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Methods for determining deep defect concentration from dependence of excess carrier density and lifetime on illumination intensity

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Abstract
Two methods are proposed for determining the deep defect concentration from dependences of excess majority carrier concentration and carrier lifetime on, respectively, illumination intensity and injection level. The methods are based on saturation of the excess majority carrier density with increasing illumination intensity and on an abrupt decrease in the lifetime of majority carriers with their increasing excess concentration, which takes place as a result of filling of the defect level by minority carriers. In contrast to the well known injection-level spectroscopy, both the methods make it possible to determine the density of a defect without knowing any of its parameters, such as energy level or recombination coefficient of electrons and holes. These methods are applied to boron-doped single-crystal silicon with radiation-induced deep defects of the phosphorus–vacancy, oxygen–vacancy and carbon–oxygen complex types. It is shown that with these methods it is possible to determine the density of only those deep defects which control free carrier density and lifetime and give rise to a significant difference between the excess concentrations and lifetimes of electrons and holes. The analysis is based on the assumption that (i) the density of deep defects is independent of the illumination intensity, (ii) processes of generation-recombination via deep defects are described within the Shockley–Read–Hall recombination theory and (iii) recombination via other defects, band-to-band recombination, Auger recombination, etc, are negligible.

1. Introduction

Determining the total impurity concentration is one of the most important problems at present. Currently several methods exist, including mass spectrometry, atomic absorption or emission spectrometry, x-ray fluorescence, nuclear activation analysis, etc [1]. The limited application of these methods and the high costs involved make them hardly suitable for routine measurements. For this reason, the carrier lifetime, sensitive to all electrically active deep impurities, is measured very frequently [2, 3]. With the lifetime determined, the deep defect density is commonly found by fitting or estimation if the recombination coefficients of electrons C_n, holes C_p and energy level of the defect E_l are already known [4, 5]. In this work, two rapid methods are proposed which can determine the deep defect concentration from the dependences of the excess carrier density and lifetime on, respectively, illumination intensity and injection level without any estimations and without knowing any of the above defect-related parameters.

2. Model considered and assumptions

We consider a single-crystalline silicon with boron concentration $N_a = 10^{15}$ cm^{-3} and radiation-induced defect–impurity complexes of the phosphorus–vacancy (E-centres), oxygen–vacancy (A-centres) and carbon–oxygen (K-centres) types. It is well known that the E-centres exist in phosphorus-doped silicon. However, it was suggested in [6] that radiation-induced diffusion of phosphorus atoms from the phosphorus-doped n^+-layer to the p-base layer occurs in n^+-p-p^+ silicon space solar cells irradiated with high-energy particles from the n^+-side. Hence, it is reasonable to study the effect of the E-centres on the properties of p-type silicon. The conclusion can then be extended to other single-level recombination centres, capturing, like the E-centres, minority carriers when in ground state. The energy level and the recombination coefficient of electrons C_n and holes C_p are taken to be E_c−0.43 eV, $C_n = 4 \times 10^{-8}$, $C_p = 4 \times 10^{-7}$ cm^3 s^{-1} for E-centres, E_v+0.36 eV, $C_n = 1.5 \times 10^{-7}$, $C_p = 2 \times 10^{-8}$ cm^3 s^{-1} for K-centres, and E_c−0.17 eV, $C_n = 8 \times 10^{-8}$, $C_p = 3 \times 10^{-6}$ cm^3 s^{-1} for A-centres [7, 8]. It is well known that the E- and A-centres may be either in neutral or in negatively charged states [7, 8], and the K-centres may be either positively charged or neutral [8]. Our estimations have been made for room temperature ($T = 300$ K) and deep defect densities $N_t = 10^{14}$, 10^{15} and 10^{16} cm^{-3}. The excess carrier concentrations and lifetimes have been estimated numerically as functions of the carrier photogeneration rate in the range from 10^{17} to 10^{23} cm^{-3} s^{-1}.

The analysis is based on the following assumptions: (i) the deep defect concentration is independent of illumination intensity; (ii) carrier recombination is described within the Shockley–Read–Hall recombination theory; (iii) the rate of recombination via the deep defects exceeds that via other defects and other channels, like band-to-band, excitonic, Auger recombination, etc.

3. Basic equations

The lifetimes of electrons τ_n and holes τ_p are estimated using the Shockley–Read–Hall recombination theory and the electroneutrality condition

$$\tau_n = \frac{1}{C_p N_t}\frac{n+n_1}{n_0\Delta p/\Delta n + p} + \frac{1}{C_n N_t}\frac{p+p_1}{n_0\Delta p/\Delta n + p} \tag{1}$$

$$\tau_p = \frac{1}{C_p N_t}\frac{n+n_1}{p_0\Delta n/\Delta p + n} + \frac{1}{C_n N_t}\frac{p+p_1}{p_0\Delta n/\Delta p + n} \tag{2}$$

$$p + \frac{N_t(C_n n_1 + C_p p)}{C_n(n+n_1) + C_p(p+p_1)} = n + N_a \tag{3}$$

where the second term on the left-hand side of equation (3) is the density N_t^+ of positively charged deep defects. If a deep defect may be either negatively charged or neutral, then we should replace N_t^+ by the density of negatively charged deep defects N_t^- with negative sign, where $N_t^- = N_t - N_t^+$. Here n_0, p_0 and Δn, Δp are the equilibrium and excess concentrations of electrons and holes, respectively, and $n = n_0 + \Delta n$, $p = p_0 + \Delta p$. The terms p_1 and n_1 are the statistical factors of the Shockley–Read recombination theory.

The equilibrium concentrations of electrons n_0 and holes p_0 are found from the electroneutrality condition (3), using the relation $n_0 p_0 = n_i^2$. The excess carrier concentrations Δn and Δp are estimated for the stationary state, with the carrier photogeneration rate G set equal to the carrier recombination rate $U = \Delta n/\tau_n = \Delta p/\tau_p$, taking into account the expressions for the lifetimes τ_n (1), τ_p (2) and the electroneutrality condition (3).

4. Method 1. Dependence of excess carrier density on illumination intensity

One of the proposed methods can be applied to measure the excess majority carrier concentration as a function of the illumination intensity. Figure 1 displays the excess concentrations of electrons Δn and holes Δp as functions of the illumination rate G in silicon with the above radiation defects. It can be seen that at low illumination intensities G, the density of excess majority carriers Δp in silicon with K-centres (figure 1(*b*)) at $N_t < N_a$ and E-centres (figure 1(*a*)) exceeds that of minority carriers Δn. At the same time, in samples with A-centres, $\Delta n \approx \Delta p$ (figure 1(*c*)). The reason is that the energy levels of the E- and K-centres are close to the midgap, while the levels related to the A-centres lie closer to the conduction band. As a result, the thermal emission rate of minority carriers from the first two defects is too low and, correspondingly, $\Delta n < \Delta p$ (figures 1(*a*) and (*b*)), while that from the A-centre is higher and $\Delta n \approx \Delta p$ (figure 1(*c*)). Note that in silicon with K-centres, $\Delta n \geqslant \Delta p$ for $N_t = 10^{16}$ cm^{-3} (figure 1(*b*)). In this case, silicon has n-type conductivity and most of the K-centres are in neutral state at equilibrium. Then the K-centres capture more excess holes than electrons. Correspondingly, the difference between Δn and Δp is small and $\Delta n \geqslant \Delta p$ for $N_t \geqslant N_a$ (figure 1(*b*)). However, the difference between Δn and Δp is greater at high densities of the K-centres, exceeding the doping level ($N_t/N_a > 20$), and extremely small N_t (below 10^{12} cm^{-3}).

Analysis of figures 1(*a*) and (*b*) shows that the excess majority carrier density Δp first grows linearly with increasing illumination intensity G, then saturates and then again grows linearly. The initial rise usually takes place at low illumination intensities G (Δn, $\Delta p < N_t$), while the final linear rise occurs at high G resulting in high excess carrier densities exceeding N_t ($\Delta n \approx \Delta p > N_t$). The dependence of Δp on G saturates because of the filling of deep defect levels by minority carriers and the resulting increase in recombination rate. Since this occurs when the excess majority carrier density is equal to the deep defect density ($\Delta p \approx N_t$), this property can be used as a rapid method for determining the deep defect concentration from the dependence of the excess majority carrier density on illumination intensity. Note that the saturation is very clear at considerable differences between the excess carrier densities. Hence, the proposed method becomes more accurate with increasing difference between Δn and Δp (see, e.g., figures 1(*a*) and (*b*)). Note that the difference grows with increasing concentration of E-centres (figure 1(*a*)) and A-centres (figure 1(*c*)), and decreases if the density of K-centres tends to the doping level (figure 1(*b*)) or is too small ($<10^{12}$ cm^{-3}). The reason is that the E- and A-centres are neutral in p-type silicon and capture most of the photogenerated free minority carriers. Hence, the higher the density of the E- and A-centres, the lower the density of excess free minority carriers and the stronger the difference between Δn and Δp. This indicates that the proposed method becomes more efficient with increasing density of deep defects, which, being neutral in ground state, capture minority carriers. Our estimates show that the lowest concentration of E-centres detectable by the proposed method is $>10^{12}$ cm^{-3}. The highest detectable concentration of this defect is determined by the

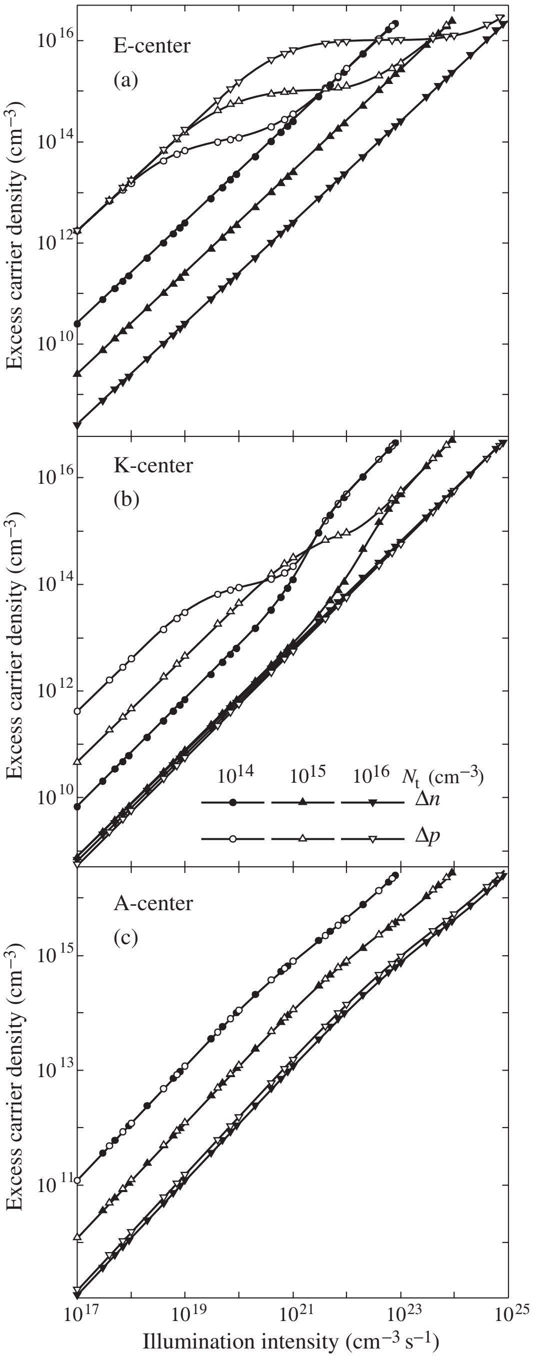

Figure 1. Excess concentration of electrons Δn (full symbols) and holes Δp (open symbols) as a function of the light intensity G in silicon with radiation-induced deep defects: (*a*) E-centres, (*b*) K-centres and (*c*) A-centres with concentrations N_t, cm^{-3}: (○, ●) 10^{14}, (△, ▲) 10^{15}, (▽, ▼) 10^{16}.

highest illumination intensity achievable at the current state of technology. The reason is that the higher the defect density, the stronger illumination intensities are required to fill the defect level with minority carriers so that saturation of the dependence $\Delta p(G)$ be observed.

At doping levels $N_a > N_t$ most of the K-centres capture majority carriers and become positively charged. At $N_a < N_t$, silicon has n-type conductivity. For this reason most of the K-centres are neutral and capture minority carriers. Correspondingly, if the K-centre density approaches the doping level N_a, the difference between Δn and Δp decreases and becomes negligible when $1 < N_t/N_a < 50$. In this range of N_t values, the defect density is undetectable by the method in question. The estimated lowest detectable N_t is about 10^{12} cm^{-3}.

Analysis of figure 1(*a*) indicates that in p-type silicon with E-centres the excess minority carrier density Δn linearly grows with increasing illumination intensity for any of the G values considered. In silicon with K-centres, Δn grows superlinearly at $N_t < N_a$ (figure 1(*b*)) and illumination filling the deep defect level with minority carriers. This depends on whether the deep defects in ground state capture majority or minority carriers. At $N_t < N_a$, all K-centres are charged positively at thermodynamic equilibrium. So, under illumination, the K-centres capture most of the photogenerated electrons. That is why the excess electron density grows superlinearly at those illumination intensities when the K-centres are already filled by electrons.

It follows from figure 1(*c*) that the excess carrier densities Δn and Δp in silicon with A-centres grow almost linearly with increasing illumination intensity G, with a minor tendency to saturate at high G, which means that the trap level is filled with minority carriers. The saturation is not so evident because thermal emission of captured electrons into the conduction band is too strong. This indicates that the method cannot be applied to determine the density of traps with energy levels lying close to an allowed band.

5. Method II. Injection level dependence of carrier lifetime

The second method proposed in this work can be used to measure the injection-level dependence of the carrier lifetime. Figure 2 shows the lifetimes of electrons τ_n and holes τ_p as functions of the excess majority carrier density Δp. It can be seen that in silicon with K-centres for $N_t < N_a$ (figure 2(*b*)) and E-centres (figure 2(*a*)), the lifetime of majority carriers, τ_p, at low injection levels (Δn, $\Delta p < N_t$) exceeds the minority carrier lifetime τ_n, which is related to the different values of the excess concentrations Δn and Δp (figure 1(*a*) and (*b*)). Indeed, dividing τ_n (1) by τ_p (2), we have

$$\frac{\tau_n}{\tau_p} = \frac{\Delta n}{\Delta p}. \tag{4}$$

Comparing figures 1 and 2, we can find a correlation supporting the above conclusion.

Analysis of figures 2(*a*) and (*b*) shows that, with increasing injection level, the majority carrier lifetime slightly decreases at low injection levels (Δn, $\Delta p < N_t$) and decreases superlinearly when $\Delta p \approx N_t$. The latter is related to the filling of the defect level with minority carriers and an increase in recombination rate. Since this occurs when $\Delta p \approx N_t$, this property can be used to determine the deep defect concentration from the injection-level dependence of the carrier lifetime. Note that the superlinear decrease in lifetime takes place in silicon with K-centres (figure 2(*b*)) at $N_t < N_a$ and E-centres (figure 2(*a*)), while in silicon with K-centres at $N_t = 10^{16}$ cm^{-3} $\tau_n(\Delta p) \geqslant \tau_p(\Delta p) \sim$ const (figure 2(*b*)). In samples with A-centres the lifetime decrease is smoother (figure 2(*c*)). This

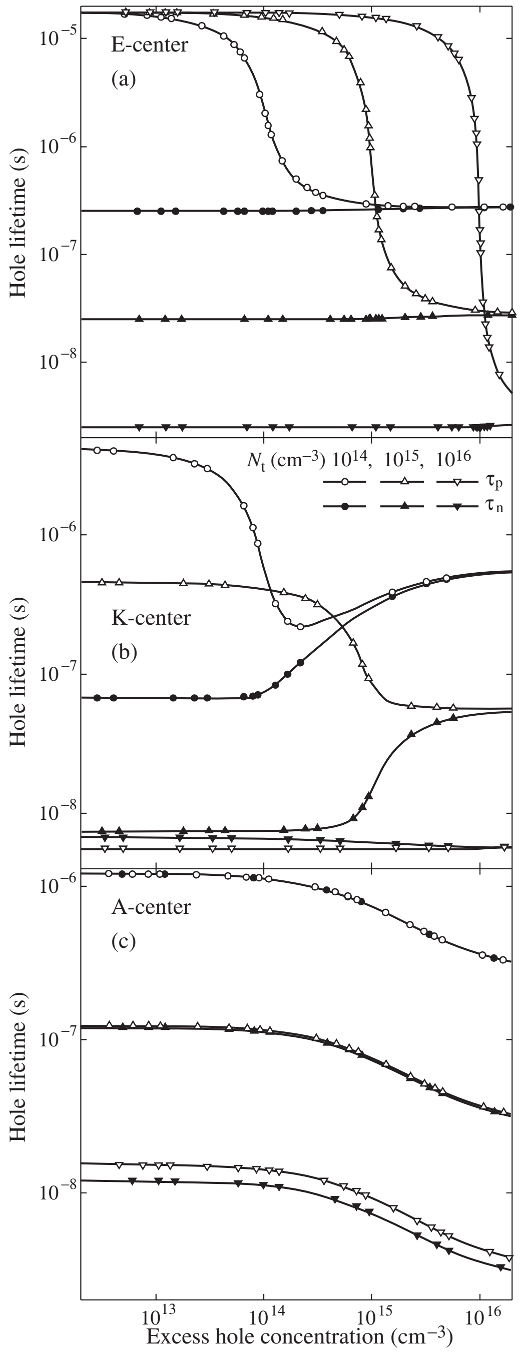

Figure 2. Lifetime of electrons τ_n (full symbols) and holes τ_p (open symbols) as functions of the excess majority carrier density in silicon with radiation-induced deep defects: (*a*) E-centres, (*b*) K-centres and (*c*) A-centres with concentrations N_t, cm^{-3}: (○, ●) 10^{14}, (△, ▲) 10^{15}, (▽, ▼) 10^{16}.

indicates that the method can be applied to determine the concentration of deep defects only if a defect gives rise to significant difference in excess concentrations and electron and hole lifetimes. The greater the difference between the lifetimes τ_n and τ_p, the steeper is the superlinear decrease in τ_p (figures 2(*a*) and (*b*)) and the more accurate is the method. Hence, as in the above case, this method also becomes more accurate with increasing density of E-centres (compare figures 1(*a*) and 2(*a*)) and with decreasing density of K-centres at $N_t > N_a$ and $N_t \leqslant 10^{12}\,\text{cm}^{-3}$ (compare figures 1(*b*) and 2(*b*)).

As shown in figure 2(*b*), at $N_t = 10^{14}\,\text{cm}^{-3}$ the majority carrier lifetime slightly increases at injection levels slightly exceeding the density of K-centres. This dependence is an inherent property of semiconductors with deep defects capturing majority carriers when in ground state and present in a concentration N_t smaller than the doping level N_a.

Analysis of figure 1(*a*) suggests that the minority carrier lifetime is independent of injection level for the entire range of injection levels considered. This is associated with a linear increase in the recombination rate, necessary to keep the balance $U = G$ when the minority carrier density grows linearly with increasing illumination intensity (figure 1(*a*)). The dependence $\tau_n(\Delta p)$ is an inherent property of semiconductors with deep defects capturing minority carriers when in ground state.

In silicon with K-centres, the minority carrier lifetime grows slightly with increasing Δp at low Δp, which takes place at excess majority carrier densities smaller than the defect density ($\Delta p < N_t$). At high holes densities, but still $\Delta p \leqslant N_t$, $\tau_n(\Delta p)$ increases superlinearly owing to the defect level filling by minority carriers, leading to a superlinear increase in the excess minority carrier density with growing illumination intensity (figure 1(*b*)). The dependence $\tau_n(\Delta p)$ saturates when the excess carrier density exceeds the defect concentration $\Delta n \approx \Delta p > N_t$ at $N_t < N_a$. When $N_t = 10^{16}\,\text{cm}^{-3}$, τ_n slightly decreases with increasing Δp. The reason is that at $N_t > N_a$ silicon is n-type and most of the excess holes are captured by the defect, resulting in $\Delta n > \Delta p$ and $\tau_n > \tau_p$.

It is well known that a semiconductor may contain several types of deep defects. Analysis of the results discussed above suggests that the proposed methods allow one to determine the density of only those defects which control the free carrier concentration and lifetime. Furthermore, the methods can detect the densities exceeding significantly the intrinsic concentration n_i. As a result, $10^{12}\,\text{cm}^{-3}$ is the lowest density of all deep defects in silicon, detectable by the proposed method at room temperature.

At high injection levels ($\Delta n \approx \Delta p > N_t$) (figures 2(*a*) and (*b*)), the carrier lifetimes are independent of the excess concentration, $\tau_n \approx \tau_p \approx 1/(C_n N_t)$. This property can be used to estimate the minority carrier recombination coefficient C_n. With this method, the deep defect density and the electron recombination coefficient have been estimated for multicrystalline silicon [4, 5] and polycrystalline $Cd_xHg_{1-x}Te$ layers [9] from the injection-level dependence of the carrier lifetime. The results are presented in table 1. For polycrystalline $Cd_xHg_{1-x}Te$ layers [9] only the deep defect density has been estimated, since the continuous spectra of deep lying energy levels make complicated the determination of other defect-related parameters in these materials.

Conclusion

In conclusion, two methods are proposed for determining the deep defect concentration from experimental dependences of the excess majority carrier density and carrier lifetime on, respectively, illumination intensity and injection level. One of the methods is based on the saturation of the excess majority carrier density with increasing illumination intensity, and the

Table 1. Bulk lifetime τ_p determined experimentally in [4, 5] and deep defect density N_t and electron capture coefficient C_n estimated using the proposed method.

Sample	Bulk lifetime[1] τ_p (μs)	Deep defect density N_t (cm^{-3})	Electron capture coefficient C_n ($cm^3\,s^{-1}$)
6A [4]	1	$(1-2) \times 10^{15}$	$(0.5-1) \times 10^{-9}$
6B [4]	50	$(4-5) \times 10^{14}$	$(4-5) \times 10^{-11}$
6C [4]	40	$(2.5-3.5) \times 10^{14}$	$(0.7-1) \times 10^{-10}$
6D [4]	2	$(1-2) \times 10^{14}$	$(2.5-5) \times 10^{-9}$
6B [5]	15	4×10^{14}	2×10^{-10}
[9]	–	1×10^{18}	–

[1] τ_p measured for $\Delta n \approx \Delta p > N_t$.

other, on the superlinear decrease in the majority carrier lifetime with increasing excess majority carrier density. Both of the effects are due to defect level filling with minority carriers, making higher the recombination rate. These two methods can be applied to study semiconductors with deep defects, giving rise to a strong difference between the excess concentrations Δn and Δp and between the lifetimes τ_n and τ_p of electrons and holes. It is shown that these methods become more accurate with increasing difference between the excess carrier concentrations and Δn and Δp and between the lifetimes τ_n and τ_p. This conclusion is valid only for semiconductors with single-level deep defects and generation-recombination via these defects described by the Shockley–Read–Hall recombination mechanism. For other types of defects, like double, metastable or extended defects, the Shockley–Read–Hall recombination theory does not work and it is necessary to make a similar analysis for each particular case.

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