Photoluminescence: A versatile characterization technique for crystalline silicon

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Introduction

Silicon wafers to be used in photovoltaic applications can generally be expected to be relatively poor light emitters with luminescence quantum efficiencies of typically $<<10^{-4}$. At first sight photoluminescence (PL) experiments on silicon therefore do not appear to be the method of choice, when it comes to sensitive measurements of material properties such as the injection level dependent effective minority carrier lifetime $\tau_{eff}(\Delta n)$. This may be one reason why quantitative analyses of PL measurements have not been too numerous in photovoltaics research in the past[1,2].

Here we review our recent PL related experimental work in which we have shown that: 1.) PL can be a surprisingly sensitive lifetime technique. 2.) PL is insensitive to various experimental artifacts that affect other techniques such as microwave reflection or photoconductance. 3.) The Suns-PL technique is discussed, which is a contactless counterpart to Suns-V_{OC} measurements and which allows the contactless determination of implied IV curves on unfinished cells. 4.) A recently introduced self consistent calibration method is described that can be applied to PL but also to other techniques.

Theory

One important characteristics of PL is that the measured signal I_{PL} is given as the *product* of minority and majority carrier densities

$$I_{PL} = B \cdot n_e \cdot n_h \approx B \cdot \Delta n \cdot (N_D + \Delta n), \quad (1)$$

whereas in other techniques the measured signal is determined by the *sum.* In Eq.1 B is the radiative recombination coefficient, N_D is the doping concentration and n_e and n_h are the electron and hole concentrations, respectively. With $n_e * n_h = n_i^2 * \exp(\Delta\eta/kT)$ the PL intensity can also be expressed as a function of the separation of the quasi Fermi energies $\Delta\eta$

$$I_{PL} = B \cdot n_i^2 \cdot \exp(\Delta\eta / kT). \quad (2)$$

The quantitative relation between the PL signal and the excess minority carrier concentration Δn expressed in Eq.1 is the basis of PL lifetime measurements. The relation between the PL signal and $\Delta\eta$ (which is equivalent to an implied voltage) is the basis for reliably determining implied voltages from PL. The direct correlation between the PL signal and an implied voltage, is also the reason why PL is very robust against various experimental artifacts as discussed below.

Sensitivity of PL lifetime measurements

Fig.1 (data taken from Ref.3) shows results from quasi steady state (QSS) injection level dependent PL and photoconductance (PC) lifetime measurements on a 260µm thick 1 Ωcm p-type wafer with a phosphorous diffusion on both sides.

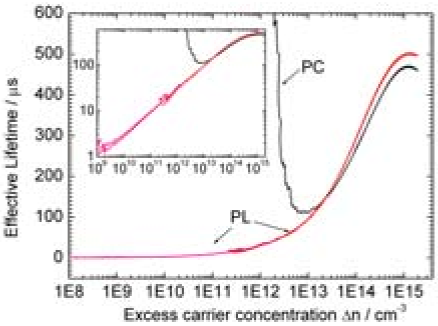

Fig.1 Effective lifetime from PL (red and pink) and from PC (black) for a 1 Ωcm p-type wafer with phosphorous diffusions on both sides.

These measurements were taken with a very sensitive combined PL and PC setup that is described in some detail elsewhere[3]. Good quantitative agreement is observed between PL and PC at injection levels > 10^{13} cm^{-3}, showing that QSS-PL measurements can indeed be used for quantitative injection level dependent lifetime measurements. Fig.1 also shows that in PL the effective lifetime could be measured down to very small excess carrier concentrations $<10^9$ cm^{-3}, which is two or three orders of magnitude below the detection limit of typical PC set ups. In our current experimental set up this somewhat unexpected sensitivity is reached in a scan that only takes a few seconds. Reaching such extremely low injection levels may not be of major interest in itself but these measurements clearly show that more relevant injection ranges can be accessed very accurately and quickly with PL. For the Suns-PL technique to be discussed below, the high sensitivity of PL results in a much wider range of implied voltages that can be determined than from any other technique.

Fig.1 also shows that PL lifetime measurements can be used to determine fairly low effective lifetimes. The lowest lifetime detectable with our setup is limited by the light intensity achievable with the LED array that is currently used for illumination and the lowest detectable PL signal. We estimate that in quasi steady state mode lifetimes on the order of τ=1 ns should be detectable with PL.

Reduced sensitivity to experimental artifacts

The effects of excess carriers accumulated in space charge regions (so called DRM effects) have recently been shown to create dramatic artificial effects on the effective lifetime in PC measurements especially at small injection levels[4,5]. Another effect that can cause artificially high apparent lifetimes in PC measurements is minority carrier tapping[6,7]. In both cases additional *free* charge carriers (majorities *and* minorities in the case of the DRM effect and only majorities in the case of trapping) are stored within the sample, which contribute to the measured signal in all experimental techniques which are linear in the *sum* of minority and majority carrier concentrations. Those carriers however, have no direct correlation with the actual free minority carrier concentration to be measured and therefore lead to an erroneous assignment of the effective lifetime. In contrast theoretical modeling[8] reveals that PL measurements should be unaffected by DRM effects, because the separation of the quasi Fermi energies can be almost constant throughout a device even in the presence of space charge regions.

The predicted insensitivity of PL against DRM effects is demonstrated experimentally in Fig.1. The PC lifetime measurement on the phosphorous doped sample (the one for which DRM effects are theoretically predicted) shows a strong and unrealistic increase of the effective lifetime at small injection levels. This increase could clearly be assigned to the DRM effect as it was not observed on an otherwise identical p-type wafer that had a boron diffusion (hi-lo junction) on both sides[3]. In contrast to the PC measurement the PL measurement on the phosphorous sample is unaffected by the DRM effect (Fig.1).

The question of the sensitivity of QSS-PL measurements to artifacts resulting from minority carrier trapping is addressed in detail experimentally and theoretically elsewhere[9].

Temperature variations are another potential source of inaccuracies in PC measurements. The problem here is that especially in samples of moderate or poor quality high light intensities are used to create small excess carrier concentrations. Resulting temperature variations, can affect not only the effective lifetime itself, but more importantly the dark conductivity via a temperature dependence of the dark carrier concentrations *and* of the mobilities. The small variation of the conductivity due to the light induced excess carrier concentrations, which is supposed to be measured, can then completely be obscured even by comparatively moderate relative variations in the much larger dark conductivity. Our experimental data indicate that PL is more robust against temperature variations, which is expected since the temperature dependence of the radiative recombination coefficient B(T) becomes very weak around room temperature. An interpolation of recently published data[10] for B(T) indicates that a temperature variation from T=290K to T=300K only results in a relative variation of B(T) of ~3%. Consequently only relatively marginal variations of the PL signal are expected due to temperature variations under typical illumination intensities.

This insensitivity of PL against various experimental artifacts is particularly advantageous at low carrier densities, where the influence on PC measurements is most pronounced. This is a crucial aspect to be considered for experimental work e.g. in advanced lifetime spectroscopy techniques such as temperature and injection level dependent lifetime spectroscopy (TIDLS)[11] which critically depend on the analysis of the lifetime at low carrier densities.

Suns-PL: Contactless measurement of IV curves

According to Eq.2 the PL signal is directly linked to $\Delta\eta$ and can thus be interpreted as an implied voltage. PL measurements in combination with measurements of the incident light intensity can therefore in principle be utilized to predict the IV-characteristics in analogy to Suns-V_{OC} measurements[12] but with the advantage that no electrical contacts, not even a solar cell structure are required.

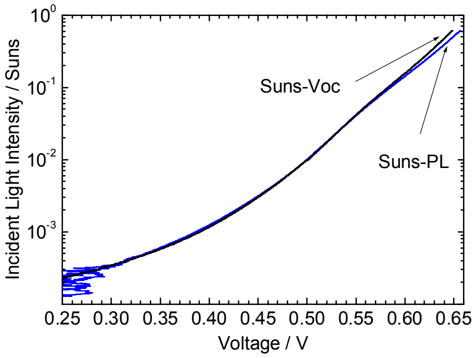

Fig.2 Sun-V_{OC} and Suns-PL curve (see text) of a bifacial double sided buried contact solar cell.

The idea to determine implied IV curves from PL is not new[13] but has only recently been demonstrated experimentally over a wide range of incident light intensities and open circuit voltages[14]. Simultaneous measurements of the open circuit voltage, the PL intensity and the incident light intensity were carried out on bifacial buried contact silicon solar cells. Fig.2 shows the resulting Suns-V_{OC} (incident light intensity as a function of the open circuit voltage) and Suns-PL curves (incident light intensity as a function of the logarithm of the PL signal), which quantitatively agree very well (data from Ref.14). The small deviations of up to 7 mV at large currents are assigned to resistive losses that occur within a solar cell even under open circuit conditions, for instance when carriers flow on a resistive path towards shaded areas under metal fingers[15]. The PL technique is more resistant against such effects, because the voltage is only reduced in the immediate vicinity of the metal contact. The PL signal is thus only affected in proportion of that affected area to the total area of the cell from which PL is collected.

Fig.3 shows the applicability of the Suns-PL technique to non-contactable silicon wafers (data from Ref.14). Here a p-type silicon wafer was measured after various processing steps towards a bifacial buried contact solar cell, i.e. a) after emitter diffusion, b) after laser scribing a contact pattern on the rear surface, c) after cleaving the edges of the cell, d) after scratching the front surface. These measurements which are discussed in more detail elsewhere[14], clearly highlight a major advantage of the Suns-PL technique, i.e. the possibility to measure the implied IV curve over a wide range of voltages after each processing step. This certainly allows the influence of individual processing steps on the material quality to be monitored and consequently these processing steps to be optimized more reliably and effectively.

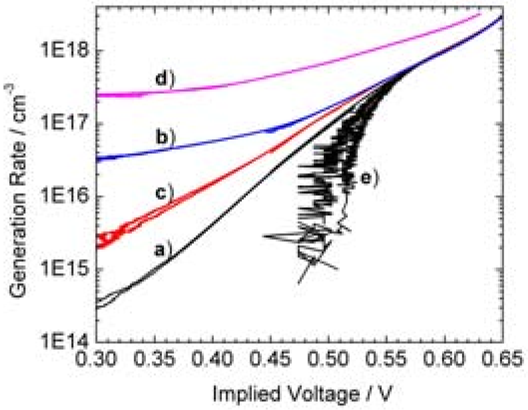

Fig.3 Suns-PL curves of a silicon wafer after various processing steps (a-d) and implied IV curve from PC data (e) measured after step a).

Implied IV curves can also be determined in contact less mode from PC measurements. However, this method is strictly limited to carrier concentrations at which trapping or DRM effects have only a marginal influence. In many relevant cases this can be a serious restriction. Curve e) in Fig.3 represents the implied IV curve resulting from a QSS-PC measurement (taken after emitter diffusion), which shows that the data below 550mV are strongly affected by DRM effects. Even in the absence of those artifacts the measurement of implied IV curves from PC data becomes very difficult at implied voltages <450 mV because the corresponding excess carrier concentrations are very small. The high sensitivity of PL is a big advantage in this context.

Calibration of PL

The calibration of a relative PL signal is an essential step in PL lifetime measurements and in the Suns-PL technique. In previous work this calibration was carried out by comparison of a PL measurement with a calibrated PC measurement taken under identical illumination conditions and at large injection conditions where the above mentioned experimental artifacts are expected to be insignificant. However, we recently also described a self consistent calibration method[16], which is not only potentially more accurate but also allows PL measurements to be

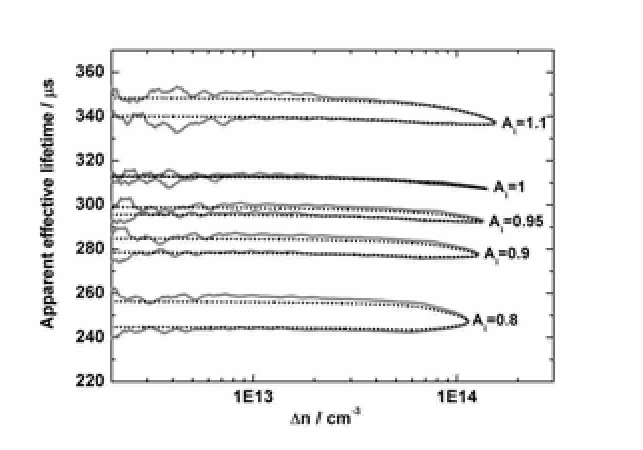

Fig.4: Theoretical (dotted) and experimental (solid) lifetime data with hysteresis effects for inaccurate choice of the calibration factor A_i.

calibrated without any separate technique for calibration. The method is based on the generalized analysis described by Nagel et al.[17] and is very similar to a method for calibrating the generation rate that we have described earlier[18]. Fig.4 shows how the calibration method works (data from Ref.16). A temporal light intensity profile with a rising and a falling branch is used for excitation. Hysteresis effects in the experimental and theoretical injection level dependent lifetime curves result from a wrong calibration of the PL signal. Minimization of such hysteresis effects by variation of a calibration constant A_i (Fig.4) allows PL or PC lifetime measurements to be calibrated.

Conclusions

PL is an unexpectedly sensitive technique that can be used for quantitative characterization of silicon wafers. It allows the contact less measurement of the injection level dependent effective lifetime and of implied IV curves and is unaffected by various experimental artifacts that affect other techniques especially at low excess carrier concentrations. With a recently introduced self consistent calibration method PL can be carried out in a self contained way without the previous need for a separate calibration technique. The advantages of PL measurements over conventional lifetime techniques discussed above also applies to *spatially resolved* PL measurements, giving a significant advantage over other spatially resolved techniques such as Carrier Density Imaging (CDI)[19,20] A practical problem with PL measurements is the requirement of high intensity monochromatic illumination over a large area. The continuous improvement of solid state light sources such as lasers and light emitting diode arrays will provide solutions to this problem. In summary we believe that given the advantages and possibilities outlined here, PL is a powerful technique, which should be used more widely for silicon characterization in photovoltaics research.

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