







On the Conversion Between Recombination Rates and Electronic Defect Parameters in Semiconductors

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Abstract—With the remarkable advances in semiconductor processing, devices such as solar cells have fewer and fewer defects that impact their performance. Determination of the defects that currently limit the device performance, predominantly by increasing the charge carrier recombination rate, has become more challenging with standard methods like deep level transient spectroscopy. To circumvent this limitation, the photovoltaic community is attempting to use the measurement of the charge carrier recombination rates to identify the remaining defects, as this approach is intrinsically sensitive to the defects that limit the cell's/sample's performance/lifetime. This article reviews this new approach, contrasting it with the developments that have occurred with deep-level transient spectroscopy, finding several critical limitations in the current assumptions, and providing suggestions for an improved strategy.

Index Terms—Photovoltaic cells, charge carrier lifetime.

I. INTRODUCTION

WITH in the past two decades, measurements of recombination rates have become the standard technique for both the study and attempted determination of defects within silicon photovoltaics; this technique is used even in preference to the gold standard deep-level transient spectroscopy (DLTS). A major driver of this shift is that the hardware for the measurement of recombination rates is widely available, contactless,

requires a measurement structure very similar to a partially processed devices, and is always sensitive to the performance limiting defect. However, unlike the more mature techniques, e.g., DLTS, the analysis performed on lifetime measurements is not as developed. Moreover, there are nuances within the presentation of DLTS results that are generally unknown by the photovoltaic community. We demonstrate that the gap between these communities is bridgeable by demonstrating agreement between separate publications work from DLTS results and lifetime measurements for two well-studied and simple defects (monovalent defects). We are specifically concerned with the conversion of measured electronic defect parameters into recombination rates or minority carrier lifetime. We focus on the electron and hole capture cross sections and the associated energy level, referred to as the electronic properties of a defect. We do not discuss other defect properties, e.g., optical capture cross sections or vibration energies. The two measurement techniques this article focuses on are lifetime spectroscopy and DLTS, both standard techniques described in textbooks [1], [2], and so, only a short description of each technique is now provided. This article seeks to bridge this knowledge gap by presenting current issues, discussing approaches for the calculation of recombination from defect parameters, and discussing how to extract reliable and generalizable defect parameters from an experiment.

DLTS is a transient technique that utilises a p - n junction's ability to increase or decrease the free electron and hole concentration (quasi Fermi energy levels) from their equilibrium value, through the application of a voltage. When changing the free carrier concentration, the number of electrons/holes in an electrically active defect also changes. DLTS operates by placing the sample in an initial condition (usually under reverse bias). Next, a voltage pulse is applied (a more forward bias), to temporally increase the number of free carriers in the depletion region, with the original voltage finally being restored after the pulse. This increase in the excess carrier density, hopefully, changes the defect's charged state and places the defect in a nonequilibrium state when the sample is returned to the initial voltage. Once back at the original voltage, the defect reestablishes equilibrium with the free carrier density via the assumed emission of a carrier. In a standard DLTS measurement, the emission rate of carriers from defects into the conduction or valence bands is monitored through probing of the sample's junction capacitance. This emission rate of carriers is then determined at a variety of temperatures, which allows the determination of both a defect's energy level and capture cross section. When only the majority

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carrier emission rate is determined, this separation into a defect energy level and a cross-section can not be accurately performed. More advanced variants of DLTS, dating to the 1980s, use the measurement of both the capture and emission rate of electrons and/or holes, which allows the complete determination of both a defect's energy level and capture cross sections [3], [4], [5]. There are additional complexities that occur in these measurements such as the effects of the electric field dependence on the emission rate, which will not be discussed in this article [2].

The currently applied lifetime spectroscopy is typically a steady-state technique that excites excess carriers into the bands and determines the average time for them to recombine. The excitation is usually performed with light, and the excess carrier density is monitored via the sample's bulk conductivity via inductive coupling or microwave reflection/absorption [1], [6]. This application of lifetime spectroscopy is contactless and requires minimal sample preparation. Similar to DLTS, lifetime spectroscopy probes the impact of a defect by changing the number of free charge carriers. However, the number of free carriers can only be increased from their equilibrium concentrations, which means the state a defect is in depends on both the capture and emission rates of both the electrons and holes. This uncertainty makes the unique determination of a defect's parameters from lifetime spectroscopy difficult. Additional benefits of the technique are that the lifetime in the bulk region of the device directly provides low-field values for defect properties, and the technique is always sensitive to what defect limits the sample's lifetime.

II. BACKGROUND

The recombination activity of defects was first described in 1952 by Shockley, Read, and Hall [7], [8] as summarized in Appendix A. The Shockley–Read–Hall recombination statistics remains the core model to describe recombination at defects today, although many nuances have been introduced to render it applicable. A significant step in our understanding of defects, and a major focus of this article, is that all the defect parameters typically change with temperature. The defect's electron (σ_e) and hole (σ_h) capture cross section and energy level (E_d), vary with temperature and this temperature dependence is both nontrivial to measure [2] and seldom measured [9], [10]. The capture cross sections can either increase or decrease with temperature, following a power law or exponential relationship, depending on the underlying physical capture mechanism [11]. The temperature dependence of the energy level E_d stems from the change in Gibbs free energy change, $\Delta H - T\Delta S$ between states with an occupied and unoccupied defect: Any change in entropy ($\Delta S \neq 0$) on moving a carrier to or from a band leads to an E_d that varies with T . Most defect parameters, measured either via DLTS or recombination lifetimes have been performed without accounting for these temperature dependencies. As a result, most published defect parameters only provide an accurate description of the measured defect properties/behavior at the measured temperatures. In other words, most published defect parameters should not be used to describe rates that were not directly measured. Moreover, they may not be used to determine

the experimentally measured property at temperatures range outside the measured ranges; an example of such as case is provided later. We refer to such incomplete characterizations of the defect's electronic properties as yielding *apparent* defect parameters. More specifically, *apparent defect parameters* are a set of parameters that can only describe a subset of the possible transitions. That is there was an insufficient set of measurements to uniquely define each defect parameter at the measured temperatures. Typically an apparent defect parameter will not be able to describe both the capture and emission rate of a charged particle. For example, a standard DLTS measurement and analysis, which again consists of measurement of the majority carrier emission rate as a function of temperature and subsequent Arrhenius analysis using (A.4) or (A.3), produces values for both the majority carrier capture cross section and an energy level. These extracted parameters accurately describe the emission rate as a function of temperature within the measured temperature range but do not predict the capture rate of the majority carriers even at the measured temperatures. As such these parameters are *apparent defect parameters*.

A short example of how the difference between apparent defect parameters and SRH defect parameters arises from DLTS is now provided. The electron emission rate is $e_e = v_{th,e}(T) \sigma_e(T) N_c(T) e^{\frac{E_c - E_d}{kT}}$. The temperature dependence of the thermal velocity $v_{th}(T)$ and the effective density of states $N_c(T)$ are known quantities, and are used to make an Arrhenius plot of $\sigma_e(T) e^{\frac{E_c - E_d}{kT}}$, where E_c is the electron energy level at the edge of silicon's conduction band. When evaluating defect parameters from an Arrhenius plot, it is tempting to misunderstand the slope in an Arrhenius plot as the energy level of the defect ($E_c - E_d$) and not as correctly as a thermal activation energy. Thus, one can not directly calculate E_d nor σ_e from it. This is as $\sigma_e(T)$ influences the slope in the Arrhenius plot, this slope. This has two consequences. First, the parameterization of the measured values (apparent defect parameters) is generally not valid for temperatures outside of the range used in the experiment. Second, even within the temperature range of the experimental data, the values derived for the capture cross section and the defect energy do not correspond to what one may call "physical reality" (here, SRH defect parameters), being σ_e and E_d . This is numerically of concern if the results of one method need to be extrapolated to the temperature regime or compared with results from another method. More mathematical detail about this specific example is outlined in Section 1 of the supplementary material.

Truly universal defect parameters would describe all of a defect's transition rates, even temperatures lying out of the measured range. We use the term *SRH defect parameter* to describe such universal defect parameters, which if all three defect parameters are known can correctly describe the four possible single-charge-carrier transitions, e.g., generation and relaxation of electrons and holes as described by (A.1)–(A.4). As such the SRH defect parameters can be used to describe each transition set out by Shockley, Read, and Hall and be used to evaluate the recombination through the defect. Continuing the aforementioned example on DLTS, to obtain SRH defect

parameters from a standard DLTS measurement requires an additional measurement of the capture rate/relaxation rate of the majority carrier, known as a pulse filling measurement [2]. The addition of this extra independent information allows unique determination of the capture cross section and energy level at each temperature. Measurement over a range of temperatures can then provide the temperature dependence of these parameters. As we will show this process is rarely performed. In fact, it is possible with DLTS, with the addition of minority carriers, to measure all three SRH parameters at a single temperature [3]. The difference between apparent and SRH defect parameters is often overlooked within the photovoltaic community. Hence, a discrepancy between measured defect parameters from DLTS and from recombination measurements are common and these differences are often considered unresolved. While the example we have just provided included the measurement of all the defect's electrical transitions to be measured, this is not always the case. For example, the capture rate only depends on a single defect parameter; the capture cross section. With knowledge of the required sample parameters, determination of the defect's SRH majority carrier cross section can be made from a single measurement.

It has also been claimed that large differences between defect parameters evaluated from DLTS and from recombination is the use of the incorrect recombination statistics [11], [12]. Whether or not it is necessary to use Sah–Shockley statistics instead of SRH statistics can be estimated with the methods outlined in [13], as listed in Appendix B. An example calculation of the errors caused by using published values of defect's in silicon with SRH statistics in place of Sah and Shockley statistics is presented in Section 3 of the supplementary material and is notably smaller than the errors arising from the use of apparent defect parameters (less than a factor of two compared with an order of magnitude). Thus, the use of alternate recombination statistics will not be discussed further in this article, and at this time should not be considered a major source of uncertainty.

In summary, while apparent defect parameters accurately describe experimental findings, such as the recombination or emission rates at the measured temperatures, they often significantly deviate from the SRH defect parameters even at those temperatures. In other words, apparent defect parameters should only be used to evaluate the data they were fit to, and should not be used to evaluate other rates, or combinations of rates, particularly at other temperatures. We want to reinforce that the measurement and reporting of apparent defect parameter is useful and should continue. For example, DLTS is used to determine apparent defect parameters (majority carrier emission rates) to chemically identify defects. The discrepancy between apparent and actual SRH defect parameters is not particularly relevant for such applications. However, when using these apparent parameters outside of such an application, their difference to SRH defect parameters does matter. There is also a trend for DLTS-focused publications to not be explicit in if they provide apparent or SRH defect parameters [14]. This can make it difficult for nonexperts to ensure they are extracting SRH parameters and not apparent parameters. The numerical difference between reported SRH defect parameters and apparent defect parameters is explored in

the next section using the data within an online resource known as the defect repository [9], [10].

III. APPARENT AND SRH DEFECT PARAMETERS

This section focuses on the numerical comparison of Apparent and SRH defect parameters, and rates calculated from them. Its focus is the highlight that errors in calculated rates of orders of magnitude appear when using these different rates. An example is shown where using the same data and different calculation procedure defect parameters results in published defect parameters that differ by five orders of magnitude. It does this through analysis of DLTS data from an open-source online repository containing defects in silicon [9].

A subset of the repository's content is used in this article that being measurements performed with DLTS and its many variants. We only use articles based on DLTS since it is a well-defined and understood technique and so are the parameters it determines. The extraction of parameters from DLTS is set out in the supplementary material. This dataset contains a wide range of defects with energetic positions throughout silicon's bandgap and covers the expected range of capture cross sections in silicon, being 10^{-13} to 10^{-18} cm². It should be noted that the SRH defect parameters are only approximately 25% of the total data. The remaining publications only report *apparent* defect parameters. Publications are taken as reporting SRH parameters if they measured a sufficient set of data that the extracted parameters accurately describe both carrier emission and capture rates, i.e., measurements of majority capture and emission rates. As such the majority of values that are reported are not SRH capture cross sections.

The distinction between apparent and SRH defect parameters is only important if there is a significant difference between these values. The deviation between the two sets of defect parameters is now investigated. The apparent and SRH cross sections are compared for all defects that had both these parameters reported from DLTS measurements, being 30 defect states. The correlation between these values is shown in Fig. 1. The colors in Fig. 1(a) indicate measurements of the same defect states. As a result of the numerous defect states considered, some colors are reused. An attempt was made to ensure that these values were in a different region of the plot. It is clear from Fig. 1(a) that there are large deviations, spanning orders of magnitude, between the apparent and SRH capture cross sections, meaning the apparent defect parameters cannot be used in place of the SRH defect parameters. A much better correlation exists between the apparent and SRH energy levels, shown in Fig. 1(b), with deviations usually less than 50 meV. However, even this apparently small error may produce large deviations in predicted recombination behavior if the Fermi energy level is close to the determined energy level.

The impact of the deviations in both σ and E_d on a calculated recombination rate/lifetime can be estimated. The recombination rate is essentially proportional to the capture cross section of one or both carriers. This means the uncertainty in σ is directly translated into the recombination or lifetime. The uncertainty in the energy level is only relevant when the lifetime is limited

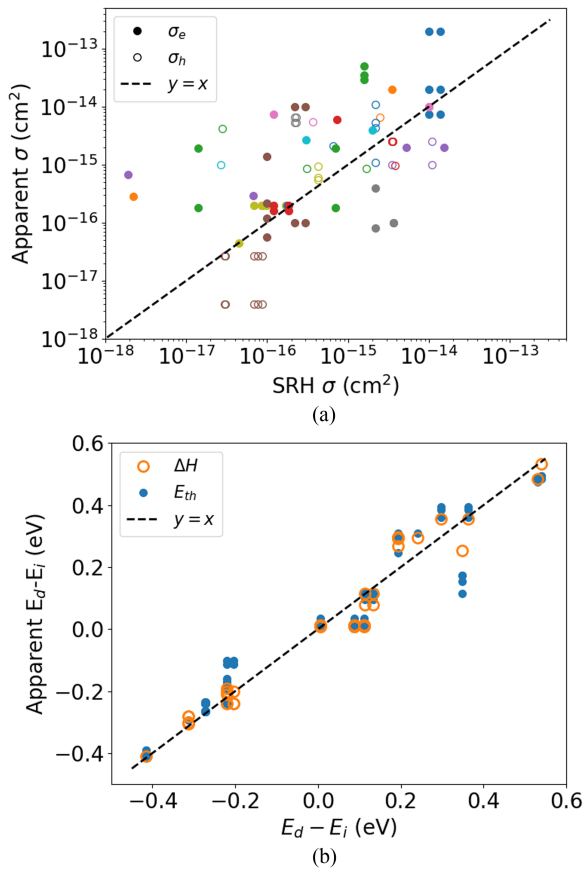


Fig. 1. Correlation between *apparent* and SRH defect parameters that have been published for the same defect. The temperature-dependent SRH defect parameters are evaluated at 300 K. (a) shows that the capture cross sections have a poor correlation, while the energy level in (b) shows a much higher correlation.

by the emission of carriers. This is more likely when the quasi Fermi energy level is closer to E_i than E_d is from E_i . It has been previously noted by the authors that using different values for the capture cross section, measured by DLTS, of interstitial iron results in over an order of magnitude difference in lifetime [15]. This difference is a result of the error that can arise when using apparent defect parameters in place of SRH defect parameters. It is also interesting to note that even for such a technologically relevant defect neither E_d (change in Gibbs free energy) nor the capture mechanism has been determined [16], and demonstrates the youth of the study of recombination rates and lifetimes.

The choice of the correct defect parameters can become even more complex, causing larger errors, when combining several characterisation techniques. This is because each technique measures its own unique apparent defect parameters. An example of this type of error is in the work of Rosenits et al., which focused on a defect in intentionally aluminium-contaminated Czochralski (Cz) silicon [17], [18]. The authors in [18] identified an inconsistency in the extraordinarily large value determined for the electron capture cross section in their original article [17], which used both DLTS and lifetime spectroscopy to obtain defect properties. In the original work, lifetime and DLTS measurements were performed on sister samples, with the lifetime measurements being performed only as a

function of injection level. The results from DLTS provided a $\sigma_h \approx 10^{-13} \text{ cm}^2$, which when combined with the results from lifetime spectroscopy resulted in a $\sigma_e \approx 10^{-10} \text{ cm}^2$, which is significantly larger than any other SRH parameters that was in the dataset used. Shortly after their original article, the same group published followed up on this work, this time using a different calculation method. The new approach replaced the use of the (majority carrier) hole capture cross section from DLTS with the defect concentration determined with DLTS. This defect density was then used in conjunction with lifetime data to calculate a temperature-independent electron capture cross section and hole capture cross section. The capture cross sections were, thereby, redetermined as $\sigma_h \approx 10^{-17} \text{ cm}^2$ and $\sigma_e \approx 10^{-15} \text{ cm}^2$, respectively. The new values for the capture cross sections are 4 to 5 orders of magnitude smaller than those in the original report and now well within the normal range of defects within the dataset (10^{-13} to 10^{-18} cm^2). The use of the defect concentration rather than the hole capture cross section was a particularly good decision as the hole capture cross section was an apparent defect parameter. This is as the hole capture cross section was evaluated from an Arrhenius plot. The switch to using a defect concentration, determined from the size of the capacitance decay, should be significantly more correct for a defect that is uniform with depth throughout the sample. This approach, combining the defect concentration from DLTS with spectroscopic lifetime to determine the capture cross sections, is promising for uniformly distributed defects. DLTS probes the properties within the reverse bias depletion region while lifetime measurements probe where the light-generated carriers recombine, throughout the device. As long as these probed volumes have the same defect concentration, these measurements can be combined. The deviations in such a concentration measurement are expected to be less than an order of magnitude, a smaller error than that occurred from using the apparent capture cross section.

The work of Rosenits continued to try to address the difference between the hole capture cross section determined by DLTS, and this new value is determined from the combination of DLTS and lifetime spectroscopy, values four orders of magnitude apart. Rosenits suggested that this difference may be a result of DLTS was measured near 200 K, while lifetime was measured near 300 K. That is the hole capture cross section changes four orders of magnitude from 200 K to 300 K. This would require an unusually strong temperature dependence of the capture cross-section. In light of the poor agreement between apparent capture cross sections reported by DLTS and the SRH parameter shown in Fig. 1(a), we suggest that the hole capture cross section determined with DLTS by Rosenits et al. is an apparent capture cross section, and could be significantly different from the actual hole capture cross section at 200 K, which would have been determined if direct capture measurements were taken. Confusingly, the likely reason leading to the deviation between the measured apparent and SRH capture cross section is that the hole capture cross section changes with temperature and that this was not taken into account in the DLTS analysis. The error was in assuming that an SRH capture cross section was determined by the standard DLTS measurement. A simple method to check for consistency between DLTS and lifetime spectroscopy in

such cases is to compare values more directly extracted from the two techniques. That is DLTS's independently determined defect concentration and majority capture cross section, with the product of these two quantities that is determined from lifetime spectroscopy. Thus, a direct comparison provides a check if the techniques are in agreement.

On a separate note, Rosenits also proposed a chemical identification of the defect they measured, relating it to aluminium and oxygen based on previous DLTS work from Marchand [19]. This assignment was made due to the close agreement of the defect energy level determined with DLTS from the two works. However, direct comparison of the emission rates from these publications shows the emission rates differ by over an order of magnitude at 190 K, being 100 s^{-1} for Rosenits versus 5.2 s^{-1} for Marchand, respectively. This difference in emission rates demonstrates that these defects are not the same defects. This type of missassignment is not uncommon, with similar occurrences happening with the well-studied defect of interstitial iron. Defects identified in DLTS measurements, were said to be the same when they had similar energy levels, however, their emission rates were orders of magnitude apart meaning some articles were not reporting on the Fe_i defect [16], [20].

This section has described that the majority of defect parameters reported in publications are not SRH defect parameters. The use of these apparent defect parameters can lead to differences in several order of magnitude in the calculated lifetime. We also highlighted that these incorrect values are used within literature. While the SRH parameters are often not reported, there are well-established methods, based on DLTS, to determine all three SRH defect parameters from a single sample, and so can be obtained. We then finished by providing an extended example of the energy large errors that can occur when combining apparent defect parameters from different techniques.

IV. VARIANCE IN REPORTED SRH PARAMETERS

With large differences between apparent and SRH defect parameters established, we now focus on the variance in reported SRH parameters for the same defect state. Previous attempts to compare such results on specific defects have shown a larger difference between reported values than the measurement error, estimated to be 20%, on the individual measurements [5], [16], [21], [22], [23]. Our results find a similar conclusion, while also noting that this variance is significantly lower than between SRH and apparent defect parameters for the same defect.

We have identified SRH parameter sets reported from DLTS studies for silver, gold, chromium, iron, molybdenum, nickel, platinum, titanium, vanadium, and tungsten. The repeatability of the reported capture cross sections of these defect states are shown in Fig. 2. Our depiction of any temperature dependent capture cross sections was evaluated at the temperature of 300 K. Deviations between repeated values are seen to extend over to a factor of 5 for a single defect state ($\text{Ag}_{s,d}$, $\text{Ti}_{i,dd}$, $\text{V}_{i,dd}$). While being significantly outside the quoted measurement error, this deviation is still significantly smaller than between the apparent and SRH capture cross sections as shown in Fig. 1(a).

The cause of large deviations (factor of 3) between reported SRH capture cross sections have been previously noted for

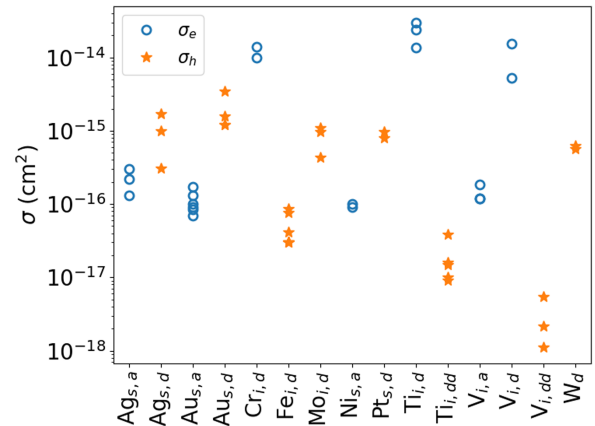


Fig. 2. Comparison of direct measurements of capture cross sections with DLTS by different groups. Measurement errors are often quoted as $\approx 20\%$, and so not visible on this figure.

substitutional gold [5], [21] and interstitial iron [22]. Possible causes for such deviations have been suggested to be: improper measurements [23], improper correction of the high fields [24], the temperature dependence of the defect's emission or capture rates [21], [25], measurement of the incorrect defect [20], [22], issues with pulse shaping [26], or the existence of two defect levels with very similar emission rates [27], [28]. The data presented in the following analysis are taken after 1980, when these effects can be considered well known by well-established groups.

The cause of some of the deviations in Fig. 2 is known. For example, vanadium's double donor ($\text{V}_{i,dd}$) hole capture cross section was measured by three different groups. The data for each group agree well with the temperature range that all the authors measured. However, when projected to room temperature, as done in Fig. 2, one value becomes significantly larger than the others. This dataset is that of Lemke, and is the dataset that spans the largest range of temperature [29]. Lemke found that with a larger measured temperature range, the functional fit used by the other authors did not represent his extended dataset, and so, changed the assumed temperature dependence. This resulted in a substantially different temperature dependence, and hence, a different value when the function form is projected to 300 K. Another example of known deviation in Fig. 2 comes from the reported hole capture cross-section of the silver donor level. The determination of the smallest value shown did not account for the variation of the capture rate in the space charge region (field-dependent emission rate) [30]. These examples were presented to highlight that significant errors (several factors) are still likely to occur, although larger factors are more likely systematic errors. In both cases, the final uncertainties, while large, are still significantly less than the several orders of magnitude that can arise from using apparent defect parameters.

Of course, the cause of all deviations in Fig. 2 is not known. Such unknown deviation exists for the hole cross section for the titanium double donor ($\text{Ti}_{i,dd}$). The work of Wang determined the highest value for the hole capture cross section and acknowledged its relatively large size. However, no reason has been given to explain why this might be the case [3]. Wang himself writes "The reason for the difference between our data and others was not clear, but we note that as long as this rate is in its given

order of magnitude and small, it has no effect on either the low- or high-level recombination rate in n- or p-Si.” This quote also highlights the sentiment within the DLTS community at the time that an order of magnitude is an appropriate uncertainty.

The impact of variation in capture cross section on the modeled lifetime, and hence, voltage of a photovoltaic device can be quantified. For simplicity, we assume that the sample is in low injection, so only minority carriers are important, and the defect in question is the dominant recombination channel. Under these assumptions, for p-type material, the minority carrier lifetime is related to the minority carrier capture cross section by

$$\tau_e = \frac{1}{\sigma_e v_{th,e} (N_{d,s} + N_{d,s+1})} \quad (1)$$

where τ_e is the minority carrier (electron) lifetime, $v_{th,e}$ is the thermal velocity of electrons, and $N_{d,s}$ is the concentration of defects in state s . A similar expression exists for holes.

The uncertainty in the terminal voltage V arising from an uncertainty in the capture, the cross section can be obtained from the relationship between the voltage and the electron and hole carrier densities (n_e and n_h), assuming a constant quasi-Fermi energy level splitting with depth

$$V = \frac{kT}{q} \ln \left(\frac{n_e n_h}{n_i^2} \right). \quad (2)$$

Substitution of the minority carrier density by the product of the lifetime and generation rate, we obtain

$$V = \frac{kT}{q} \ln \left(\frac{G \tau n_h}{n_i^2} \right). \quad (3)$$

The uncertainty in the voltage can be obtained by taking the difference of the expected voltages with lifetimes τ_1 and τ_2 as

$$\Delta V = \frac{kT}{q} \ln \left(\frac{\tau_1}{\tau_2} \right). \quad (4)$$

Substitution of the minority carrier lifetime defined in (1), under the assumption that only the minority capture cross sections differ between τ_1 and τ_2 , provides

$$\Delta V = \frac{kT}{q} \ln(\sigma_2/\sigma_1). \quad (5)$$

This result predicts a change in expected voltage of ≈ 18 mV at room temperature from a factor of two uncertainty in the capture cross section. This difference is significant, especially considering that in some samples the reported capture cross sections vary by a factor of five, resulting in 42 mV uncertainty in expected device voltage. The same calculation can be performed for an n-type sample with identical results.

This large variation in terminal voltage may suggest that measurement of a device’s open-circuit voltage or implied voltage may be a route to improve the accuracy of the reported capture cross sections. While this is technically possible, it also requires knowledge of the defect concentration, the number of charge states, and the number of different defects that impact the lifetime of the sample. These conditions have so far provided difficult to achieve, especially to result in an error less than a factor of two [4]. This difficulty is similar to the problem with

TABLE I
COMPARISON OF DEFECT PARAMETERS MEASURED SEPARATELY WITH DLTS AND LIFETIME TECHNIQUES

Defect	Method	Energy level (eV)	Capture cross section (cm ²)
Cr _i	DLTS [31], [32], [33] lifetime[34], [35]	$\Delta H = E_c - 0.22$	$\sigma_e = 1 \cdot 10^{-14}$
		$\Delta H = E_c - 0.24$	$\sigma_e = 2 \cdot 10^{-14}$
Fe _i	DLTS[20], [36]	$\Delta H = E_v + 0.39$	$\sigma_h = 8 \cdot 10^{-17}$
	DLTS[20], [36]		$\sigma_e = 2 \cdot 10^{-14}$
	lifetime [37], [38], [39] lifetime [37], [38], [39]		$\sigma_h = 7 \cdot 10^{-17}$ $\sigma_e = 7 - 20 \cdot 10^{-15}$

extracting cross sections from lifetime measurements. Values reported by lifetime measurements for three of the four capture cross sections of gold are over five times larger than those reported by DLTS [5], significantly outside the consistency observed with DLTS.

This section has demonstrated that there is an inconsistency between reported SRH parameters determined by DLTS measurements outside its quoted error. This technique is the gold standard for the electrical characterisation of defects, and as such its uncertainty may be considered a limit to which electronic defect parameters are known. The size of this variation leads to significant differences in recombination rates and modeled device performance. Possible causes for some of the remaining variances were outlined. It is important to note that this variance is still significantly lower than when using apparent parameters or those reported by other techniques such as lifetime spectroscopy.

V. CONSISTENCY BETWEEN PARAMETERS DETERMINED FROM DLTS AND LIFETIME SPECTROSCOPY

One purpose of SRH statistics is to predict the recombination lifetime of a defect, and yet the SRH defect parameters extracted by DLTS have to date not been shown to allow quantitative prediction of lifetimes. We now demonstrate that SRH defect parameters can be used to calculate recombination rates and vice versa. We compare independent measurements on the same type of sample with the two techniques. If the different techniques provide the same defect parameters, judged as being a factor of two difference for the capture cross section and 20 mV for energy level, then the two techniques will be considered in agreement with each other. Then, it can be said that the determined parameters are truly SRH parameters. Two monovalent defects are now analyzed, the first being interstitial chromium and the second being interstitial iron. These defects are chosen as they are both well-studied defects with many publications focusing on them to draw data for this review. The values which are considered to be in good agreement are shown in Table I.

Interstitial chromium is a monovalent defect in silicon with a temperature-independent σ_e . Its defect parameters, $\Delta H = E_c - 0.22$ eV, and $\sigma_e = 1 \times 10^{-14}$ cm², have been measured with DLTS at ≈ 100 K [31], [32], [33]. Two high-quality studies have used lifetime measurements to obtain defect parameters of interstitial chromium. These publications performed lifetime measurements as a function of injection level and temperature by Schmidt [34] and injection level and doping by Sun [35]. The defect’s energy level was calculated by different methods in

both articles with Schmidt calculating it from measurements of an n-type sample as a function of temperature (300–450 K) [34] and Sun calculating it from measurements of several samples with varying doping types and concentrations at a fixed temperature [35]. Both studies determined the energy level be $E_c - 0.24$ eV.

We now compare the reported capture cross section for interstitial chromium. The σ_e has been determined from lifetime spectroscopy from the absolute value of the sample's lifetime assuming a known defect concentration. Schmidt determined the defect concentration with DLTS [34], while Sun determined it from the total chromium content added to the melted silicon during ingot growth [35]. Both approaches provided similar values for $\sigma_e = 2 \times 10^{-14}$ cm², very similar to the DLTS values of 1×10^{-14} cm². As these values are within a factor of 2, we consider them in agreement, especially since there is a 200 K temperature difference between the temperatures at which DLTS and lifetime measurements were performed. While it is clear that Sun's σ_e measurement is independent of the DLTS results, it may not be clear that Schmidt's measurement is also independent of DLTS. While Schmidt's determination of σ_e used data from the DLTS measurement, that data are independent of the extraction of the majority carrier capture cross section. Hence, it is still an independent measurement. More specifically, Schmidt's result combined the defect concentration determined from DLTS and combined with the product of the defect concentration and capture cross section provided by lifetime spectroscopy, to determine the capture cross section. The defect concentration is determined by the magnitude of the capacitance change in DLTS, while the determination of the capture cross section is obtained from the capture rate of a defect. An alternative phrasing is that the product of the capture cross section and the defect concentration determined from DLTS can be used to calculate the electron lifetime determined by Schmidt, and this is again in agreement. No measurements of the σ_h are known to have been performed by DLTS-based techniques, although good agreement (a factor of 2) is seen between the different groups performing lifetime spectroscopy, being in the range, $0.4 - 1 \times 10^{-14}$ cm².

Interstitial iron is another well-studied monovalent defect in silicon, for, as we will see, which good agreement can be seen between DLTS and lifetime spectroscopy. Unlike interstitial chromium, interstitial iron has a temperature-dependent capture cross section (σ_h) appearing with an Arrhenius energy barrier of 60 meV. DLTS has measured $\Delta H = E_v + 0.39$ eV [20], [36], and $\sigma_h = 8 \times 10^{-17}$ cm² and $\sigma_e = 2 \times 10^{-14}$ cm² at 300 K. Interstitial iron has been measured using lifetime spectroscopy by varying the temperature, doping, as well as toggling iron between its metastable states of interstitial iron and iron-boron. Unlike chromium, different groups have reported varying parameters being extracted from both DLTS and lifetime spectroscopy [1], [22], [38], [39], [40], [41]. This variation in the published DLTS work arises from not accounting for the variation of SRH defects parameters with temperature, i.e., they determined apparent defect parameters. Similar variation from apparent to SRH parameters is expected to exist within the data

produced from lifetime spectroscopy. We now demonstrate that good agreement can be found between these techniques if careful and a systematic approach is taken.

Good agreement occurs between DLTS and lifetime spectroscopy at room temperature, with values determined from lifetime spectroscopy as $\sigma_h = 7 \times 10^{-17}$ cm² (DLTS provided $\sigma_h = 8 \times 10^{-17}$ cm²) and $\sigma_e = 0.7 - 2 \times 10^{-14}$ cm² (DLTS provided $\sigma_e = 2 \times 10^{-14}$ cm²), respectively [37], [38], [39]. The temperature dependence of the capture cross sections have also been determined with both DLTS and lifetime spectroscopy. This process was done via independent determination of the capture cross section at each temperature. The lifetime spectroscopy of Paudyal et al. [39] matches well with the DLTS work of Lemke [36], being an exponential temperature dependence for the hole capture cross section and power law for the electron capture cross section. The determination of the capture cross section of holes from Paudyal's lifetime data and Lemke's DLTS data was done isothermally, i.e., a value of the hole capture cross section was determined at each temperature using only data at that temperature. For this reason, the determined values are not impacted by the temperature dependence of the capture cross sections. Paudyal did not determine the energy level of iron.

We have not used the defect parameters of interstitial iron determined by Rein [42], who is well known for doing some of the most thorough work on lifetime spectroscopy to date. Given the respected quality of this work, we now address why we did not use his data. Rein measured lifetime as a function of injection level and separately temperature in p-type silicon with a doping density of 2.9×10^{14} cm⁻³. Rein found interstitial iron to have $\sigma_e \propto e^{\frac{0.024}{kT}}$ and $E_{th} = 0.418 \pm 0.005$ eV, resulting in $\Delta H = E_v + 0.395$ eV. While the energy level (enthalpy) would appear correct the value and the function determined is in contrast to measurements from both DLTS and lifetime spectroscopy mentioned earlier, which had $\sigma_e \propto T^{-1.5}$. A possible explanation for this discrepancy is a breakdown in one of Rein's experimental assumptions. Specifically, that the sample was at sufficiently low injection such the lifetime is limited by the capture of electrons. According to our estimation, Rein would have required the carrier density to be below 10^{11} cm⁻³ at room temperature, which might have been impossible to reach experimentally. The limit on the maximum excess carrier density for this assumption to hold also decreased with temperatures. If the excess carrier density is above this value, the lifetime of the sample will increase above its low injection value, resulting in a capture cross section that appears to increase with temperature, as observed by Rein. It is suspected that this was not seen by Paudyal as the sample doping he used was roughly two orders of magnitude higher, relaxing this effect.

We have compared defect parameters determined from DLTS and carrier lifetimes for the simple defects of interstitial chromium and interstitial iron. These independently measured parameters are found to agree when proper measurement and analysis is performed. As such, it is expected that a set of SRH defect parameters can be found to describe both the recombination rate and individual transitions of defects, i.e., their SRH defect parameters.

VI. DISCUSSION

From a review of published data, this article has demonstrated that accurate calculation of recombination properties from defect parameters determined with DLTS is possible. Also, that lifetime spectroscopy is able to provide accurate values of defect parameters. The accuracy to which this is assumed to be currently possible is within two to three times for a capture cross section and 10 s of millivolts for the energy level. While this variance could still be considered quite large, as it could represent a doubling of the expected recombination, it is significantly less than the expected variance if apparent defect parameters are used. The large variation of values for the apparent parameters cited in literature illustrates their “apparent nature.” They do not describe the properties of the defect, such as “true defect parameters” would, and instead the apparent parameters describe the experimentally measured property for the specific defect and experimental conditions, such as temperature. Therefore, it is a mistake to intemperately these values as actual “defect parameters.” Such a mistake would result in recombination rates that differ by four to five orders of magnitude, as we have shown previously. This result suggests that the conclusions of previous studies may have to be reexamined. This situation raises the question: for what can we use apparent parameterization? We will now provide an overview of the two current techniques DLTS and lifetime spectroscopy, what they are currently being used for, and what they could be potentially used for.

DLTS is predominantly used for determining emission rates and measuring defect concentrations. DLTS provides a direct measure of these. From this measured data, several analyses can be performed, e.g., the correlation of an emission rate to a chemical species, investigating the concentration of the defect with other processing, and correlating the level with device performance. This is a very robust approach and is only limited by the sensitivity of DLTS, being typically five orders of magnitude lower than the doping density for detection and four orders of magnitude for characterization [43]. DLTS has more rarely been used to determine the SRH parameters of defects [14], although it is possible. While we have shown that it is possible for agreement to be achieved between DLTS and lifetime spectroscopy, there are reasonable arguments to expect such agreement to not be generally possible, particularly for more exotic defects. DLTS measurements are performed at quite different conditions from those at which the recombination rate is generally acquired. DLTS is performed in the space charge region with $n_e n_h \ll n_i^2$, while lifetime measurements are dominated by the bulk properties during which $n_e n_h \gg n_i^2$. This translates to DLTS being measured with essentially no minority carriers, usually under high fields, and at lower temperatures, while lifetime measurements are performed with many excess carriers, low fields, and typically in a higher temperature range. While the temperature dependence of the SRH parameters can be treated appropriately, carrier-induced band-gap narrowing, electric field dependence, or other unknown effects could alter the capture/emission processes, so the results determined under DLTS conditions become nonpredictive of behavior in devices. To confirm or disprove such concern requires studies focused on using values extracted from DLTS and using them

to estimate the recombination in a device, with comparisons to lifetime measurements. We are not aware of any such systematic studies, which would be invaluable for a deeper understanding of both the characterization techniques and recombination physics.

Lifetime spectroscopy has risen within the photovoltaics community as a characterization technique that is used to address some of the perceived barriers posed by DLTS. It directly measures the recombination rates, and then, attempts to determine the defect parameters of a single or collection defects assumed to be dominating the material recombination. There are two main reasons for lifetime spectroscopy’s rise in popularity. The first is that the measurement of a device’s lifetime was already a standard measurement in solar cell laboratories although it was not used for the study of defects. Lifetime measurements were already being used to provide an estimate of a devices voltage potential and current collection probability on a partially processed device. The second is that lifetime spectroscopy measures the dominant recombination sources, hence, it is sensitive to the performance limiting and most relevant defects for the solar cell performance. This means that lifetime spectroscopy is always sensitive enough to measure the lifetime-limiting source, a point that should not be underestimated as some lifetime-limiting defects in solar cells, e.g., interstitial iron, approach concentrations below 10^{10} cm^{-3} [42]. These arguments are often presented to validate the use of lifetime spectroscopy over more deterministic methods such as DLTS or EPR, i.e., techniques from which different defects will provide a unique signal. However, especially designed samples can be made that provide more conclusive results, for example, silicon samples have been made that allowed defect concentrations $< 10^{10} \text{ cm}^{-3}$ to be measured with DLTS [44].

Lifetime spectroscopy is usually performed with two main aims. One aim is to identify the defect that is limiting a device/material performance by extracting defect electrical parameters and comparing those with known parameters from DLTS. Considering the points raised in this article, it is clear that this approach requires care on several fronts. Specifically, this analysis must account check for multivalent defects and temperature dependence of the defect parameters, and be sure they are compare with SRH defect parameters from DLTS . One method to avoid these complications, which is slowly occurring, is to create a set of reference samples and measure how specific defects impact the recombination of a device. From this set of data, lifetime spectroscopy will obtain its own set of apparent defect parameters, which may serve as specific fingerprints of a defect. This is a similar approach to how standard DLTS is currently able to determine what impurity is in a semiconductor, as neither technique intrinsically provides information about the chemical nature of defects.

The other aim of lifetime spectroscopy is to improve the accuracy of SRH parameters. This goal requires temperature-dependent values or values defined at specific temperatures to be determined, along with knowledge of the defect/s concentrations. These are nontrivial requirements, but they can be accomplished. However, without all this prior knowledge, lifetime spectroscopy can still provide a direct measurement

of the temperature dependence of the minority carrier capture cross section and an assumed temperature-independent energy level (enthalpy), as long as one defect always dominates and its concentration does not change during the measurement. This application of lifetime spectroscopy is referred to as temperature-dependent lifetime spectroscopy and measures the lifetime of the sample under low injection conditions as a function of temperature. Note that this version of temperature-dependent lifetime spectroscopy provides apparent defect parameters different to that determined by DLTS and other variants of lifetime spectroscopy, e.g., injection level and doping density-dependent lifetime spectroscopy. However, such apparent parameters may still provide significant value, in the same manner as E_{th} and σ_{∞} do for DLTS. In this form, they represent apparent defect parameters that accurately describe recombination as a function of temperature, and hence, may be used to discover what defects limit a sample lifetime.

VII. CONCLUSION

This article has reviewed data published on defect properties in silicon, with a focus on relating the electronic parameters of defects to the defects' recombination rate. By describing published defect parameters as either apparent defect parameters or SRH defect parameters, we have demonstrated that large errors have been possible in the calculation of transition rates, including recombination rates. From a combination of publications on DLTS and separate publications on recombination rates, we have found that SRH defect parameters can accurately describe all the transitions for a defect. While apparent defect parameters can cause errors in the prediction of rates that have not been measured on the scale of orders of magnitude, these errors have been a direct result of apparent parameters being determined from an incomplete fit to a subset of the rates.

The main cause of differences between SRH and apparent defect parameters has been that the determination of the apparent defect parameters has been performed assuming no temperature dependence of at least some of the reported defect parameters, or assume an incorrect functional form of the temperature dependence, e.g., exponential instead of the power law. As a result, apparent defect parameters, measured with DLTS, can lead to inaccuracies of several orders of magnitude when used to calculate recombination rates. A key strategy to overcome such inaccuracies has been to ensure that all the parameters have been evaluated under the assumption that they have been temperature dependent, or have the defect parameters determined with data taken at a single temperature, as occurs for DLTS when SRH parameters have been determined. Another approach has been to only use apparent defect parameters in the same condition as they have been measured, although these parameters may be hard to find for a specific case.

This article has also demonstrated that it has been possible for SRH parameters determined by DLTS to be able to predict the recombination rate caused by the defect. Specifically, this has been shown with the relatively simple defects of interstitial iron and interstitial chromium. This has opened the path to use such measurements for the prediction of photovoltaic

device performance from independently determined SRH defect parameters.

Finally, this article has highlighted that the current analysis of recombination rates has provided apparent defect parameters that should not be directly compared with values from other techniques, as it is likely their specific apparent defect parameters deviated from the SRH parameters in a different way.

These determined parameters should not be used to provide a general description of the recombination behavior, although they can still be considered useful as they are easier to determine and act as a fingerprint for which defects for similar material to which they have been measured in.

APPENDIX A

This section discusses some of the essential concepts to enable accurate prediction of a defect's recombination properties from a combination of different measurements.

The SRH recombination statistics is the most basic description of recombination through a defect. Following Shockley and Read, we consider a semiconductor with a single defect species that has only two charged states: neutral and ionized. It changes between these states via capture or emission of an electron or hole. The volumetric relaxation rates of electrons and holes into a defect are, respectively, given by

$$R_e = \sigma_e v_{th,e} n_e n_{d,h} = c_e n_e n_{d,h} \quad (A.1)$$

$$R_h = \sigma_h v_{th,h} n_h n_{d,e} = c_h n_h n_{d,e} \quad (A.2)$$

where c_e and c_h are the capture coefficients of electrons and holes, $v_{th,e}$ and $v_{th,h}$ are the thermal velocities of electrons and holes, n_e and n_h are the free electron and hole carrier density, n_i is the intrinsic carrier density, $n_{d,e}$ and $n_{d,h}$ are the concentration of electrons and holes in the defects, and σ_e and σ_h are the capture cross section of electrons and holes. The capture rate is also often used. The capture rate is the capture coefficient multiplied of a carrier type by the excess carrier density of that carrier.

Similarly, the volumetric generation rates of free electrons and holes from a defect are related to R_e and R_h by detailed balance and given by

$$G_e = \sigma_e v_{th,e} n_{d,e} n_i e^{(E_d - E_i)/kT} = e_e n_{d,e} \quad (A.3)$$

$$G_h = \sigma_h v_{th,h} n_{d,h} n_i e^{-(E_d - E_i)/kT} = e_h n_{d,h} \quad (A.4)$$

where e_e and e_h are the emission rate for electrons and holes, E_i is the value of the Fermi energy in an intrinsic semiconductor in the dark, k is Boltzmann constant, and T is temperature. E_d is the energy needed to emit one electron from the defect and is thus the chemical potential difference between having an electron bound to the defect and having that electron free with the defect ionized. It, therefore, is the change in Gibbs free energy at any constant pressure and temperature [45], [46]. The recombination rate is the relaxation rate minus the generation rate. The assumption that in a steady state, the recombination rate for electrons must equal that of holes, leads to the SRH formalization of recombination (R) that relates the recombination rate through a defect

to the defect's parameters

$$R = \frac{n_e n_h - n_i^2}{\frac{n_e + n_i \exp((E_d - E_i)/kT)}{N_d \sigma_h v_{th,h}} + \frac{n_h + n_i \exp(-(E_d - E_i)/kT)}{N_d \sigma_e v_{th,e}}} \quad (\text{A.5})$$

or in terms of quasi-Fermi Energy levels of electrons and holes ($E_{f,e}$ and $E_{f,h}$, respectively) instead of carrier densities

$$R = \frac{n_i (e^{(E_{f,e} - E_{f,h})/kT} - 1)}{\frac{e^{(E_{f,e} - E_i)/kT} + e^{(E_d - E_i)/kT}}{N_d \sigma_h v_{th,h}} + \frac{e^{(E_i - E_{f,h})/kT} + e^{(E_i - E_d)/kT}}{N_d \sigma_e v_{th,e}}} \quad (\text{A.6})$$

APPENDIX B

Since Shockley–Read–Hall recombination statistics was set out in 1952, there has been substantial improvement in our knowledge of defects. One such improvement has been that most defects have more than two different charge states [26], with measurements of up to five states existing for a single defect [47]. As an example, 22 out of 26 transition metals in silicon have more than two charge states [33]. Such defects are usually referred to as multivalent defects, as opposed to monovalent defects, which are the basis of SRH statistics. A monovalent defect has only two charge states and as such can be described with a single energy level, while multivalent defects have more electron charge states and cannot be described with a single energy level. The recombination statistics to describe multivalent defect were set out by Sah and Shockley (SS) in 1958 [48]. While the predictions of the recombination rates can be different when using SS statistics and SRH statistics, these differences are much smaller than the incorrect use of apparent defect parameters. A worked example of these differences are provided in the supplementary material. Moreover, in 1970, Choo provided a check to confirm if SRH statistics are sufficient to describe the recombination rates through a multivalent defect [13]. That is, a multivalent defect can be considered as several independent monovalent defects with energies $E_1 < E_2 < \dots$ when

$$e^{\frac{E_j - E_i}{kT}} \gg \frac{C_{e,i}}{C_{e,j}} \gg 1 \quad (\text{A.7})$$

$$e^{\frac{E_j - E_i}{kT}} \gg \frac{C_{h,j}}{C_{h,i}} \gg 1 \quad (\text{A.8})$$

for $j > i$. However, this check is not performed although it is often fulfilled. An example of the difference between the calculated lifetimes for a multivalent defect is provided in the supplementary material. The calculations there show a difference in recombination rates of approximately a factor of two. Given this a relatively small value (factor of 2) and that Choo's work provides a check for this assumption, this error will not be discussed further within this article.

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