Quantum dot photoluminescence as charge probe for plasma exposed surfaces

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Abstract
Quantum dots (QDs) are used as nanometer-sized in situ charge probes for surfaces exposed to plasma. Excess charges residing on an electrically floating surface immersed in a low-pressure argon plasma are detected and investigated by analysis of variations in the photoluminescence spectrum of laser-excited QDs that were deposited on that surface. The experimentally demonstrated redshift of the PL spectrum peak is linked to electric fields associated with charges near the QDs’ surfaces, a phenomenon entitled the quantum-confined Stark effect. Variations in the surface charge as a function of plasma input power result in different values of the redshift of the peak position of the PL spectrum. The values of redshift are detected as 0.022 nm and 0.073 for 10 and 90 W plasma input powers, respectively; therefore indicating an increasing trend. From that, a higher microscopic electric field, $9.29 \times 10^6$ V m$^{-1}$ for 90 W compared to $3.29 \times 10^6$ V m$^{-1}$ for 10 W input power, which is coupled to an increased electric field in the plasma sheath, is sensed by the QDs when plasma input power is increased.

Keywords: quantum dot, photoluminescence, surface charge, low pressure plasma, plasma charging, dusty plasma

(Some figures may appear in colour only in the online journal)

1. Introduction

Plasmas containing nano- to micrometer-sized dust particulates, designated as complex or dusty plasmas, are of immense importance due to either the potential threat or advantageous role of the nanoparticles in different research areas and technologies. Dust particles are, for instance, advantageous for the creation of self-organized plasma crystals [1] and plasma-assisted fabrication of nanostructures and polymers [2, 3]. Recently, detrimental effects of dust particulates for contamination control purposes in high-tech [4] and semiconductor [5] industries have been observed and studied. Plasma charging of particles, either levitated or adhered to surfaces, is the process that determines the dynamics of contaminating particulates in ionized media such as those in lithography scanners [6] or those with respect to spacecraft charging during the atmosphere re-entry [7]. Connected to that, electrically floating surfaces are known to accumulate negative charge, i.e. an excess of electrons, when exposed to, for instance, radiofrequency (RF) [8, 9] or extreme ultraviolet-induced [10] plasmas since the electrons possess higher mobility compared to ions. Charge accumulation on these surfaces is studied to account for various phenomena such as particle
lofting [11]. Crucial in these applications is the fundamental understanding of charging of particle-laden surfaces immersed in plasmas, for which so far a comprehensive model predicting the charging dynamics does not exist. Also, experimental data on electric fields surrounding the surfaces as well as accurate surface charge measurements are scarce.

The amount of (negative) charge on a surface in contact with plasma is determined by the balance of incoming and outgoing ion and electron fluxes; those can be measured experimentally [12] and modeled numerically [13]. Furthermore, particle charge on a surface can be calculated using the ‘shared charge model’ [14]. According to this model, the charge density depends on the plasma sheath electric field around the surface. This sheath electric field was modeled by Sheridan et al., assuming a planar, collisionless and dc sheath in a plasma where the electrons are described by a bi-Maxwellian distribution [14]. Simulations of Kim and Economou illustrate a two-dimensional sheath profile at an interface between an insulator-conductor floating surface exposed to a high-density plasma [15].

The sheath electric field was measured spatially resolved in RF driven argon plasmas by using either microparticle probes under hypergravity conditions [16] or by deploying laser-induced fluorescence-dip spectroscopy by Barnat and Hebner [17]. In the latter technique, laser-excited Argon Rydberg levels are Stark-shifted due to the electric field around the probe. Similarly, Stark-shifted energy states of an ‘artificial atom’, i.e. of a quantum dot (QD), can in principle be used for electric field measurements near a surface since their discrete energy level structure is also subject to electric-field-induced shifts and alterations [18].

Although the electric field profiles around an electrically floating and biased object were measured [19], an in situ measurement of the plasma sheath electric fields on a particle-laden surface facing a plasma has not been performed yet. Experimentally investigating the plasma sheath electric fields with surface-deposited QDs would provide unique insights into the charging mechanisms of nanoparticles. Experimental data regarding the charging of nanoparticles are scarce in the literature, partly because a particle’s charge decreases with its size, which necessitates high-resolution diagnostic methods [20]. The problem of charging of particles residing on plasma-facing surfaces was considered both theoretically [21] and experimentally [22] only for micrometer-sized particles and not for nanometer-sized particles which pose an increasing challenge in future contamination control applications.

Pioneered recently by Marvi et al. [23], photoluminescent nanoparticles have been used to visualize interactions between plasma and a substrate surface. In that work, the idea of using the photoluminescence (PL) of semiconductor QDs as a diagnostic method for surface charging of nanoparticles due to plasma interaction was proposed. Furthermore, Pustylnik et al. [24, 25] have theoretically shown that a layer of QDs deposited on the surface of a microparticle could provide the possibility of measuring the surface charge of microparticles in plasmas.

In this paper, we further develop the diagnostic tool that visualizes the charging of a plasma-exposed surface using PL spectra of nanometer-sized QDs. For this purpose, PL spectra of QDs deposited on an electrically floating substrate have been recorded before, during, and after plasma exposure. Distinctly, in this study, reproducible measurements are performed to quantify the values of the electric-field-induced redshift of the peak of the PL spectrum of the QDs, previously characterized as Stark shift [23]. These values of Stark shift are measured at various plasma conditions (i.e. at different input powers). Moreover, the measured values of Stark shift are interpreted using a statistical surface charge model. A Langmuir probe is used to extract plasma parameters (e.g. electron temperature) at the conditions of the Stark shift measurements. These plasma parameters are then used for estimations of the sheath electric field using traditional RF sheath theory.

The current present paper is organized as follows: First, an overview of the experimental methodology is presented in section 2. Together with a detailed description of the experimental setup, the measurements of the PL spectra of the QDs, are explained in that section. Next, in section 3, the experimental results and observations of QD PL spectra from these nanocrystals as exposed to low-pressure RF plasma in various conditions are provided. Finally, section 4 contains the interpretation of the experimentally investigated phenomena.

2. Methods

2.1. Quantum dot photoluminescence

QDs are semiconductor nanocrystals characterized inherently as zero-dimensional quantum wells for charge carriers. The optical characteristics of these QDs are dependent, among other parameters, on their size. QDs typically have a core–shell structure. The main semiconductor in the core determines the properties, whereas the shell stabilizes those. A QD nanocrystal is optically excited upon receiving a photon whose energy exceeds the energy gap between the valence and conduction bands, followed by the generation and confinement of an electron–hole pair. In the next stage, the electron–hole pair relaxes back to the bound states of the QD’s corresponding quantum well; finally, the recombinination of the electron and hole leads to the emission of a photon with an energy equal to the width of the band gap. As a consequence of charge carrier relaxation, the energy of an emitted photon is lower than that of an excitation photon. Since in this work, the emission from an ensemble of QDs with a certain size distribution is observed, the associated PL peak is broadened corresponding to the size distribution. A PL emission peak of an ensemble of QDs can be characterized by three values: The central wavelength, the integrated intensity, and the full-width at Half-Maximum (FWHM).

Measurements of the QD PL spectrum and analysis of the above-mentioned values allow using QDs as in situ charging probes. In this work, the QDs are deposited on a substrate and exposed to a low-pressure RF argon plasma. Optical excitation is performed by a laser. The charges on the surface of an electrically floating substrate create the electric field. This electric
field affects the PL of the QDs due to the quantum-confined Stark effect [26], which allows to obtaining the information on charging from the PL spectra.

The QDs used in this work were commercially available (NanoOpticalMaterials) colloidal CdSSe-ZnS gradient-alloyed shell QDs. In this specific type of QDs, blinking effects were nearly suppressed and the quantum yield was enhanced by constructing a band structure that confines the exciton within the core [27, 28]. Therefore, the Auger effect, as a non-radiative process responsible for blinking, was suppressed. The peak of the PL of the QDs was at $\lambda_p = 540 \pm 10$ nm and FWHM = 34 nm; their core radius and shell thickness were 2.2 nm and 0.9 nm, respectively, and their molecular mass $1.21 \times 10^8 \text{ mg mol}^{-1}$. For each QD sample, 1 $\mu$l of the original colloidal solution with $4 \text{ mg ml}^{-1}$ concentration was drop-cast on a reflective silicon substrate, therefore resulting in a surface density of about $1.1 \times 10^{-11}$ mol mm$^{-2}$ and a layer thickness of 350 nm, assuming the QDs were homogeneously dispersed. The relative dielectric constant of the QDs was approximately [29] $\varepsilon_r = 6.19$. After total evaporation of the solvent, a layer of QDs remained on the substrate. The silicon substrate with the QDs was clamped to a stainless-steel substrate holder which was electrically insulated from the grounded walls of the vacuum vessel. Therefore, in this configuration, the QD sample acquired floating potential with respect to the surrounding plasma. The PL of the drop-cast QDs on the sample stimulated by laser excitation was continuously recorded before, during, and after plasma exposure. The PL was temporally and spectrally resolved with 0.075 s and 1.5 pm maximal temporal and spectral resolution, respectively, using the experimental setup described below.

2.2. Experimental setup

A schematic representation of the experimental setup is shown in figure 1. The experiments were conducted in a cylindrical vacuum vessel, 30 cm in diameter and 45 cm in height. Illumination laser light was introduced into the chamber through a quartz window. The PL of the QD-sample was observed at 90° with respect to the illumination through another quartz window. The vessel lid contained a gas inlet which was used together with a mass flow controller to feed a steady flow of 1 SCCM Argon gas to the experimental volume. Simultaneously, the vessel lid contained an electrode that was electrically insulated from the rest of the vessel by a Teflon ring. This 12 cm diameter circular electrode was driven with a sinusoidal voltage of 13.56 MHz. This voltage was delivered by an RF generator (Barthel RFG-13-100-L) synchronized with an automatic matchbox (Barthel MCI-300) with powers ranging from 10 to 90 W. The rest of the vessel served as a grounded electrode.

The vacuum vessel was pumped out at the bottom by a turbo-molecular pump backed by a rotary roughing pump. The base pressure inside the vessel was $3 \times 10^{-3}$ Pa. During the experiments, the pressure inside the vacuum vessel and thus inside the measurement volume was set to 4 Pa by a butterfly valve (VAT 61332-KAAH) operated in the vacuum line—bypassing the turbo-molecular pump—between the vacuum vessel and the rotary roughing pump.

The plasma exposed QDs on the sample was excited using a temperature-controlled pulsed laser system consisting of a laser diode (Thorlabs L405G1) with a wavelength of 405 nm, together with a laser diode driver (Thorlabs ITC4005) enabling pulse-width modulation and pulsing of the laser diode corresponding with square pulses delivered by the signal generator (Keysight 33509B). The laser beam was collimated and directed to the QD layer deposited on the silicon substrate using a mirror and a collimator lens.

PL of the QDs was collected using a pair of confocal lenses (with identical focal lengths of $f_1 = f_2 = 200$ mm, see figure 1) and focused onto the 250 $\mu$m wide entrance slit of the monochromator (Acton Research SpectraPro275), where it
was spectrally resolved. Afterwards, the spectrum was recorded by an ICCD camera (Andor iStar 334 T) mounted directly behind the monochromator. The camera recorded a time series of spectra synchronized with the laser pulses. The laser was pulsed in order to allow the recording of both the background emission and the PL signals of the excited QDs for consecutive pulses. A band pass filter (central wavelength = 540 nm, FWHM = 50 nm) ensured the collection of PL emission light only, by attenuating most of the plasma emission which could otherwise induce additional noise.

As the PL spectra of the QDs are temperature-induced effects [30] resulting from, in our case, heat fluxes from the plasma, measurement and recording the temperature of the QDs is essential. Therefore, a temperature sensor (PT-1000) was installed in the substrate holder to record the temperature trend. The data were stored in a PC and analyzed with in-house developed scripts. A delay generator (Stanford Research Systems DG645) was used for temporal modulation of the input RF signals driving the plasma as well as synchronization of the pulsed laser and the ICCD camera system.

 Plasma parameters such as the electron temperature ($T_e$), the floating potential ($V_f$), and the plasma potential ($V_p$) were measured using a Langmuir probe (Impedance P2516i). The software delivered by the supplier interpreted the I–V characteristic curves of the probe and calculated the aforementioned plasma parameters. The Langmuir probe and the floating substrate were simultaneously inside the chamber where the probe was positioned a few centimeters apart from the sample with the QDs. This configuration enabled the measurement of the local values of the bulk plasma parameters in the vicinity of the floating substrate. The aforementioned plasma parameters were used to approximate the electric fields in the plasma sheath formed around the floating substrate, as will be discussed later.

### 2.3. Measurement and fitting procedure

Figure 2 represents a typical measurement of a PL spectrum together with the fit for a pristine QD sample. The fitting procedure will be described below. For the measurements, the ICCD camera served as a master device with which the plasma and laser pulses were synchronized via the delay generator. In order to acquire a sufficient amount of PL light and to ensure optimal signal-to-noise ratio, each acquisition consisted of 100 accumulated individual spectra, repeated consecutively for background (without laser excitation) and PL (with laser excitation) measurements. Each PL measurement was subtracted from the average of its previous and next background measurement to reconstruct the PL spectra (black dots in figure 2).

The position of the PL peak was determined using the following fitting procedure. After averaging the data over 100 repeated measurements, the PL peak was fitted using a double skewed Voigt function developed specifically for this procedure (see appendix A). This double skewed Voigt distribution ($\phi_V$) consisted of a weighted distribution of a Gaussian and a Lorentzian probability density function ($\phi_G$ and $\phi_L$) multiplied by their respective cumulative distribution functions ($\Phi_G$ and $\Phi_L$) as indicated in the following expression:

$$
\phi_V(x) = 2(1-\eta)\phi_G(a_Gx)\Phi_G(a_Gx) + 2\eta\phi_L(a_Lx)\Phi_L(a_Lx),
$$

where $\eta$ is the Voigt weight factor and $a_G$ and $a_L$ are the skew parameters of the Gaussian and Lorentzian probability density functions, respectively. This double-skewed Voigt distribution approximated the data with $R^2$ of 0.9998. The primary reason for developing this specific set of fitting functions was asymmetry in the measured data caused by non-linearities of the image intensifier of the ICCD camera, skewing the spectrum of the PL emission. The PL peak position was assigned to the peak and the PL intensity to the integral of the skewed Voigt function resulting from the fit.

Next, variations of the PL peak position and peak intensity were determined during each experiment. Figure 3 exemplary shows two respective PL peaks: One at the beginning of a typical experiment, and the other the QDs’ PL emission after 76.5 s of plasma exposure (red dots). It is visible that the peak slightly shifts towards a longer wavelength, indicating a ‘redshift’, while the peak intensity slightly decreased.

Multiple trials of exposing QDs to plasma were performed, during which the PL peak positions were measured in several plasma pulses of equal duration and subsequently averaged over these pulses. This averaging scheme was designed to track the PL peak position and intensities precisely, enabling further quantitative analysis when the input power of the plasma was subject to change. With this procedure, the PL peak position was determined with a 0.002 nm error.
Figure 3. PL emission spectrum of the QDs before (blue dots) and after 76.5 s (red dots) of plasma exposure: the peak has experienced a 0.15 nm shift. The peak intensity has slightly declined.

3. Results

3.1. Time-resolved PL spectra: the ‘slow shift’ and the ‘fast shift’

As illustrated in figure 4, the two main features of the PL spectrum, the peak position, and the peak intensity are subject to change due to exposure of the QDs to plasma. At the beginning of the experiments, before any plasma exposure, both the peak position and the peak intensity are constant. At the moment when the plasma is switched on, an immediate shift of about 0.04 nm in the peak position towards longer wavelengths is observed (see figure 4(a)). Afterwards, a gradual, ramp-like, and relatively slow shift of 0.11 nm in total proceeds as the plasma affects the QDs on an extended time scale of 76.5 s. Marking the switching off of the plasma, an immediate shift of the peak position is observed, which is symmetrical—equal in magnitude but reverse in direction—to the initial immediate shift. Finally, a gradual and again, relatively slow shift towards the initial values sets in. However, the peak position reaches a stable value slightly higher than that for the pristine QD sample. Similarly, the trend in the integrated intensity of the PL peak appears to show a gradual decrease during plasma exposure. Both slow trends—of the PL peak position and of the integral intensity—are characterized by very similar time scales. The PL intensity also does not recover to its value for the pristine QD sample (see figure 4(b)).

We term the immediate increase/decrease of the PL peak position at the moment of switching the plasma on/off ‘fast shift’. The gradual and ramp-like shift occurring on the longer time scale, we term the ‘slow shift’. Obviously, the trend in the slow shift follows the trend in the substrate temperature (see figure 4(a)) which rises during plasma exposure and exponentially declines after the exposure is stopped. Therefore, we attribute the slow shift to temperature-induced effects caused by the thermal plasma load on the substrate surface. The time scale of the fast shift is much shorter than that of the temperature evolution of the substrate and, therefore, we attribute this shift to the quantum-confined Stark effect caused by plasma-induced surface charges.

The substrate temperature is measured to rise 1.1 K during 76.5 s of plasma exposure. The rate of the temperature-induced redshift is approximately 0.1 nm K$^{-1}$ according to this measurement. This value was cross-checked by externally heating the substrate with the QDs without any plasma exposure, where the trend of the slow shift corresponded exactly to that of the temperature while the fast shift observed in the plasma exposure experiments did not occur. Recently, a detailed evaluation of the thermal balance of surface-deposited QDs was published. The results practically rule out any transient thermal effects that could obscure the quantum-confined Stark effect.

According to the observations described above, the fast shift and the (temperature-induced) slow shift occur on...
different timescales which allows us to undoubtedly distinguish between them. The following section presents a different set of experiments in which we could reduce the slow shift to negligibly small magnitudes in order to better investigate the fast shift.

3.2. Stark shift

To isolate the Stark shift, the time during which the QD sample was exposed to the plasma was shortened step by step. As the plasma exposure time was decreased, the QDs had lesser time to attain temperature rise, which would induce observable redshifts. Initially, the QDs, and the substrate they were deposited on, were exposed to the plasma for 76.5 s (see figures 3 and 4). In further experiments, the exposure time was consecutively set to 30, 18, and 4.5 s as can be seen in figures 5(b)–(d) respectively. As demonstrated in figure 5, the slow shift is still clearly visible at the plasma durations of 76.5, 30, and 18 s. The temperature of the substrate and, therefore, of the QDs was measured to rise 1.1, 0.6, and 0.3 K during 76.5, 30, and 18 s of plasma exposure, respectively (see figures 5(a)–(c)). For the last experiment (figure 5(d)), the exposure time was set to 4.5 s only, which was sufficient to gather enough data and, at the same time, to diminish the temperature effect. Also, at 4.5 s plasma duration, the PL peak position recovered to the value it had before the plasma exposure. Hence, for a sufficiently short plasma exposure time (4.5 s and shorter), the temperature effects become negligible and pure Stark shift can be observed. The PL peak intensity, nevertheless, has a longer (about 20 s) recovery time and relaxes to a value that is slightly below the initial one (figure 5(d), red dots). This effect was already reported by Marvi et al [23] and can be attributed to the damage of the QDs by impinging plasma ions.

3.3. Quantifying Stark shift

To quantify the Stark shift of the PL peak position, a more enhanced set of experiments involving averaging over multiple cycles of measurements was conducted. The QDs were then exposed to 100 short plasma pulses each lasting 0.7 s. Temperature increase over multiple plasma pulses was prevented by separating the exposure periods by \(\approx 15\) s, allowing the
Figure 6. Stark shift measured for a short plasma exposure. The QDs’ PL peak position during plasma exposure (0.7 s, pink dots) and non-exposure (yellow dots) time intervals. The pink and yellow areas and lines indicate the standard deviation and the average of the data points, respectively. For the specific plasma parameters of 50 W and 4 Pa, the Stark shift is measured to be 0.046 nm.

temperature of the substrate to decrease. As a result of this averaging scheme, the PL peak position was determined within a maximum standard error of the mean of just 0.002 nm. The value of Stark shift was, afterwards, calculated by subtracting the average peak positions during plasma exposure from those during non-exposure time intervals. As illustrated in figure 6, the value of Stark shift for specific plasma parameters of 50 W input power and 4 Pa gas pressure is measured to be 0.046 nm. In figure 6, the PL peak positions for each measurement are represented with pink (plasma exposure time interval) and yellow (non-exposure time interval) dots. Besides that, the heights of the colored areas correspond to the standard deviations for respective measurement intervals and the solid lines indicate the average of the respective measurement intervals.

3.4. Stark shift depending on the plasma input power

We applied the procedure described in the previous subsection to systematically measure the dependence of the Stark shift on the plasma input power. The input power of the plasma ranging from 10 to 90 W was increased in steps of 10 W and the value of the Stark shift was measured for each input power. In this set of experiments, the gas pressure was maintained constant at 4 Pa.

As figure 7 shows, the plasma-induced shift of the peak position of the QD PL spectrum with varying plasma input powers is represented by black circles. An increasing trend is observed in the value of the Stark shift as a function of input power. For the lowest power value of 10 W, the Stark shift of the PL peak position was measured to be 0.022 ± 0.002 nm. This value of the Stark shift gradually rises to the value of 0.073 ± 0.001 nm at the plasma input power of 90 W.

4. Discussion

First, the slow shift is attributed to the temperature effects of the plasma on the substrate and the QDs. As depicted in section 3.1, a monotonous redshift on long timescales of tens of seconds is observed when the QD sample is immersed in the low-pressure plasma environment. Concomitant with this redshift of the PL peak position, the integrated intensity of the PL peak is observed to decrease with a similar linear trend on long timescales. Lattice dilation, i.e. thermal expansion of the QDs, contributes to the slow shift of the PL peak position [31]. The reduction in PL peak intensity is comprised of a recoverable and a non-recoverable part. The recoverable part is ascribed to temperature effects [32], whereas effects of ion damage play the main role in the non-recoverable part of the PL peak intensity [23].

Experiments with short plasma exposure times allowed to exclude the slow shift and to investigate the dependence of the fast shift on the plasma input power. This fast shift is attributed to charging effects, i.e. to the electric fields generated by charged species, in this case, electrons, residing on the QD-coated substrate. The reason for the accumulation of electrons on the substrate, once it is immersed in the plasma, is that the mobility of electrons is much higher compared to that of ions. At steady state surface charge density, the electron and ion fluxes towards the surface are balanced. The latter condition can only be satisfied when the floating potential, V_f, is negative with respect to the surrounding plasma [33]. The electric field, induced by the surface electrons, will cause the quantum-confined Stark effect (QCSE) [34–36] on the discrete quantum states of the QDs.

The electric-field-induced fast redshift (∆λ) is expressed as [37]:

$$\Delta \lambda = 0.03 \lambda^2 (hc)^{-1} \left( m_e^* + m_h^* \right) a^4 \left( \frac{2 \pi eE}{h} \right)^2,$$

(2)
where \( e, h, a, m_e^*, \) and \( m_i^* \) indicate the elementary charge, Planck’s constant, the QD core radius, the effective electron mass, and the effective hole mass, respectively. The QCSE is caused by modification of the electron and hole energies as a result of which, the recombination energy becomes lower. The electric field ‘pulls’ the electron and hole to the opposite sides inside the QDs, leading to a reduction of the band gap and therefore to a redshift in the overall PL spectrum [38]. We use this effect for sensing the surface charges in plasma.

Marvi et al [23] proposed a model explaining quantitatively how the experimentally observed Stark shift is correlated to plasma charging of the floating surface. Using this ‘discrete charge model’, it was confirmed that the observed Stark shift can be explained by the electric field created by surface charges.

As the electrically floating substrate, with QDs deposited on it, is immersed in the plasma, a sheath is formed around it. The average normal component of the plasma sheath electric field on the substrate surface is \( E_{\text{sheath}} = \sigma / \epsilon_0 \), where \( \sigma \) is surface charge density. The local electric field is, however, subject to fluctuations. Therefore the actual value of the electric field sensed by the QDs is larger. The fluctuations are mainly due to the redistribution of electron configurations on the sample and the inherently discrete nature of the charge process [21, 39].

We calculate the statistics of the local electric field resulting from the surface charge by taking into account multiple random configurations of electrons on the surface at constant \( \sigma \) and evaluating the electric field at the position of a single point-like QD. The resulting Stark shift of the PL peak position caused by the microscopic electric field of each randomly dispersed configuration of electrons is then calculated using equation (2). Typically, a few million random electron configurations are evaluated to calculate the statistics of the local electric field—each configuration consisting of thousands of quasi-static electrons. The observed fast shift is measured over long (typically 0.7 s) measurement time and is therefore averaged over all possible electron configurations and over many radiation acts. It was shown [23, 24] that in this case the measured Stark shift—\( \delta_{\text{mean}} \)—would correspond to the average of the Stark shifts of all electron configurations. In other words, \( \delta_{\text{mean}} = \Delta \lambda (E_{\text{rms}}) \), where \( E_{\text{rms}} \) is the root-mean-square electric field averaged over all the electron configurations.

The discrete charge model allows the calculation of the local electric field for a given \( \sigma \) which is connected with the average normal component of the sheath electric field. The sheath electric field, in its turn, is calculated assuming a quadratic potential drop profile across the sheath thickness, leading to a linearly increasing electric field [40] in the sheath from the bulk plasma towards the surface. Plasma parameters measured by the Langmuir probe (appendix B) are used to determine the potential drop and roughly estimate the sheath thickness using Child-Langmuir law for RF plasmas [41]. The sheath thickness estimations are cross-checked with camera images taken from the plasma sheath close to the substrate. The potential drop across the floating sheath of an RF plasma, also known as the floating potential under RF bias, is expressed as [8]:

\[
V_{\text{fsr}} = \frac{kT_e}{e} \left[ \frac{1}{2} \ln \left( \frac{2\pi m_e}{M} \right) \right] - \ln I_0 \left( \frac{eV_1}{kT_e} \right),
\]

where \( T_e, m_e, M \) and \( V_1 \) are the electron temperature, electron mass, ion mass (in this case, argon), and the amplitude of the RF voltage across the sheath, respectively. Here, \( I_0 \) is the zero-order modified Bessel function. The first term on the right-hand-side of equation (3) represents the floating potential under DC conditions while the second term represents the RF self-bias. \( T_e \) is measured by the Langmuir probe. \( V_1 \), however, cannot be reliably measured for a floating electrode. Therefore, to obtain an absolute upper limit estimation of \( V_{\text{fsr}} \) (and corresponding \( E_{\text{sheath}} \)), we used the amplitude of the RF signal \( (U_{RF}) \) measured by the oscilloscope on the RF electrode. The actual value of \( V_{\text{fsr}} \) lies therefore between the DC floating potential measured by the Langmuir probe and the voltage obtained from equation (3) with \( V_1 = U_{RF} \).

From the Langmuir probe measurements, the electron temperature is \( T_e = 1.5 \text{ eV} \pm 0.1 \text{ eV} \) and the amplitude of the RF signal (measured by an oscilloscope) is \( U_{RF} = 178 \text{ V} \) for 50 W plasma input power. Together with a sheath thickness of \( d_s \approx 0.6 \text{ mm} \), the plasma sheath electric field at the location of the substrate is approximated to be \( E_{\text{sheath}} = 5.8 \times 10^5 \text{ V m}^{-1} \), for the conditions explained in detail in section 3.3. Illustrated in figure 8 is a statistical evaluation of the microscopic electric field that is yielded by the discrete charge model for the above-mentioned values and conditions of the plasma. In figure 8(a), a histogram of the electric fields associated with \( 10^6 \) configurations of 3000 electrons on the surface, randomly distributed on a \( 10^{-10} \text{ m}^{-2} \) square sample in the center of which a QD resides. A root-mean-square electric field of \( E_{\text{rms}} = 6.8 \times 10^6 \text{ V m}^{-1} \) would consequently induce a Stark shift of the PL peak position of \( \delta_{\text{local}} = 0.05 \text{ nm} \) (figure 8(b)). Also, as the corresponding Stark shift values in figure 8(b) indicate, the average sheath electric field would induce only a non-observable Stark shift of \( \delta_{\text{sheath}} = 3.4 \times 10^{-4} \text{ nm} \).

The measured value of Stark shift of the PL peak position was 0.046 nm (see figure 6) for the conditions mentioned in section 3.3 is very close to the maximal Stark shift value \( \delta_{\text{local}} = 0.05 \text{ nm} \) figure 8. The same statistical calculations are performed assuming the absolute minimum for the floating potential (i.e. DC floating potential). In this case, the minimum \( \delta_{\text{local}} = 0.0034 \text{ nm} \) would be one order of magnitude lower than in the case assuming the upper limit \( V_{\text{fsr}} \), resulting in the calculated Stark shift value to fall below the experimental detection limit of 0.01 nm.

As the Stark shift values are measured at different plasma input powers, the effect of the plasma conditions on the detected value of Stark shift is demonstrated (see section 3.4). It has been observed that the value of the Stark shift increases with the plasma input power (see figure 7). In order to study the effect of these plasma parameters on the charge of the surface, the plasma sheath electric field and the microscopic electric field are calculated using the discrete charge model

\[
\delta_{\text{mean}} = \Delta \lambda (E_{\text{rms}}),
\]
Figure 8. Statistical evaluation of the microscopic electric field $E_{\text{rms}}$ at the location of a QD associated with quasi-stationary electrons on the substrate surface (a) and the corresponding histogram of QD photoluminescence Stark shifts (b). Over $10^6$ different electron configurations are integrated for these evaluations.

Figure 9. Maximum (red upward triangles) and minimum (blue downward triangles) calculated values of Stark shift based on the discrete charge model as a function of plasma input power at the constant pressure of 4 Pa together with the measured values of Stark shift (black circles). The minimum calculated values all fall under the experimental detection limit.

5. Conclusions

QDs, deposited on the surface of an electrically floating substrate immersed in a low-pressure RF plasma, were used as nanometer-sized surface charge probes. In conclusion, the experiments have shown that:

- The fast (Stark) redshift of the PL peak position of the laser-excited QDs was caused by electric fields originating from electrons residing on the surface of the substrate.
- The previously designed discrete charged model \[23\] correctly calculated the electric field, typically $6.8 \times 10^6$ V m$^{-1}$, formed by the surface electrons and the associated Stark shift of 0.05 nm.
- Increased plasma input power led to an increased value of Stark shift, 0.073 nm, which was associated with increased surface charge density as a result of higher plasma input power of 90 W.
• The Stark shift of the PL of the QDs deposited on a plasma-facing surface was therefore capable of tracking the variations in the surface charge density.

The plasma parameters were measured by a commercial Langmuir probe and used to estimate plasma sheath electric fields and the values of Stark shifts by the discrete charge model. The uncertainty in the RF self-bias measurements led to calculating only the maximal and minimal possible values of Stark shifts. The experimentally measured values of the Stark shift were found to lie close to the maximal calculated values.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Appendix A. Double skewed Voigt fitting

In this appendix, the derivation of the double-skewed Voigt distribution function is explained in detail. A Voigt distribution function, or a Voigt profile, is a convolution of a Gaussian and a Lorentzian distribution.

Since the acquired data had an asymmetrical component, the Voigt profile was modified, accordingly, to be a combination of a skewed Gaussian distribution and a skewed Lorentzian distribution, resulting in a double skewed Voigt distribution as used to analyze the data in this paper. This double-skewed Voigt distribution had the form:

\[
\phi_V(x) = 2(1-\eta)\phi_G(x)\Phi_G(a_Gx) + 2\eta \phi_L(x)\Phi_L(a_Lx). \quad (A1)
\]

The Gaussian probability density function around the mean \(\mu\) with variance \(\sigma^2\) is expressed as:

\[
\phi_G(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{x-\mu}{\sigma})^2}, \quad (A2)
\]

and the cumulative distribution function belonging to this Gaussian probability density function is:

\[
\Phi_G(x) = \frac{1}{2} \left[1 + erf\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\right], \quad (A3)
\]

here, \(erf\left(\frac{x-\mu}{\sigma\sqrt{2}}\right)\) is the Gauss error function defined as:

\[
erf(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-t^2} dt. \quad (A4)
\]

The probability density function of a skewed Gaussian distribution with skew parameter \(a_G\) is then given by:

\[
f_G(x) = 2\phi_G(x)\Phi_G(a_Gx). \quad (A5)
\]

When \(a_G = 0\) the function is equal to a regular Gaussian distribution whereas for \(a_G > 0\) and \(a_G < 0\) the distribution is skewed towards the right and left, respectively.

The same procedure is used for a Lorentzian distribution with a probability density function:

\[
\phi_L(x) = \frac{1}{\pi\gamma} \frac{1}{1 + \left(\frac{x-\mu}{\gamma}\right)^2}, \quad (A6)
\]

where \(\mu\) is the location parameter, specifying the location of the peak, and \(\gamma\) is the scale parameter equal to the FWHM of the Lorentzian distribution function.

The cumulative distribution function of the Lorentzian distribution function is:

\[
\Phi_L(x) = \frac{1}{\pi} \arctan\left(\frac{x-\mu}{\gamma}\right) + \frac{1}{2}. \quad (A7)
\]

Multiplying the probability density function with the cumulative distribution function results in the skewed Lorentzian distribution function with skew parameter \(a_L\):

\[
f_L(x) = 2\phi_L(x)\Phi_L(a_Lx). \quad (A8)
\]

These skewed Gaussian and Lorentzian distributions can be combined with weight factor \(\eta\) to find the double skewed Voigt distribution of equation (1) or in abbreviated form:

\[
\phi_V(x) = (1-\eta)f_G(x) + \eta f_L(x). \quad (A9)
\]

Appendix B. The electron temperature and the floating potential

The electron temperature (\(T_e\)) and the floating potential under RF bias (\(V_{fr}\)) are measured and calculated using the data from the Langmuir probe and equation (3) for the same values of plasma parameters (i.e. input power and gas pressure) discussed in the paper. As illustrated in figure B1, the electron temperature follows a downward trend, starting from \(T_e = 2.2\) eV for input power of 10 W and descending to \(T_e = 1.32\) eV for 90 W, whereas the floating potential almost linearly increases from \(V_{fr} = 84\) V for 10 W to \(V_{fr} = 240\) V for 90 W of input power. The gas pressure is kept constant at 4 Pa throughout these measurements.

These values and their respective trends as a function of input power and gas pressure of the plasma are essential for the estimation of the plasma sheath electric field (\(E_{sheath}\)) and interpretation of the results regarding Stark shift values in the same plasma conditions.
Figure B1. Electron temperature ($T_e$, blue circles, left axis) and the floating potential ($V_{fp}$, red triangles, right axis) as a function of input power. The gas pressure is set at 4 Pa.

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