), the more chance to escape from the sample these high-energy photons have. As a result, the impact of the carrier profile on the emitted photons is more significant at shorter wavelengths. On the other hand, \( \alpha_{BB} \) is small at longer wavelengths, and the generated photons are not reabsorbed when moving toward the front surface. Thus, the carrier profile plays a little role on the shapes of the spectra at longer wavelengths. In terms of the temperature dependence, once again, \( \alpha_{BB} \) increases with temperature, and thus, the variation becomes larger and shifts to longer wavelengths at higher temperatures. The very good match between the modeling and the experimental data verifies these findings. We, therefore, conclude that the carrier profile has an increasing impact on the spectrum shapes at higher temperatures.

VI. COMBINED IMPACT OF INTERNAL REFLECTION AND CARRIER PROFILE ON PHOTOLUMINESCENCE SPECTRUM SHAPE

In Sections IV and V, the internal reflection and the carrier profile have shown opposing impacts on the PL spectrum shape at different temperatures. The enhanced rear reflectance shifts down the low-wavelength side of the normalized spectra, while the inhomogeneous carrier profile shifts this side up. However,
Fig. 3. Comparison of modeled normalized PL spectra between the symmetric optics and carrier profile case (blue-dashed lines) and the combined effect case (see black-dotted lines), in which the optics and the carrier profile are both asymmetric. The experimental data of the combined effect case (black squares) agree with the modeling. The normalized spectra with the effects of the enhanced rear reflectance from Section IV (red-dashed-dotted lines) and of the inhomogeneous carrier profile from Section V (green solid lines) are also plotted, again to facilitate the comparison.

in practice, these two effects often happen simultaneously, since these two properties are usually altered together during the sample processing steps. Therefore, we here inspect their combined effects on the spectrum shapes, as a function of temperature.

We deposited a 100-nm layer of silver on the rear of the second sample. This thick silver layer not only provides a very high SRV, but also makes the reflectance of the rear approach unity. Thus, this sample displays the properties of both inhomogeneous carrier profile and asymmetric optics on both surfaces. The spectra were then both captured and modeled.

Fig. 3 compares the modeled normalized spectra in this case with the symmetric optics and carrier profile case. The spectra with the effects of the enhanced rear reflectance from Section IV and of the inhomogeneous carrier profile from Section V are also plotted, again to facilitate the comparison. In this figure, the normalized spectra present a combination of both effects, the net effect of which lies in between the two cases in isolation, due to their opposing nature. At room temperature, the carrier profile has less impact on the spectrum shape, and the combined normalized spectrum shows a greater impact of the rear reflector. When the temperature increases, the impact of the carrier profile is more significant at low wavelengths, in particular near the wavelength of 1000 nm, and thus cancels out the effect of the rear reflector. However, when the wavelength increases, this impact is reduced, and the spectrum eventually displays the signature of the enhanced rear reflectance case again. Fig. 3 also shows the experimental spectra of this sample; they are identical to the modeling. This agreement has validated the combined model explained above.

VII. IMPACT OF INTERNAL REFLECTION ON $\alpha_{BB}$ AND $B$

We have confirmed that the internal reflection and the carrier profile can have significant impacts on the PL spectra at different temperatures. In addition, as can be seen from (5), the band–band absorption coefficient $\alpha_{BB}$ is a critical input parameter in spectral PL models. Since the values of this parameter have been reestablished recently using spectral PL measurements [12], it is supposed that the internal reflectance and the carrier profile may, in principle, have a significant impact on the measurement of $\alpha_{BB}$ in [12] and, hence, $B$ in [14], which in turn affect our modeled spectra here. However, since the carrier profile in [12] was shown to be uniform, and the determination of $B$ was based solely on the data of $\alpha_{BB}$ [14], here, we examine only the potential effect of the internal reflection on $\alpha_{BB}$.

The long wavelength escape tail of the measured reflectance spectrum in silicon wafers is a commonly known artifact. However, in [12], we employed the measured reflectance without correcting the reflectance spectra at longer wavelengths. Thus, a question arising is whether this reflectance discrepancy significantly affects the established values of $\alpha_{BB}$. To elucidate this question, using the same technique as in [12], we recalculated $\alpha_{BB}$ at various temperatures around room temperature using the modeled internal reflectance and compared with the data in [12], in which $\alpha_{BB}$ was computed using the measured external reflectance. The internal reflectance of the silicon sample used in [12] was modeled using the optical simulator OPAL [21], [22]. The results are shown in Fig. 4(a), whereas the deviation between two cases is plotted in Fig. 4(b). At longer wavelengths, $\alpha_{BB}$ is determined solely by the absorptivity, which has a constant deviation between the two works due to different scaling factors. Thus, the deviation in Fig. 4(b) trends up or down depending on the changing relative impact of these two variables. Nevertheless, the deviation is
mostly less than 5%. Therefore, the reflectance does not affect the data of $\alpha_{BB}$ in [12] in the wavelength range of interest, despite the significant discrepancy between the measured and modeled reflectances.

VIII. CONCLUSION

We have experimentally demonstrated the separate impacts of the internal reflection and the carrier profile on the PL spectra. The enhanced rear reflectance compresses the low-wavelength sides of the normalized spectra, while the inhomogeneous carrier profile enhances them. These effects are more pronounced at shorter wavelengths and higher temperatures, giving an incentive to use higher temperatures to enhance the accuracy of some established spectral PL tools. In addition, we have shown the aggregate influence of these two properties on the spectra in which the enhanced rear reflectance has offset the impact of the inhomogeneous carrier profile caused by the increased rear-surface recombination velocity. Finally, we have demonstrated that the reflectance has little impact on the data of the band–band absorption coefficient, and hence, the radiative recombination coefficient, despite significant deviation between the measured and modeled reflectances at longer wavelengths.

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Authors’ photographs and biographies not available at the time of publication.