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Blinking Statistics of Silicon Quantum Dots

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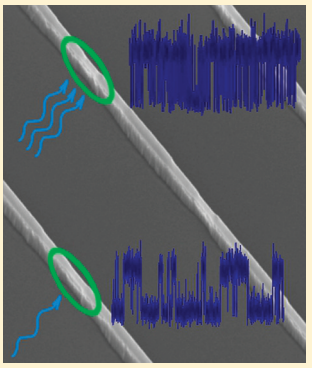
ABSTRACT: The blinking statistics of numerous single silicon quantum dots fabricated by electron-beam lithography, plasma etching, and oxidation have been analyzed. Purely exponential on- and off-time distributions were found consistent with the absence of statistical aging. This is in contrast to blinking reports in the literature where power-law distributions prevail as well as observations of statistical aging in nanocrystal ensembles. A linear increase of the switching frequency with excitation power density indicates a domination of single-photon absorption processes, possibly through a direct transfer of charges to trap states without the need for a bimolecular Auger mechanism. Photoluminescence saturation with increasing excitation is not observed; however, there is a threshold in excitation (coinciding with a mean occupation of one exciton per nanocrystal) where a change from linear to square-root increase occurs. Finally, the statistics of blinking of single quantum dots in terms of average on-time, blinking frequency and blinking amplitude reveal large variations (several orders) without any significant correlation demonstrating the individual microscopic character of each quantum dot.



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Blinking, also known as emission intermittency, refers to the switching of a quantum emitter between a bright (on) and a dark (off) state, or even between more (gray) states.[1] It is expected to be a common phenomenon that follows the same rules in all quantum emitters, ranging from single dye molecules to semiconductor nanocrystals. Even though advantageous for identifying emitters as single fluorophores (for an ensemble of emitters the random intermittency of individual emitters will be smeared out resulting in an average brightness), it causes severe problems for applications, such as a reduction in quantum efficiency leading to loss of energy efficiency, diminished brightness and possibly poorer reliability. Since the first report of blinking in CdSe quantum dots (QD) by Nirmal et al.,[2] a vast number of papers on the subject have been published. The first model by Efros and Rosen[3] ascribes the dark state to a charged QD state, where a single hole remains in the core, while an electron becomes trapped in the vicinity. Upon further excitations, the core contains two holes and one electron causing very fast nonradiative Auger de-excitation, the dark state. Assuming a fixed trap state energy, this model predicts purely exponential on- and off-time distributions in the emission trace and has been further developed into a manifold of models to account for observed power-law distributions and a number of additional phenomena (see, e.g., ref 4 and 5). For most systems covered in the literature on- and off-times are distributed according to a power-law. Almost all power-law exponents between 1.2 and 2.0 have been measured.[5] The Efros and Rosen model can be modified to account for this if a trap state density is assumed with a distribution in energy levels. Power-law blinking has been shown to cause ensembles of emitters to statistically age, that is, to suffer from decreasing intensity as time progresses.[6,7] This is a natural consequence of such trap state energy distributions where, as time progresses, the electron will eventually fall into a very deep state causing the emitter to be in the off state for very long times. Indeed, mathematically the expectation value of the intensity from such an emitter with a power law distribution (and $m(\mathrm{on}) > m(\mathrm{off})$) goes to zero when extrapolated to very long times.

Because of the indirect bandgap nature of silicon and a relatively long exciton lifetime (about 4 orders of magnitude higher than for many active materials, i.e., 10−100 μs), Si-QDs do not emit as many photons per unit time as their direct bandgap counterparts. Therefore, observation of blinking is restricted to time scales much longer than, for example, CdSe nanocrystals. Depending on excitation strength and measurement method, this means tens of milliseconds[8] at high excitation power densities of several kW/cm^2, simultaneously creating many excitons per nanocrystal, or even seconds, as in this work, presenting a lower limit to the temporal resolution. In direct bandgap materials, on the other hand, millisecond resolution can be achieved already at low excitation. Cichos et al.[8] observed power-law blinking and statistical aging in silicon nanocrystals fabricated by electrochemical etching. While their observation time spans roughly 4 orders of magnitude, starting with 10 ms, Sychugov et al.,[9] working with nanocrystals fabricated by lithography, etching, and oxidation, concentrate on a regime of several seconds and find purely exponential blinking behavior. Both argue in favor of Auger-assisted photoluminescence quenching. Finally, Valenta et al.[10]

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observed a combination of power-law with exponential tail (for longer periods) in electrochemically etched Si particles. Despite extensive efforts, many aspects of blinking are hardly understood yet and there seems to be a lack of statistical approaches where large numbers of individual dots are analyzed. This is particularly important as many parameters of blinking, for example, frequency, duty cycle, intensity, and so forth span a large parameter interval between different individual QDs.

In this paper, blinking studies conducted on single silicon quantum dots fabricated by electron beam lithography (EBL), reactive ion etching (RIE), and oxidation are presented. On our samples, we have identified about 2000 luminescing QDs and analyzed blinking statistics for around 250 individual dots. The excitation intensity has been varied covering a range between the regime significantly below an average excitation of one exciton per QD and up to several excitons ($\leq$6) per QD. While most articles find power-law distributed on- and off-times usually truncated by an exponential tail at long times, in this work purely exponential distributions were found for a significant number of nanocrystals. In line with this, statistical aging could not be observed in the quantum dots under investigation. In addition, a linear increase in switching frequency with laser excitation intensity was observed. This contradicts generally accepted models based on Auger-mediated luminescence deactivation. Instead, we propose direct tunneling to a trap state as a cause for the ionization of the core.

As described in previous work,[11] samples were fabricated using EBL, RIE, and oxidation in the self-limiting regime (900 °C). In short, silicon walls were defined by EBL and etched followed by a series of gentle oxidations that first resulted in nanowire cores that subsequently broke up into individual luminescent quantum dots. A set of seven experiments at different excitation power densities (2, 7, 10, 20, 30, 40, and 60 W/cm^2) was performed using a 405 nm Omicron Phoxx diode laser in cw mode. An Andor iXon-X3 888 EMCCD camera, connected to a Nikon Optiphot-150S microscope (Nikon 100× objective lens, 0.9 NA) and a Triax 180 spectrometer in imaging mode, captured almost 6000 frames per experiment with an acquisition time of 1 s and a dead time of less than 0.3 s between two adjacent frames. Note that the excitation beam entered the sample directly (not through microscope lens which is the common approach) at an angle of ~30° with respect to the sample surface. In this way, the full imaged area was illuminated at a relatively constant power density. The excitation power density value was calculated from the area the laser beam was focused on (viewed with a 10× objective lens), initial laser power and optical loss in the beam delivery system. It should be noted that the polarization of the laser beam might not have coincided with the nanocrystal orientation, which can lead to reduced absorption efficiency[12,13] and therefore shift the expected power density value for the simultaneous creation of several excitons per nanocrystal. The raw image data was imported into a home-built java code embedded in the ImageJ[14] framework for analysis. Small sample drifts during data acquisition were corrected, an extraction mask was defined in the form of squares around all detected luminescing dots, and that mask was used to extract all intensity traces from all single experiments. Figure 1 shows a photoluminescence (PL) measurement of the sample (a), an extraction mask (b), and examples of extracted intensity traces (c) and their integrated histograms (d). Dot 653 is typical for a single emitter while dot 505 clearly shows a double dot (both emitters accidentally having similar amplitude). On- and off-level intensity, and

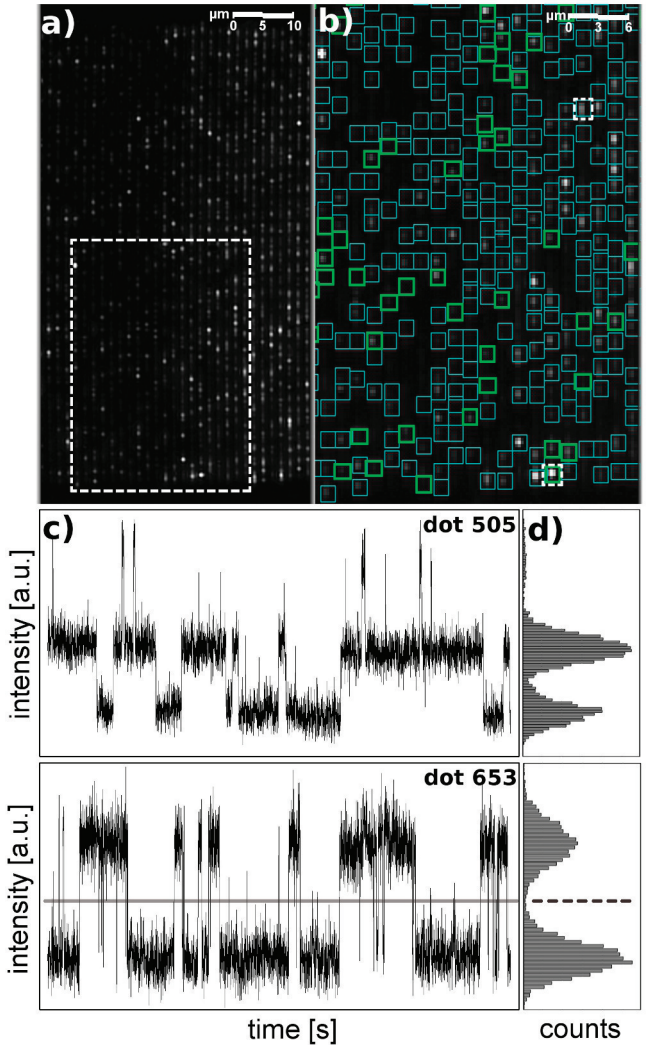

Figure 1. (a) Photoluminescence image of a sample that contains quantum dots arranged in a matrix pattern. (b) Magnification of the part indicated in (a) with a data extraction mask as overlay. Green squares indicate dots with distinct two-level blinking. (c) Intensity traces of the two dots indicated in (b). The data is extracted from an image sequence (6000 frames, 1 s bin) using the data extraction mask. (d) Histograms of the traces in (c) demonstrating distinct states. The threshold between on- and off-state is indicated by a line in the two-level case.

therefore blinking amplitude, can be determined from a histogram. A threshold approach transforms the intensity trace into binary states and therefore makes identification of blinking events possible. The number of blinking events, or the blinking frequency, and on- and off-times (and therefore their distributions, correlation, and the average on-time) can be extracted from the binary trace. In total, almost 2000 dots were identified by the software, of which only a fraction exhibited clear emission intermittency with quantized intensity levels. For blinking amplitude, frequency, and average on-time histograms 250 single dots (showing two-level blinking) from the 20 W/cm^2 experiment were used. Investigations of properties' dependency on excitation power density were performed on a subset of 30 single dots.

Blinking traces enable an easy distinction of background and nanocrystal emission, which yields higher quality data than a simple time-integrated intensity measurement. The background

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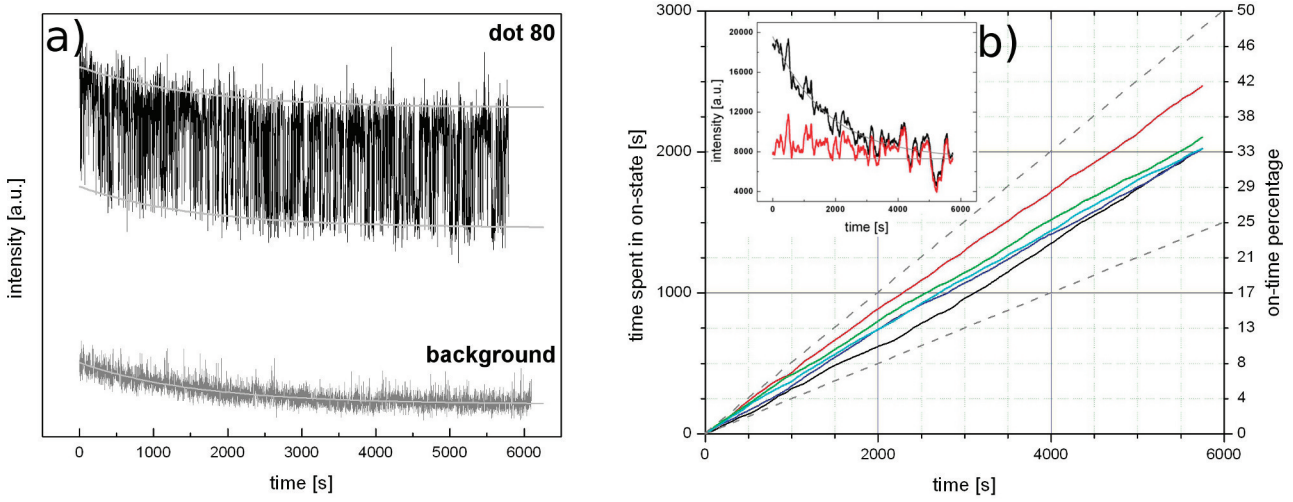

Figure 2. (a) Single dot blinking trace at high excitation (black line), photoluminescence trace recorded on a flat surface on the same sample but far away from the nanostructures (dark gray line) and single exponential fits to the latter with arbitrary offset (light gray lines). (b) Accumulated on-time of a dot ensemble versus passed time (7, 10, 20, 30, and 40 W/cm^2 represented by black, red, green, blue, and turquoise curves, respectively). Bleaching and statistical aging would cause the lines to bend downward. The inset shows a sum of 30 dot traces at 40 W/cm^2 without background subtraction (black line) and with single exponential background subtraction (red line). The gray lines show a single exponential decay and the offset for that fit.

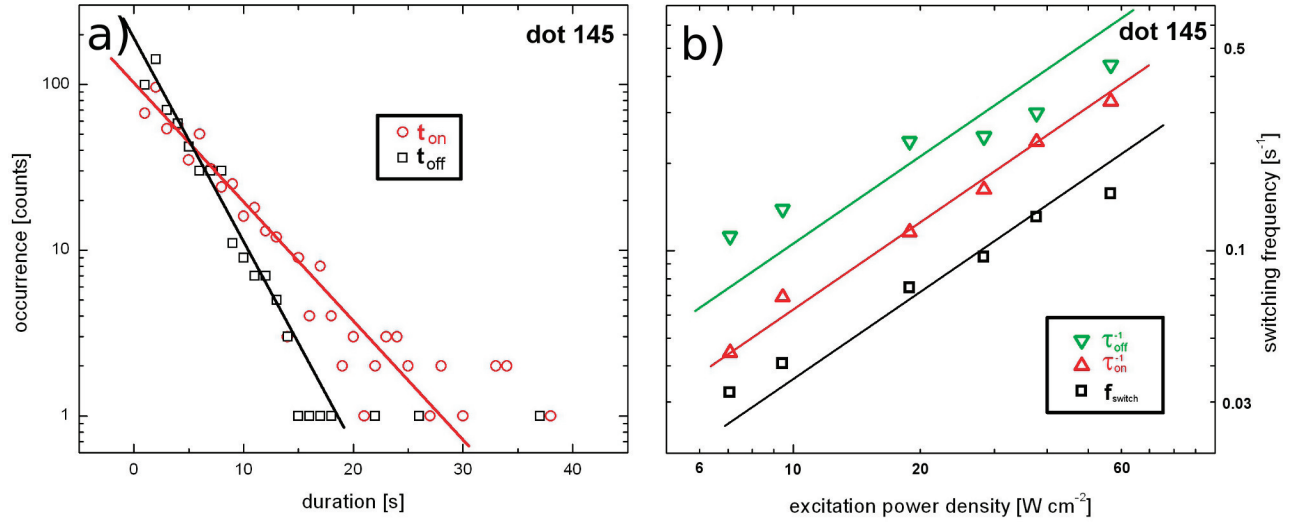

Figure 3. (a) On- and off-time distributions (red circles and black squares, respectively) of a single nanocrystal at 30 W/cm^2 excitation power density. Continuous lines indicate single exponential fits. (b) Inverted characteristic times of the single exponential fits for on-times (red upward triangles) and off-times (green downward triangles), as extracted from (a), and switching frequency from the total count of blinking events in an image sequence (black squares). Straight lines indicate linear increase (also see Figure 4).

signal of all 250 quantum dots under investigation was increasing linearly with excitation power density, which is most likely due to non-filtered excitation light and luminescence from the optics. Some intensity decrease with time could be observed in the background at high excitation, which raises the question if this part is scattered light emitted by neighboring nanocrystals. However, measurements on a flat surface on the same sample, but sufficiently far away from any patterned structures, revealed the same behavior, which can be fit with a single exponential function. The loss of intensity therefore cannot originate from any nanocrystals and is much more likely caused by oxide defect luminescence (note that there is a thin oxide layer all over the surface, also on the reference point). To strengthen the point, a look should be taken at the blinking amplitude. Figure 2a reveals that even though the average signal decreases, the blinking amplitude of a single dot does not, which means that the nanocrystals do not suffer from decreasing emission intensity. Statistical aging, as found, for example, by Brokmann et al.,[6] cannot be observed when plotting the average on-time of a single nanocrystal versus experimental time. Figure 2b shows that the average on-time of almost all 30 single quantum dots under investigation is roughly constant and not, as would be expected for bleaching or aging emitters, decreasing with time. These results are in contrast to many other publications, which present statistical aging in QD ensembles in accordance with power-law blinking statistics. In this work, 30 dots have been analyzed with respect to their on- and off-time distributions and most of them clearly exhibit single exponential behavior. Figure 3a shows such data for a representative dot. In contrast to power-law blinking, purely

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single exponential blinking behavior is not expected to lead to practically infinitely long dark states and therefore aging. The inset in Figure 2b shows that the sum of a few intensity traces is indeed unstable but does not decrease on average. The fact that there is no average intensity decrease at the beginning of the experiment shows that not all dots are initially in a bright state, which is in accordance with our own blinking trace analysis and also with Krauss et al.,[15] who found that about half of their nanocrystal population is initially in the dark state. Both on- and off-time distributions seem to be somewhat dependent on excitation power, but usually off-time distributions are less affected. As can be seen in Figure 3b, the characteristic falloff time decreases with increasing excitation power, which means that the switching frequency increases. That the switching rate is indeed dependent on excitation power has already been shown by Pistol et al.[16] and (for Si-QD) by Sychugov et al.[9] Also note at this point that Nirmal et al.[2] observed blinking on a 0.5 s time scale for CdSe nanocrystals, while most following publications report much shorter time scales (milliseconds) consistent with the use of high laser powers. Accordingly, Cichos et al.[8] found blinking on rather short time scales even for silicon nanocrystals under high excitation. When Auger processes are not suppressed, they are increasingly likely to happen with stronger excitation, leading to a quadratic increase of switching frequency with excitation,[3] which is indeed found by some experimenters.[16,17] In contrast, in this study a linear increase is found, as shown in Figure 4. This result is in line with experiments by Krauss at al.,[15] who found a linearly increasing quantum dot ionization rate with increasing excitation power.

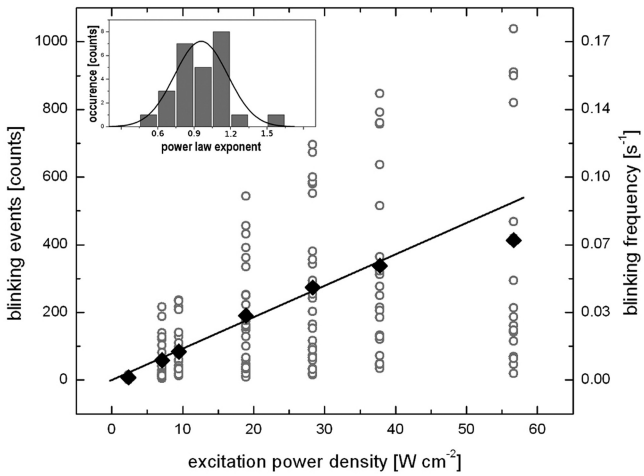

Figure 4. Number of blinking events (or, alternatively, blinking frequency) versus excitation power density for 30 single nanocrystals (gray circles) and the mean values (black diamonds). The straight line is a guide for the eye, demonstrating linear increase. The inset shows a histogram for the exponents obtained from power-law fits to all single emitters and a Gaussian fit with its maximum at unity.

There are three properties that could be extracted from single dot intensity traces: (i) switching frequency, (ii) average on-time, and (iii) blinking amplitude. None of them seems to correlate with the other demonstrating the individuality of different dots and their trap state configurations. Figure 5 shows all correlation plots (a,c,e) and all histograms (b,d,f). The switching frequency is roughly evenly distributed in the frequency domain (Figure 5f) over 3 orders of magnitude. Similarly, on-time duty cycles span the whole range from 0–100% (Figure 5b). There seems to be a peak at low average on-time values approaching a constant value from 50%. It should be noted, however, that there is a considerable fraction of non-blinking QDs (on-time of 100%). These have been omitted here since their intensity is more difficult to analyze than the QD blinking amplitude and since these may also be intermixed with other luminescent centers than QDs, for example, defects. The blinking amplitude for individual QDs in an ensemble (Figure 5d) is distributed according to a log-norm function. This is commonly found for nanocrystal size distributions, although geometrical features of the nanocrystals cannot necessarily be regarded as the cause for this. Remarkably, nanocrystals with very similar emission energy peaks can differ by almost an order of magnitude in intensity in their on-state. We see no clear explanation for this but argue that individual shape and microscopic configuration may have a large influence on the oscillator strength.

Turning to excitation power dependence, Auger processes do seem to play an important role in PL saturation experiments. Figure 6a presents the development of blinking amplitude with excitation power density, where a clear change in slope can be seen at 12 W/cm^2. Below this value the QD signal increases linearly with excitation, whereas the increase follows a square root dependency above it. These general trends of linearity below the threshold and square-root dependence above are analyzed for individual QDs in the form of histograms in Figure 6b. Calculations show, assuming an average exciton lifetime of 20 μs[18] and a nanocrystal absorption cross section of 3×10^{-15} cm^2,[19] that such value of excitation power density corresponds to a mean occupation of one exciton per nanocrystal.

The linear increase of switching frequency with excitation requires more discussion, since most experiments on blinking quantum dots find a different (quadratic) increase of the inverse characteristic on-time that represents Auger-mediated switching from the on- to the off-state. A linear dependency on the other hand means that Auger processes do not play a major role for blinking in these nanocrystals, which is in line with the conclusion from a previous paper[12] that such Auger processes are suppressed due to geometrical QD features (elongation). Protasenko et al.[20] argue that mobile charges in the vicinity of a quantum dot influence their emission significantly, being able to put the nanocrystal, or parts of it in their case, into a dark state. The charge distribution around a quantum dot can be rearranged by absorption of a photon, which explains a linear dependency of blinking events on excitation power. Altering the charge distribution on the nanocrystal surface inevitably shifts the local field and therefore energy levels, causing spectral shift in the QDs emission spectrum. Such a correlation of spectral shift and blinking events has been found by Schlegel et al.[21] It is conceivable that a charge redistribution could open (or close) midbandgap trap states, providing (or removing) alternative paths for exciton recombination. In another line of thought, the alignment of energy levels, caused by charge redistribution, enables resonant carrier tunneling to or from a trap state. This resembles the diffusion controlled electron transfer (DCET) model of Tang and Marcus.[22] An alternative interpretation of the linear dependence of the blinking frequency with excitation power is a direct transfer process whereby an electron has a certain probability to directly transfer to a trap state. The remaining hole would then prevent radiative recombination by enabling Auger processes. The direct transfer of the electron may be enhanced by the initial electron energy

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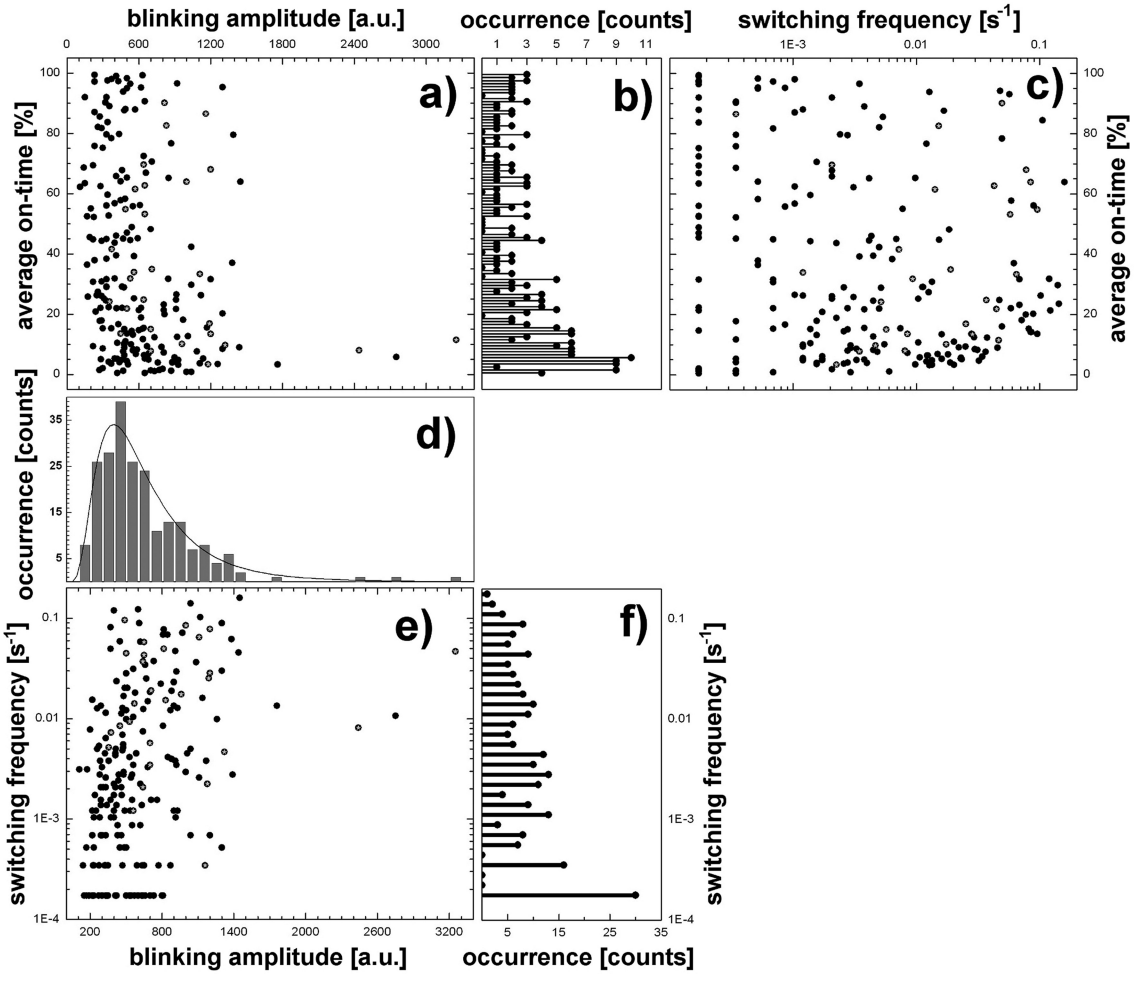

Figure 5. (a) Correlation graph for average on-time and blinking amplitude of 250 single nanocrystals. (b) Histogram for average on-times. (c) Correlation graph for average on-time and switching frequency of the same crystals as in (a). (d) Histogram for blinking amplitudes. The curve is a log-norm fit. (e) Correlation graph of blinking amplitude and switching frequency of the same crystals as in (a) and (c). (f) Histogram of the switching frequencies. (a–f) An excitation power density of 20 W/cm^2 was used for the measurement. (a,c,e) The circles marked with gray stars are dots that were used for Figures 2b, 4 and 6.

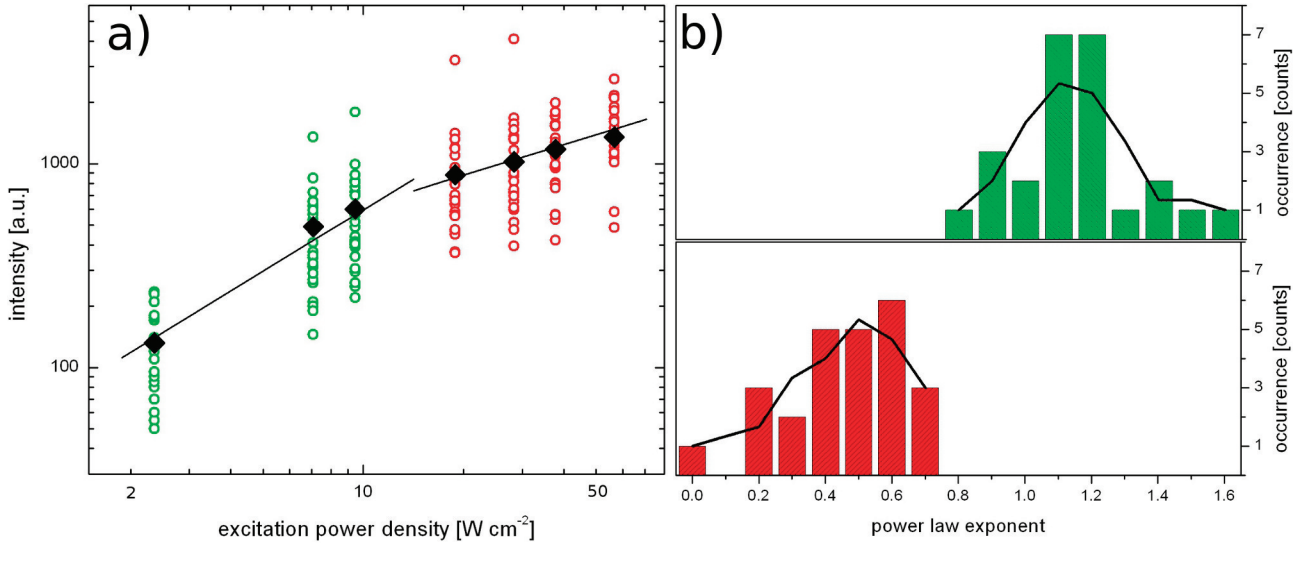

Figure 6. (a) Blinking amplitude for different excitation power densities for 30 single dots (green and red circles), average values (black squares) and guides to the eye with slopes 1 and 0.5 in double-logarithmic scale (black lines). (b) Histograms of slopes for all single dots determined by power-law fitting. The upper panel shows power-law exponents for the green region (three lowest excitations), while the lower panel shows data for the red region (four highest excitations). The black curves were obtained by smoothing the distributions (adjacent averaging, one neighbor).

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before relaxation to the QD quantized levels. As a result, the effect may be dependent on photon energy. Most single nanocrystals exhibit rather individual behavior and while some are not emitting light most of the time, interrupted by short emissive states, others almost never switch off. A possible explanation for this behavior is a differing stability of different charge distributions, of which some create nonradiative recombination centers in the bandgap and some allow the excitons in the quantum dot to recombine radiatively. A measure for the stability of a certain type of charge distribution would be its lifetime, given by the on- and off-time distributions obtained from the blinking statistics. In the most simple case there are two configurations, yielding purely single exponential distributions. In more complex cases several exponential distributions could add up to power-law distributed on- and off-times, as has been shown by, for example, Bochud et al.[23] A so-called truncated power-law would result from a superposition of several exponential functions, where the tail is dominated by the exponential with the longest characteristic time. When arguing in terms of trap states in the vicinity of the quantum dot core, the characteristic times in the distributions would strongly be influenced by the distance between trap and quantum dot core and the shape of the distribution by the number and distribution of different traps (see, e.g., ref 24 for an according model). Almost all nanocrystals under investigation in this work exhibit single exponential on- and off-time distributions, which would mean that there is a very small number of possible charge distribution configurations or only one single dominating trap state close to the dot. This could be caused by very good passivation, which is provided by a thick high quality oxide shell around the silicon core created by careful oxidation in the self-limiting regime. A change in PL increase with excitation power, represented by the at-least-one-exciton-per-nanocrystal threshold at 12 W/cm^2 in Figure 6, has been observed before[10] and has been attributed to a nonradiative, Auger-mediated recombination channel for excitons that competes with the radiative recombination channel. It suggests that bimolecular Auger processes are still allowed (even though suppressed to a certain extent) despite the nanorod shape of the silicon nanocrystals. However, a complete saturation of PL is not observed allowing for multiexciton occupancy in single silicon QDs. This is in accordance with some studies [ref 10 and references therein] but in contrast to others.[25]

In conclusion, we have analyzed the statistics of blinking of a large number of silicon quantum dots, fabricated by lithographic techniques. It could be shown that these quantum dots mostly obey single exponential laws in their blinking on- and off-times. Statistical aging of an ensemble, after subtraction of the background, is not observed. We conclude that bimolecular Auger recombination is not the dominant cause for blinking, but switching between on- and off-state is governed by single photon absorption processes. This suggests a direct electron transfer to a trap state to be effective leaving the QD core charged (by the hole). Mobile charge distributions in the vicinity of the nanocrystals may also play an important role here. Furthermore, photoluminescence saturation could not be observed with increasing excitation power. Instead, light emission increases with a square root dependency over a certain pumping threshold defined by the creation of one exciton per nanocrystal on average. All these effects are believed to be related to good passivation and nonspherical nanocrystal shape and make this type of silicon nanocrystals suitable for a broad range of applications, especially in lighting technology. The fact that there is a large number of apparently non-blinking quantum dots should be investigated further, since it is important both from a scientific and applications point of view. Analyzing the statistics of many quantum dots, as in this work, brings many general conclusions as discussed above. However, the large variation between individual dots in terms of switching frequency (>3 orders), average on-time (0−100%) and blinking amplitude (>1 order) is striking and calls for careful microscopic modeling. It is believed that individual QD shape, size, interface quality, oxide thickness, and oxide trap states all contribute to this vast scenario.

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REFERENCES

(1) Ma, X.; Tan, H.; Kipp, T.; Mews, A. *Nano Lett.* **2010**, *10*, 4166.
(2) Nirmal, M.; Dabbousi, B. O.; Bawendi, M. G.; Macklin, J. J.; Trautman, J. K.; Harris, T. D.; Brus, L. E. *Nature* **1996**, *383*, 802.
(3) Efros, Al. L.; Rosen, M. *Phys. Rev. Lett.* **1997**, *78*, 1110.
(4) Lee, S. F.; Osborne, M. A. *Chem. Phys. Chem.* **2009**, *10*, 2174.
(5) Frantsuzov, P.; Kuno, M.; Jankó, B.; Marcus, R. A. *Nat. Phys.* **2008**, *4*, 519.
(6) Brokmann, X.; Hermier, J.-P.; Messin, G.; Desbiolles, P.; Bouchaud, J.-P.; Dahan, M. *Phys. Rev. Lett.* **2003**, *90*, 120601.
(7) Margolin, G.; Protasenko, V.; Kuno, M.; Barkai, E. arXiv:cond-mat/0506512v2 (2008).
(8) Cichos, F.; Martin, J.; von Borczyskowski, C. *Phys. Rev. B* **2004**, *70*, 115314.
(9) Sychugov, I.; Juhasz, R.; Valenta, J.; Linnros, J. *Phys. Rev. B* **2005**, 115331.
(10) Valenta, J.; Fucikova, A.; Vácha, F.; Adamec, F.; Humpolícková, J.; Hof, M.; Pelant, I.; Kusová, K.; Dohnalová, K.; Linnros, J. *Adv. Funct. Mater.* **2008**, *18*, 2666.
(11) Bruhn, B.; Sangghaleh, F.; Linnros, J. *Phys. Status Solidi A* **2011**, *208*, 631.
(12) Bruhn, B.; Valenta, J.; Linnros, J. *Nanotechnology* **2009**, *20*, 505301.
(13) Valenta, J.; Bruhn, B.; Linnros, J. *Phys. Status Solidi C* **2011**, *8*, 1017.
(14) http://rsbweb.nih.gov/ij/(accessed November 5, 2010).
(15) Krauss, T. D.; O'Brien, S.; Brus, L. E. *J. Phys. Chem. B* **2001**, *105*, 1725.
(16) Pistol, M.-E.; Castrillo, P.; Hessman, D.; Prieto, J. A.; Samuelson, L. *Phys. Rev. B* **1999**, *59*, 10725.
(17) Peterson, J. J.; Nesbitt, D. J. *Nano Lett.* **2009**, *9*, 338.
(18) Sangghaleh, F.; Bruhn, B.; Linnros, J. Materials Physics, School of ICT, Royal Institute of Technology, Electrum 229, SE-16440 Kista-Stockholm, Sweden (2011), unpublished work.
(19) Kovalev, D.; Diener, J.; Heckler, H.; Polisski, G.; Künzner, N.; Koch, F. *Phys. Rev. B* **2000**, *61*, 4485.
(20) Protasenko, V.; Gordeyev, S.; Kuno, M. *J. Am. Chem. Soc.* **2007**, *129*, 13160.
(21) Schlegel, G.; Bohnenberger, J.; Potapova, I.; Mews, A. *Phys. Rev. Lett.* **2002**, *88*, 137401.

(22) Tang, J.; Marcus, R. A. *J. Chem. Phys.* **2005**, *123*, 054704.
(23) Bochud, T.; Challet, D. arXiv:physics/0605149v2 (2006).
(24) Verberk, R.; van Oijen, A. M.; Orrit, M. *Phys. Rev. B* **2002**, *66*, 233202.
(25) Timmerman, D.; Izeddin, I.; Gregorkiewicz, T. *Phys. Status Solidi A* **2010**, *207*, 183.