Insights on the electronic parameterisation of defects in silicon obtained from the formation of the defect repository

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ABSTRACT: Defects in semiconductors have been studied for over 60 years. In this time there has been significant progress in measuring and understanding of these defects. This development has led to various types of defect parameters being reported. A large proportion of these are not suitable to accurately determine the impact of a defect on the performance/lifetime of a device. This paper outlines these developments and different values that have been reported. It then suggests a path so that the correct values important for lifetime can be determined.

The impact a defect has on a semiconductor lifetime in steady state was originally described by Shockley, Read, and Hall (SRH) [1], [2] in 1952, almost 70 years ago. Since then the parameterisation used to describe defects has not significantly changed, as they can still accurately describe all capture and emission processes. The parameterisation consists of three temperature dependent parameters, being: a capture cross section for electrons (σ_e) and holes (σ_h), which is a measure of how easily an electron/hole can move between the defect and the conduction/valance band respectively; and an energy level of the defect (E_d), which affects the emission of electrons and holes from the defect. However, what these terms mean and how they should be measured has changed significantly over this ~70 year period. Unfortunately, this evolution of concepts and measurement techniques is not well known within the general photovoltaic community. Moreover, this paper highlights that there are actually very few defects for which electronic parameters are accurately known, thus allowing the defects impact on a devices lifetime to calculated. An example used in this paper highlights the use of incorrect values results in an order difference in the recombination activity. This lack of data has led to the use of incorrect comparison of published data. This paper will outline these theoretical developments as well as highlight methods by which the electronic defect properties have been accurately measured. The review of this paper is limited in scope to the data on 170 different defects captured within the defect repository [3].

HOW HAVE WE BEEN MEASURING DEFECT PARAMETERS?

Halfway through the 20th-century, interest arose in defects in semiconductors, as they were found to be impacting the performance of semiconductors. Rapidly a host of techniques arose to measure the properties of these defects, with junction-based techniques becoming the techniques of choice for the measurement of their electronic properties. An example of this is Sah's work[4] on the substitutional gold defect in silicon, where three different junction-based techniques were used to measure defect emission rates at different temperatures. They reported the data as inverse emission rates spanning over 9 orders of magnitude from 10 µs to over 1 ks. [4] Of these junction-based techniques, transient capacitance measurements, with their simple analysis [5] and high sensitivity, quickly become the technique used to study the electronic nature of defects. This technique is more commonly known as deep level transient spectroscopy (DLTS).

Deep level transient spectroscopy has since been the technique of choice for the determination of electronic properties and concentration of defects for the semiconductor community. Unfortunately, DLTS is most commonly used to only find the emission rate of carriers from defects. PV applications are most interested in the recombination rate, which can be determined if the SRH parameters are known. The most commonly performed DLTS experiments, however, do not measure SRH defect parameters and thus do not allow accurate prediction of capture rates.

A more direct approach to determine the impact of contaminants on finished solar cell performance has also been used. Such an approach has been to intentionally contaminate silicon feedstock with known quantities of impurities, then use this standard processing to make solar cells and measure the final sample/device performance/properties [23]–[26]. While this approach does not give defect parameters, it is truly invaluable for determining the sensitivity of a manufacturing process to a particular contaminant.

WHAT HAVE WE BEEN MEASURING?

A large issue for evaluation of recombination properties of defects from published data exists, as most published data

are not SRH defect parameters, but rather "*activation*" or "*apparent*" defect parameters [6]–[8]. A description of the difference between these types of parameters follows later in the paper, but arises as SRH parameters are temperature dependent though this is not always account for.

To exemplify that SRH defect parameters are rarely reported, both types of defect parameters that exist within the defect repository are shown in Figure 1. The *apparent* parameters cannot be used within the Shockey Read and Hall framework to determine the recombination activity of a defect and as such quantify the defect's influence on device performance. An example of the errors this can result in is provided later in the document. These *apparent* electronic parameters have been reported because they can be determined from a single DLTS measurement. While *apparent* values do not allow the calculation of recombination of a defect, they do allow a consistent identification of the defect as well as its concentration, which is arguably the more useful value.
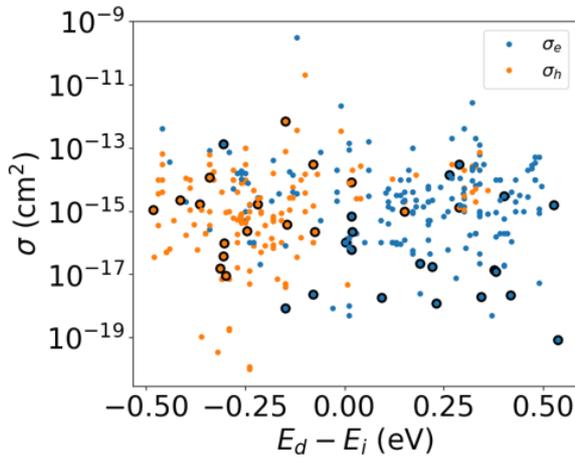

Figure 1: Comparing the number of published *apparent* to SRH defect parameters currently in the defect repository. The SRH values are highlighted with a black border. The vast majority are found to be *apparent* defect parameters.

The reporting of different types of defect parameters (SRH or *apparent*) is well established, being noted in textbooks for almost 30 years. [8] A brief overview of this difference, how it specifically affects DLTS, and its impact on the calculation of lifetime is now provided. The SRH energy level of a defect is the free energy change for ionization of the state change, i.e. the Gibbs free energy (ΔG) [6]:

$$E_d = \Delta G(T) \qquad (1)$$

where T is temperature. It can be expressed in terms of a change in enthalpy (ΔH) and a change in entropy (ΔS).

$$E_d = \Delta H - T\Delta S \qquad (2)$$

The change in entropy arises from both changes in the lattice and electronic re-configuration of the defect. For an n-type material DLTS directly measures the electron emission rate (e_e):

$$e_e = v_{th,e}\sigma_e(T)N_c \, e^{-\frac{E_d(T)}{kT}} \qquad (3)$$

where $v_{th,e}$ is the thermal velocity of electrons and N_c is the density of states in the conduction band and E_d is relative to the conduction band edge. Substitution of Equation 2 provides

$$e_e = v_{th,e}\sigma_e(T)N_c e^{-\frac{\Delta H}{kT}} e^{\frac{\Delta S}{k}} \qquad (4)$$

$$ln\,(e_e) - ln\left(v_{th,e}\sigma_e(T)N_c\right) = -\frac{\Delta H}{kT} + \frac{\Delta S}{k} \qquad (5)$$

A type of energy level for the defect is then typically determined from a linear fit of the natural log of emission rate to 1/T. There are two complications in the determination of an energy level from such a fit. The first is that the term containing ΔS does not have an inverse temperature dependence. Thus, the energy determined for the fit is limited to ΔH. The second complication arises from the unknown functional form and values for the temperature dependence of the capture cross-section. If the capture is thermally activated, i.e., changes exponentially with inverse temperature, $\sigma_e \propto e^{-\Delta E_\sigma/kT}$, then we arrive at the common form of the emission rate used for DLTS,

$$e_e = v_{th,e}\sigma_{e,app}N_c \, e^{-\frac{\Delta H + \Delta E_\sigma}{kT}} \qquad (6)$$

where $\sigma_{e,app}$ is a temperature independent apparent electron capture cross section and ΔE_σ is the energy barrier for carrier capture. As ΔH and ΔE_σ cannot be separated, DLTS extracts a thermal activation energy (ΔE_{th}). While this parameterisation does not give SRH defect parameters, it does accurately represent the emission rate as a function of temperature.

It may appear that the determination of all three SRH defect parameters is a hard problem to overcome, fortunately this problem was surmounted in the 1980's with the use of DLTS variants [11], [12]. At the core of this problem is that there are two electronic defect parameters that impact a DLTS measurement, both of which are unknown functions of temperature. To determine both values, two measurements are required to be performed at the same temperature. This can be done by measurement of the capture rate as well as the emission rate. Measurement of the capture rate may be done with DLTS by varying the filling-pulse time or pulse height. Issues can arise when the capture rate is very fast, e.g. capture rates faster than 1 ns. The remaining SRH parameter, the minority carrier capture cross-section, can then be determined with a modified DLTS measurement, where minority carriers are injected during the "filling pulse" [11], [12]. Note that when determining any type of defect parameters, it is also suggested to do it on a single sample, as there can be sample to sample variations [11], [12]. At the time of writing this paper we have only found data with both capture and emission rates measured for a handful of

defects, being: gold and gold hydrogen [11], [13], titanium [12], [14], [15] silver [16], iron [10], nickel and nickel related defects [17], carbon [18], and nitrogen-related defects [19]. The small amount of defects listed highlights the inability of data for accurate simulation the impact of defects on device performance. Please note that we do not claim this is an exhaustive list but rather the result of our ongoing literature survey.

PROBLEMS WITH RELATING DEFECT PARAMETERS TO LIFETIMES

The impact of using apparent parameters over SRH parameters for the determination of lifetime can be quite large. An example of this can be found for the well-studied interstitial iron defect, where values have been reported both accounting and not account for its temperature dependent capture cross section. Its defect parameters originally reported by Gerson were $E_d=E_v+0.45$ eV with a temperature independent $\sigma_h=$ 4x10^{-18} cm^2 [9], rather than the more accurate values from Istratov [10], as they do account for the temperature dependence of the capture cross section of $E_d=E_v+0.38$ eV and $\sigma_h=$ 6.9x10^{-17} cm^2 at 300 K, where E_v represents the valence band edge. Calculating the lifetime in low injection for a n-type sample with $N_d=5x10^{15}$ cm^{-3} and an interstitial iron concentration of 1x10^{12} cm^{-3} gives 15 ms and 0.9 ms respectively, a discrepancy larger than a factor of 10. This highlights the importance for using the correct values for the calculation of lifetime.

Even with the three electronic parameters of a defect determined it may not be necessarily sufficient to calculate the defect's recombination activity. To completely determine the impact of a defect on the lifetime/performance, even more information is usually required, as most defects have either multiple energy levels or are bi/metastable. A defect with multiple energy levels simply means the defect can have different charge states, e.g. it can have a net negative, neutral or positive charge. As most defects have multiple energy levels [4], accurate prediction of the lifetime requires a) the number of defect levels are known and b) each level must have the three defect parameters known. The first point may appear trivial, but as recently as 2015 the assignment of different charge states of the well-studied titanium defect [20] in silicon has been questioned. Unfortunately, this adds another layer of difficulty, one which DLTS is not able to conclusively determine. This inability to calculate the impact on a devices lifetime from defect parameters also reflects that it is very difficult to determine SRH defect parameters solely from lifetime measurements.

The impact of bi/metastable defects also complicates the calculation of the recombination strength of a defect. For such cases, not only do the electronic properties of both defects need to be known, but the reaction kinetics between the two states needs to be understood. A common example is the impact of the single-level defect of interstitial iron and its metastable transition to iron acceptor pairs. It is well known that this creates a metastable defect with boron and that the fractions of iron in interstitial or paired form changes during standard solar cell operating conditions [21]. Another

well-known example is the so called DX centres in III-V semiconductors. [22]

CONCLUSION

Reviewing the data within the defect repository has resulted in several key points that will aid our in progress defect characterisation. These include that there are several different types of electronic defect parameters being reported and that it is important to understand the difference between these. The difference between these parameters is if their temperature dependence has been accounted for. This difference results in parameters that can only be used for the calculation of specific rates, e.g. of the emission rate. Unfortunately, the values that can be used to determine the recombination of a defect on a device, are the values that are rarely reported. However, there are established methods to determine these values using mature methods such as DLTS. Even when the correct values are reported, further complications exist for the determination of the recombination strength, as the number of energy level of a defect must be known, and how to account for possible bi/metastability. All these problems occur for both the calculation of lifetime from defect parameters, but are equally relevant for trying to determine defect parameters from lifetime measurements.

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