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Spectroscopic investigations of dark Si nanocrystals in SiO₂ and their role in external quantum efficiency quenching

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The percentage of dark silicon nanocrystals, i.e., the nanocrystals that are not able to radiatively recombine after absorption of a photon, is investigated by combining measurements of external and internal quantum efficiencies. The study is conducted on samples prepared by co-sputtering and subsequent heat treatments. We show that the external quantum efficiency is mainly limited by the presence of dark nanocrystals, which induce losses after direct excitation and also, as we propose, by indirect excitation enabled by energy migration. The percentage of dark nanocrystals can be decreased by high quality surface passivation as a result of low-temperature annealing in ambients of O₂ and H₂. By using a non-passivated sample as a reference, the relation between the size of a nanocrystal and its probability of being dark is studied. Larger nanocrystals are demonstrated to function more likely as dark centers. The study shows that high external quantum efficiencies of Si nanocrystal ensembles can be realized for small, well passivated Si nanocrystals under suppression of excitation diffusion. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4818580>]

I. INTRODUCTION

The photovoltaic conversion efficiency of single-junction solar cells is limited to approximately 30%, as derived in the well known Shockley-Queisser limit.¹ The so-called detailed balance limit is calculated under assumption that electron-hole pairs generated by photon absorption recombine only radiatively. Evidently, in that situation, the efficiency limitation arises mostly due to two reasons: the low-energy photons do not have enough energy to excite electrons from the valence to the conduction band and therefore are not absorbed, and photons with energies exceeding the bandgap generate losses in the form of heat. Therefore, a significant solar cell efficiency increase could be achieved by the proper spectral shaping of the incoming light in order to better match the characteristics of the device. Up-conversion, where two low-energy photons are combined into a single high-energy one, can be used for the low-energy range. On the other end of the solar spectrum, a down-conversion process, where a high-energy photon is split into one or more low-energy ones, can decrease the losses induced by thermalization. For down-conversion lanthanide ions are widely studied and energy conversion efficiencies of up to 86% have been demonstrated.² Silicon nanocrystals (NCs) can also be used for that purpose and offer several advantages when compared to lanthanides:

1. A much larger absorption cross-section. Since the optical properties of lanthanides arise due to the inner 4f-electron shell, their cross-section for optical absorption is very small and typically excitation “sensitizers,” in the form of defects or nanostructures of other materials, need to be used.³ With Si NCs, this is not necessary, with absorption

and emission of photons occurring in the core, avoiding the unnecessary complication of different materials in the system.

2. Tunability by quantum confinement. This implies that emission energies can be freely tuned to match the high-efficiency regime of a solar cell, rather than being limited to specific bands predetermined by the spin-orbit coupling within the 4f-electron shell.

In addition to the above, Si NCs offer a very interesting option of the space-separated quantum cutting process^{4,5} in which multiple carriers can be created in neighboring NCs upon absorption of a single high-energy photon. This process can induce an even more powerful down shift at the high-energy end of the solar spectrum. Moreover, as a result of their spatial separation in different NCs, the Auger interaction between individual electron-hole pairs is suppressed, and they all will have single-exciton lifetimes, making radiative recombination possible.

Despite of these advantages actual implementations of Si NCs as conversion layers in practical photovoltaic devices have not appeared yet. The major reason is the external quantum efficiency (EQE), the ratio of the number of emitted and absorbed photons, which is not adequate for increasing the total system's efficiency. Which EQE values eventually should be reached depend on the quality of the solar cell; however, in order to realize the net increase in the number of emitted photons by the conversion layer, the EQE of emission (measured at low excitation energies, i.e., not involving the afore-mentioned space-separated quantum cutting process) should be well in excess of 50%, herewith yielding an EQE of at least 115% for the high energy end of the solar spectrum.⁶ Previous research showed that while individual Si NCs can reach near 100% efficiencies,⁷ the ensembles do not. The two major and mutually connected reasons for this discrepancy are the so-called “blinking” and formation of

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“dark” Si NCs (dNCs).^{8,9} The effect of blinking is well known for molecules and involves periodic switching between states of different optical activity, usually with very different radiative rates, as, e.g., a singlet and a triplet state for an exciton. This implies that on a level of a single Si NC, emission is characterized by a statistical sequence of “on” and “off” periods; obviously, on an ensemble level, this effect leads to the overall lower emission, reducing its EQE. In contrast, the dNCs are characterized by a very efficient nonradiative recombination channel; therefore, these dNCs absorb photons but convert them into heat, with very detrimental effect on the EQE of an ensemble (from this perspective, a blinking NC can be reckoned as a dNCs when it is in the “off” state). The existence of these very efficient channels of nonradiative recombination is directly confirmed by ultrafast emission and induced absorption experiments, which reveal prominent presence of pico- and sub-picosecond transients.⁸ The dNCs are the object of this study, where we undertake a quantitative investigation of their influence on the EQE of the ensemble. We elucidate details of their role in the EQE quenching and then use this knowledge to find a route towards development of efficiently emitting Si NCs for ensembles with high EQEs. In order to achieve this goal, we measure effective recombination rates, EQEs, and absorption spectra of differently prepared Si NC layers. Based on the detailed analysis, we identify the dNCs for different samples and evaluate the actual fraction of the dNCs with respect to the ensemble participating in optical absorption, in that way demonstrating their significance in the EQE reduction. Second, we study the effect of surface treatment on the percentage of dNCs appearing in the ensemble. Third, we investigate a possible relation between the size of a NC and its probability of being dark. By combining all three aspects, we aim to obtain a recipe on how to produce thin films of Si NCs with high EQEs, with the prospect to be used as spectral converters for photovoltaics.

II. EXPERIMENTAL DETAILS

The experiments have been conducted on thin film Si NC samples. NCs were dispersed in an SiO₂ matrix by magnetron co-sputtering using high purity Si (99.99%) and SiO₂ (99.99%) targets. The sputtered films (400 nm thick) were annealed for 1 h at 1250 °C in nitrogen atmosphere. This high-temperature heat treatment induces phase separation between Si and SiO₂.¹⁰ With the chosen stoichiometry, this produces Si NCs with an average size of 5 nm. For detailed investigations, a specific sample has been chosen with the emission spectrum centered in the high conversion efficiency range of typical Si solar cells and the effective emission lifetime representative for solid state dispersions of Si NCs with high crystalline quality in SiO₂. This sample is further labelled as sample A. Subsequent low-temperature annealing for 1 h at 450 °C in an ambient of O₂ (sample B) and H₂ (sample C) was performed in order to passivate the surface of the NCs and quench the non-radiative recombination channels without enabling further silicon diffusion and aggregation. Photoluminescence (PL) intensity and EQE measurements were performed in an integrating sphere in order to avoid possible influences of light

scattering and reflections and also of directionality of emission.¹¹ We have used a xenon lamp as a stable excitation source. The xenon lamp was combined with a M136 (Solar LS) monochromator enabling the excitation at $\lambda_{exc} = 302$ nm. Time-resolved PL measurements have been performed with an optical parametric oscillator (OPO) pumped by the third harmonic of a 100 Hz Nd:YAG laser with a pulse duration of 5 ns set at $\lambda_{exc} = 300$ nm. Both setups used an M266 (Solar LS) monochromator coupled to either a silicon CCD (for the spectral resolution) or a photo multiplier tube (for the time-resolved measurements). Absorption measurements were carried out using a UV-vis Lambda900 spectrometer in combination with an integrating sphere, accounting for reflection and scattering effects. All spectra are corrected for the system response curve.

III. PRELIMINARY CONSIDERATIONS

As stated in the Introduction, the prime object of this study is the influence of dNCs on the EQE of an ensemble. The dNCs influence the EQE by participating in photon absorption. On the other hand, the internal quantum efficiency (IQE) of PL of dNCs is practically zero (no emission), and therefore, the experimentally determined IQEs only relate to the emitting Si NCs. Consequently, by combining EQEs and IQEs, it is possible to calculate the percentage of dNCs for a particular ensemble. The IQE is given by

$$IQE(\lambda) = \frac{\Gamma_{rad}(\lambda)}{\Gamma_{eff}(\lambda)}, \quad (1)$$

where Γ_{rad} and Γ_{eff} represent the radiative and effective recombination rates, respectively, the latter being given by the sum of the radiative and non-radiative recombination rates ($\Gamma_{rad} + \Gamma_{nonrad} = \Gamma_{eff}$). Past investigations established that the radiative rate of Si NCs is predominantly determined by the level of quantum confinement, i.e., the size of a NC, with only minor changes due to particulars of the preparation procedure.⁷ Consequently, the IQE of Si NCs is emission wavelength dependent. Equation (1) implies that in order to determine the IQE for a specific emission wavelength (i.e., a particular NC size), it is necessary to uncouple the measured effective recombination rate into the radiative and non-radiative recombination components. Miura *et al.*⁷ determined radiative rates for Si NCs of different sizes by measuring their emission in vicinity of an Au layer, which modifies the radiative rates, leaving the nonradiative recombination unaffected. Since the materials used in the present study have been prepared in the same way, we will assume that the radiative rates determined in Ref. 5 apply to our samples and use these in further considerations.

The IQE and EQE are linked by the percentage of emitting NCs

$$\frac{N - N_d}{N} IQE_{ave} = EQE, \quad (2)$$

with $EQE = \frac{\#Em_{ph}}{\#Abs_{ph}}$. Here, N and N_d represent the number of absorbing (total) and dNCs, respectively. The numbers of

FIG. 1. Effect of low-temperature annealing on the optical characteristics. (a) PL spectra for c.w. low intensity excitation at $\lambda_{exc} = 302$ nm inside an integrating sphere. Surface treatment of the sample in an ambient of O_2 (sample B) and H_2 (sample C) increases PL intensity with a factor of 1.5 and 2.9, respectively. (b) Absorption spectra for the heat treated samples show identical behavior implying identical absorption cross sections.

emitted and absorbed photons are represented by $\#Em_{ph}$ and $\#Abs_{ph}$, respectively. From here, the percentage of dNCs can be derived. We note that the IQE used above represents a value averaged over the whole ensemble. This is necessary in view of the definition of the EQE, which is experimentally measured for the ensemble, over the complete spectral range of emission. The average IQE is obtained by scaling the IQE value for every emission wavelength with the spectral weight, referred to as ρ (the relative number of emitting NCs at that particular wavelength with respect to the whole emission spectrum), normalized so that $\sum_{spectrum} \rho = 1$, where differences in emission efficiencies are taken into account. Therefore, we get

$$IQE_{ave} = \sum_{\lambda} IQE(\lambda) \times \rho(\lambda). \quad (3)$$

IV. EXPERIMENTAL RESULTS

In this section, we give a brief account of the data measured in this study. Further analysis of the experimental results and conclusions will be addressed in Sec. V. Looking for the physical origin of dNCs, we recall that it has been often proposed that these could appear due to efficient nonradiative recombination mediated by Si dangling bonds at the Si-SiO₂ interface (the so-called P_b centers^{12,13}). In that case, it should be possible to reduce the number of dNCs by decreasing the number of Si-dangling bonds through their passivation. Past research^{14–16} proved that this can be efficiently achieved by low-temperature annealing in H_2 or O_2 atmosphere. Nesbit showed that the diffusion constant of silicon in SiO₂ decreases exponentially with the inverse of annealing temperature.¹⁷ Therefore, we can expect that in principle the Si NCs produced during high-temperature annealing should stay intact at the temperature of 450 °C, and the low-temperature annealing procedure will only affect the surface. The effect of low-temperature annealing on the PL intensity and absorption spectra is displayed in Fig. 1.

As mentioned Sec. II, PL has been measured in an integrating sphere and therefore the integrated intensities obtained for different samples can be directly compared with

each other, as emission directionality and/or possible misalignment of sample positions are automatically corrected for. Fig. 1(a) displays the PL of sample A followed by the low-temperature annealing in ambients of O_2 (sample B) and H_2 (sample C). As can be seen, O_2 and H_2 passivation increases PL intensities with factors 1.5 and 2.9, respectively. EQEs of these samples, presented in Table I, show a similar increase from 9.3% for sample A, to 15.8% for sample B and 27% for sample C, that is, with factors of 1.7 and 2.9, respectively. The fact that the EQE enhancement follows closely the increase of PL intensity depicted in Fig. 1(a) can be understood by the data in Fig. 1(b), where the absorption spectra are shown for samples B and C. Within the investigated range, the absorption is indeed the same for both samples. We conclude that the absorption cross section of the NCs is not influenced by the low-temperature treatment. As a result, an EQE increase reflects directly a PL intensity enhancement. We would like to stress that the observation that the absorption cross section of Si NCs is not affected by surface passivation is a crucial result which is further on used to derive the probability of dNC formation as a function of size.

Figure 2 shows PL transients as measured for three different emission wavelengths of 769, 840, and 970 nm for sample A. The intensity scale is logarithmic, and we directly conclude that in all cases, PL decays have multi-exponential character, evidencing superposition of different contributions. Anticipating that the measured transients represent contributions from NCs of different sizes, symmetries and, a huge spread in nonradiative recombination rates (further on elaborated), we have fitted them with the so-called “stretched exponent” function allowing for a distribution of time

TABLE I. External quantum efficiency as measured in an integrating sphere.

Sample	EQE (%)
A	9.3
B	15.8
C	27.0

FIG. 2. PL transients obtained for sample A with excitation set to $\lambda_{exc} = 300$ nm measured at $\lambda_{PL} = 760$, 840, and 970 nm. The laser pulse duration was $\Delta t = 5$ ns. A clear multi-exponential decay is observed for all three emission wavelengths.

constants. In that case, scaling of the fitted lifetimes with the Gamma function¹⁸ is necessary to compute the average effective lifetime for an ensemble

$$\tau_{ave} = \tau \frac{1}{\beta} \Gamma\left(\frac{1}{\beta}\right). \quad (4)$$

The fitted β values varied from 0.6 to 0.8, implying a significant spread of effective lifetimes for a given emission wavelength. In Fig. 3, the effective recombination rates measured for samples A, B, and C are presented as a function of the emission wavelength. For completeness, the relation between the emission wavelength and Si NC diameter obtained by Takeoka *et al.*¹⁹ is given in the inset. We conclude that larger NCs exhibit lower effective recombination rates. Such a trend is expected for the radiative recombination rate, which increases for smaller Si NCs as the momentum conservation is gradually relaxed due to the Heisenberg uncertainty relationship and the so-called pseudo-direct transitions appear. However, it is only fair to mention that such an enhancement can also indicate a more important role of nonradiative recombination channels for smaller NC sizes. Here, we make two notions. First, the effective recombination rate obtained for large NCs is very close to the expected radiative rate.

FIG. 3. Comparison of the effective recombination rate of Si NCs as a function of emission wavelength for different surface qualities (samples A, B, and C). A general trend is observed with higher rates for shorter emission wavelengths, i.e., smaller NC sizes. The dashed lines function as guides to the eye. The relation between the emission wavelength and Si NC diameter is displayed in the inset of sample A, obtained from Ref. 19. The experiment is conducted with excitation pulses of $\Delta t = 5$ ns and $\lambda_{exc} = 300$ nm.

Second, the transients measured for a particular wavelength are different for the different samples (which is possibly better visualized in Fig. 4). Since the radiative rate should be essentially determined by the NC size, the fact that these PL transients differ evidences that the nonradiative channel is affected by the heat treatment.

V. FURTHER ANALYSIS AND DISCUSSION

In order to elucidate the effect of dNCs in the emission from thin layers of Si NCs, we calculated the IQE in the investigated samples as a function of emission wavelength. We do that by using Eq. (1) and the radiative recombination rates as reported by Miura *et al.*⁷ As already mentioned, the results for samples A, B, and C, plotted in Fig. 4, clearly demonstrate that the heat treatment significantly increases the average IQE. This follows from the overall improvement of surface passivation of NCs and not to their size transformation and/or agglomeration.

By detailed inspection and comparison between the individual samples, two important insights are obtained:

1. The IQE shows values intermediate between those which characterize totally dark (IQE = 0) and totally “bright” (IQE = 1) NCs. This indicates that a non-radiative recombination channel is also available to those NCs which contribute to PL. However, the experimentally determined high IQE values imply that these non-radiative recombination channels are not very efficient, with rates being of the same order as those of the spontaneous emission. This is then very different from the rapid non-radiative quenching characteristic for dNCs. It is worth mentioning that this competition of radiative and non-radiative recombination channels in emitting NCs is also observed by means of single quantum dot spectroscopy.²⁰ As a consequence, we conclude on the coexistence of strong and weak non-radiative recombination channels: (i) an efficient non-radiative recombination with characteristic rates of an order of 10^{12} s^{-1} (approximately 8 orders of magnitude higher than the radiative rates²¹) which could be induced by defects, e.g., a Si dangling bond on the NC/SiO₂ interface and which gives rise to the phenomenon of dNCs and (ii) a weak non-radiative channel, which diminishes the IQE of emitting NCs. The latter should have a different origin and rates comparable with the

FIG. 4. IQE as a function of emission wavelength measured for the samples with and without surface passivation. For samples A and B, IQE increases towards longer wavelengths (larger NCs), whereas for sample C (H_2 heat treatment), a constant IQE level is achieved.

spontaneous emission rate. Its contribution is included in the effective recombination rate (Fig. 1) and in the evaluated IQE (Fig. 3).

2. A distinct dependence of IQE on the emission wavelength can be observed: when coming from shorter to longer wavelengths, i.e., from smaller to larger NC sizes, the IQE initially grows and then slightly decreases again (samples A and B) or stabilizes (sample C) for the biggest NCs.

These two characteristic features found here for the IQE hint to a possibility of excitation diffusion between NCs as a possible mechanism responsible for the weak non-radiative recombination channel. Such a possibility has been suggested in the past^{7,22,23} and concerns exciton diffusion between NCs by means of energy transfer resulting from dipole-dipole interaction,²⁴ the Förster resonant energy transfer (FRET). The nonradiative recombination is accomplished by energy transfer from an emitting NC to a dNC, which then effectively terminates further diffusion. Because the time-scale for the dipole-dipole energy transfer is typically in the microsecond range, which is many orders of magnitude slower than the nonradiative recombination in dNCs, it is the diffusion process which controls the experimentally measured quenching of luminescence. As a result, the rate of this diffusion-induced weak non-radiative recombination channel is comparable with that of the spontaneous radiative emission. Further, since energy transfer between NCs is likely to occur with small losses to phonons, this implicates its directionality from smaller to bigger NCs; in that way, the rise of the IQE with emission wavelength, i.e., for larger NCs, is readily explained. Following this reasoning, it immediately implies that the IQE is not a property of the NC itself but rather a combination of the NC with the environment. We would like to stress that the diffusion itself is not an energy relaxing process (besides small losses originating from the accompanying phonon emission), with the energy dissipation appearing due to participation of dNCs. In that way, this channel of non-radiative recombination can be regarded as indirect excitation of dNCs through diffusion, and its efficiency reflects both the total number as well as proximity of dNCs. Similar increase of IQE towards longer emission wavelengths has also been reported by Miura *et al.*,⁷ indicating the similarities in the produced systems. This indeed can be expected for the indirect excitation of dNCs being the origin of the weak

nonradiative recombination. The slight decrease observed for long wavelengths in samples A and B might hint on other effects competing with the spontaneous emission rate, which could explain why the IQE does not reach 100% for the longest emission wavelengths. We note also the much larger error margin for these data points.

We will now proceed to establish the contribution of dNCs to the PL quenching. From Table I, we see that the EQE of 9.3% has been found for sample A. While the particular measurement has been conducted with the excitation set to 302 nm, the EQE value turned out to be independent of the excitation wavelength. This implies that effects such as excitation-dependent trapping and the space-separated quantum cutting process frequently reported for Si NCs,^{4,5,25} and leading to variation of EQE upon excitation energy, are not present in the samples investigated in this study. This indicates large NC separation precluding coupling of high energy states between NCs. We want to emphasize that the space-separated quantum cutting process and the excitation diffusion have completely different mechanisms. Quantum cutting, theoretically predicted to occur on a picosecond time-scale,²⁶ is arising from a high-energy state and successfully competes with the Auger recombination. In contrast, exciton diffusion is governed by dipole-dipole interactions from the first excited state and takes place in the microsecond regime. Using the measured EQE, the percentage of dNCs in sample A is calculated with Eq. (2) as $N_{dNC}^A = 83.3\%$. Therefore, we conclude that the direct excitation quenching by the strong non-radiative recombination channels of the dNCs is the decisive effect responsible for the low EQE of PL in sample A. Furthermore, by combining the percentage of dNCs with the measured value for EQE of 9.3%, we deduce that the remaining loss of 7.4% arises from the weak channel of nonradiative recombination which in our interpretation is induced by excitation diffusion towards (larger) dNCs. From the above, it is clear that the major route towards enhancement of the EQE leads via the reduction of the dNC population. Moreover, since both direct (strong non-radiative channels) and indirect (weak non-radiative channels) excitations of dNCs affect the EQE, then reducing the number of dNCs will simultaneously enhance the average IQE.

By using Eq. (2) in combination with the data from Table I, the percentage of dNCs after O_2 and H_2 passivation is calculated to be $N_{dNC}^B = 73.7\%$ and $N_{dNC}^C = 68.5\%$, respectively, with the loss to other processes of (weak)

non-radiative channels being 10.5% (sample B) and 4.5% (sample C). Therefore, we conclude that dNCs can effectively be transformed into emitting ones by thermal treatment in gas atmospheres, most probably through surface passivation. This is consistent with the assumption that the strong non-radiative recombination is caused by defects. It is worth noting that the primary reason for the ~ 3 -fold increase of the EQE is the reduction of the percentage of dNCs, with the percentual loss due to weak nonradiative recombination decreasing as well. Therefore, we conclude that indirect excitation of dNCs becomes less efficient when the number of dNCs is decreased (which is indeed directly confirmed in Fig. 4, where samples B and C have higher IQE_{ave} values).

Having established the essential role of dNCs for the EQE, we now turn to investigate whether a relation exists between the size of the NC and the efficient non-radiative recombination channel, i.e., whether the size distribution of dNCs is different from that of the whole ensemble. We note that under laser illumination in the low flux regime, the PL intensity can be approximated as²⁷

$$I \propto \sigma \phi IQE_{ave} N_{em} V_{exc}, \quad (5)$$

where σ and ϕ represent the absorption cross section of a NC and the photon flux, respectively. The product of the two can be viewed as the average number of photons absorbed per NC, per second (note that $\sigma \phi \ll 1$ in the low flux regime). N_{em} refers to the concentration of NCs which can emit and V_{exc} reflects the excited volume. The product of N_{em} and V_{exc} describes the amount of emitting NCs within the excitation range, which contribute to PL. Under assumption that the absorption cross-section σ remains unaffected upon surface passivation (concluded from Fig. 1(b)), the ratio of bright NC concentration in two samples B and A or C and A can be obtained by comparing their PL intensity under illumination with an equal photon flux²⁷

$$\frac{N_{em}}{N_{em,ref}} = \frac{I}{I_{ref}} \frac{IQE_{ave,ref}}{IQE_{ave}}, \quad (6)$$

where “ref” corresponds to the reference sample, which in our case is sample A. In Fig. 5, the percentage of bright NCs that are able to emit is plotted as a function of the emission wavelength, normalized to sample A. We see that while by annealing in both O_2 and H_2 the fraction of emitting NCs is increased, H_2 passivation is much more efficient. The graph can be interpreted as a relation between the conversion yield from dark to bright NCs and the NC size. Under the assumption that the size of a specific NC does not affect passivation of surface defects, an important insight can be retained: because the dNC conversion yield is increasing as a function of size, the fraction of dNCs is higher for larger sizes, implying that large NCs have a higher probability to be dark. One could rationalize this observation by noting that larger NCs have a larger surface area and thus a higher chance for a surface defect to appear (dangling bond at the Si/SiO₂ interface). On the other hand, it could be argued that free carrier localization on the surface would be higher for smaller NCs, increasing their coupling to the defect. However, the latter

FIG. 5. Conversion yield from dark to bright NCs as a function of the emission wavelength (i.e., size). Both heat treated samples show a decreased number of dark NCs, with the reduction being stronger for the H_2 passivation, sample C. From the rising ratios towards longer emission wavelengths, we conclude larger NCs have higher probabilities to be dark.

effect should be of a lesser importance in view of the very efficient character of defect-related non-radiative recombination channels.²¹

VI. CONCLUSIONS

In this paper, we investigate a route towards realization of high PL efficiency from Si NCs. We conclude that the formation of dark Si NCs is the main effect limiting the EQE of Si NC layers prepared by thermal annealing of (co-)sputtered sub-stoichiometric oxide layers. In a particular as-prepared sample representing state-of-the-art for this preparation technique, we established that 83.3% of all the Si NCs are dark, i.e., do not emit light while participating in photon absorption. We therefore conclude that an effective reduction of the concentration of dNCs, and their conversion to the emitting (bright) ones, is necessary for an EQE enhancement. We demonstrate that one way in which this can be realized is by an additional low-temperature annealing in an ambient gas atmosphere. In particular, we show that in the investigated sample, the dNC percentage can be reduced to 68.5% by H_2 passivation treatment. This result points to a direct link between formation of a dark NC and the presence of defect states at the surface of a NC. We investigate NCs of various sizes and show that large NCs are more likely to be dark than small ones. This, we argue, is a result of their larger surface area and consequently a higher chance of defect presence. Further we argue that, next to the direct excitation quenching, dNCs play also an additional role in EQE mitigation; based on the experimental findings and their analysis, we propose that dNCs quench the EQE in an indirect way by their participation in excitation diffusion, as enabled by, e.g., FRET.

Therefore, we conclude that in order to enable highly efficient PL, Si NCs need to be (i) small, (ii) with well-passivated surface (preferably by H_2), and (iii) excitation diffusion between them should be suppressed in order to avoid indirect excitation of dNCs. The latter could be achieved, e.g., for free-standing, sufficiently separated, and/or appropriately capped NCs. With an eye on possible

applications of Si NCs in photovoltaics, future research should clarify whether the insights provided by this research will enable sufficient increase of EQEs of Si NC layers, such that these could be applied for spectral conversion.

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