Probing Charge of plasma exposed surfaces with quantum dots photoluminescence

M. Hasani[1], G. Klaassen[1], M. Pustylnik[2], Z. Marvi[1], J. Beckers[1]

[1]*Department of Applied Physics, Eindhoven University of Technology, Eindhoven, 5600 MB, The Netherlands*

[2]*Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt, Cologne, Germany*

Introduction

Plasmas containing micro- to nanometer sized dust particulates, called dusty or complex plasmas, are of particular interest due to either the advantageous roles or the potential threats the dust particles may pose to plasma related applications. The advantageous roles include polymer formation and synthesis in plasmas using hydrocarbon gaseous discharges [1] while the main potential threat of dust particles in plasma is posed in contamination control applications, for instance in the semiconductor industry [2]. Here, plasma-charging of small dust particles is the essential phenomenon determining the dynamics of the particles in, for instance, spatial afterglow plasmas [3]. Once in a plasma environment, dust particles are either levitated, in the bulk or in the sheath region, or surface deposited. Negatively (plasma-)charged surfaces with dust particles deposited on them are known to exhibit phenomena such as particle lofting [4]. For studying plasma charging of particle-deposited surfaces, so far, only simplified models and scarce data are available.

Recently, photoluminescent semiconductor nanoparticles, called quantum dots (QDs), were used to visualize the charging of particle-laden surfaces when immersed in a radio-frequently (RF) driven plasma [5]. For this purpose, the photoluminescence (PL) spectra of laser-excited QDs were recorded time-resolved before, during and after pulsed plasma exposure. Proven in that study was the feasibility of the pioneering idea that the PL emission peak position of QDs on a charged surface was subject to a wavelength shift driven by the so-called quantum-confined Stark effect. The wavelength of the PL peak was found to be shifted towards longer wavelengths due to the electric fields originating from the charge carriers, in this case electrons, residing on the surface in the proximity of the QDs. Moreover, it has been theoretically proven that the same mechanism can be used for measuring the overall charge of plasma-levitated micrometer-sized particles in the case these microparticles were coated with QDs [6].

The current study presents further investigation of using QDs as nano-probes for an electri-

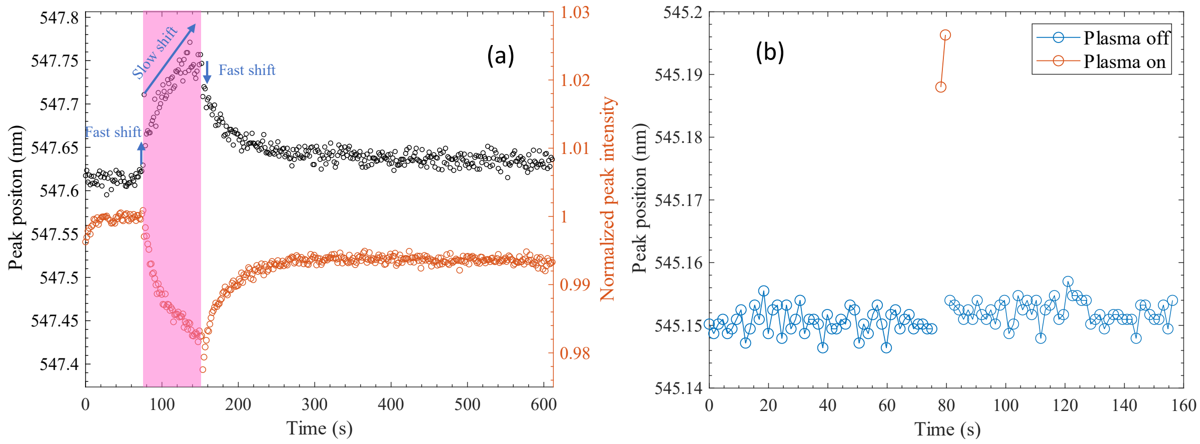

Figure 1: (a) The position of the PL peak emission (left axis, black dots) together with the normalized integrated peak intensity (right axis, orange dots) recorded time-resolved. The sample was exposed to plasma for 76.5 s (pink region) (b) Distinguished Stark shift of 0.04 nm measured for short (0.75 s) exposure times and for plasma parameters of 40 W and 4 Pa.

cally floating surface immersed in a low pressure RF plasma. PL emission spectra from surface deposited QDs were recorded spectrally resolved and analyzed for various plasma conditions (i.e. for different input powers). Furthermore, the surface charge induced by the plasma was analyzed and estimated by extracting internal plasma parameters (e.g. electron temperature) using a Langmuir probe.

Results and discussions

CdSSe/ZnS gradient-alloyed core-shell quantum dots with a total diameter of 6 nm were deposited on a silicon sample. This sample was exposed - in an electrically floating manner - to a low pressure RF plasma for different durations and plasma conditions. The used experimental setup is illustrated and explained in the work of Marvi *et al.* [2]. In the preliminary set of experiments, the sample was exposed to plasma for a total duration of 76.5 s and the QDs' PL emission spectra were recorded temporally resolved and further analysed. The analysis of the obtained PL emission spectra provided, temporally-resolved, the spectral peak position of the emission spectrum and its integrated intensity. The PL peak position and the normalized integrated peak intensity are illustrated throughout one typical experiment of plasma exposure in Figure 1-a. As illustrated in the figure, the PL peak experiences a wavelength shift towards longer wavelengths (i.e. redshifts) on two distinguished time scales. First, a fast redshift of 0.04 nm occurres upon the moment the plasma is switched on. Second, a slow redshift of 0.11 nm can be observed as the plasma affects the QDs during the total exposure time of 76.5 s. At

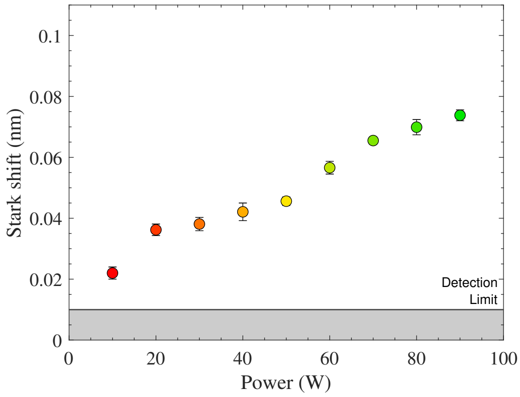

Figure 2: The measured amounts of Stark shift of the QDs' PL peak position as a function of plasma input power at a constant pressure of 4 Pa.

the moment the plasma is switched off, a reverse and symmetrical fast shift towards shorter wavelengths was detected. Finally, for longer time scales, the PL peak position slowly returns towards its initial spectral position (i.e. times before any plasma exposure).

The slow shift can be attributed to temperature effects, while the fast shift upon plasma ignition can be attributed to the quantum-confined Stark effect caused by the appearance of local electric fields induced by accumulated negative (plasma-)charge on the surface. This net negative charge (i.e. a surplus of electrons) is accumulated on the surface as a result of the relatively higher mobility of electrons compared to that of the ions. The electric fields originating from the excess electrons residing on the surface and in proximity of QDs' surfaces, cause the alteration of electron-hole band-gap energies inside the QDs. As a result, a redshift of the PL emission of the QDs can be observed. The slow temperature-induced redshift appeared to follow the temperature of the sample on which the QDs were deposited. The increase of the sample's temperature is explained by the plasma's heat load (i.e. impinging ions that have been accelerated in the plasma sheath near the surface and recombination heat). The temperature-induced redshift - although interesting - was outside of the main focus of the study; therefore the bulk of the experiments was redesigned to exclude this effect.

The electric field induced Stark shift of the PL emission was distinctively observed for sufficiently short plasma exposure times. As illustrated in Figure 1-b, the QD deposited sample was exposed to a short plasma pulse of 0.75 s, before, during and after which the PL peak position was recorded. Since the temperature increase was measured to be only 1% of the case for longer plasma exposure times in Figure 1-a, it can be concluded that - on these short time scales - the temperature effect is negligible compared to the electric field induced stark shift. This technique enables to examine and measure the sensitivity of the QDs' response to the plasma for varying parameters such as plasma input power.

Once reproducible measurements of the Stark shift of the QDs' PL emission were made possible, the amount of Stark shift upon plasma exposure was measured for different operating conditions of the plasma. In the next set of measurements, the input power of the plasma was changed and the respective amount of Stark shift was measured as a function of input power. Figure 2 shows that the amount of Stark shift is directly proportional to the input power of the plasma; i.e. the increasing trend in the input power is followed by an increase in the amount of Stark shift due to a higher charge density on the surface.

Conclusions

Local electric fields resulting from the surface charge on an electrically floating surface immersed in a low pressure plasma are detected using the spectral shift of the photoluminescence emission from QDs. The spectral PL emission peak position of the surface-deposited and laser-excited QDs appears to be subject to Stark shift, a mechanism that could be used as sensor for the surface charge. The variation of the amount of Stark shift for different plasma conditions indicates different amounts of surface charge density and confirms the ability to use this method for versatile nanoprobes for surface charge. Extrapolating this observation to the ever-lasting problem of microparticle charge measurements in the fields of dusty and complex plasma physics, one could use PL emission measurements from plasma-immersed QD-coated microparticles as an in-situ probe for their charge, as proposed by Pustylnik et al [6] and experimentally confirmed by the experiments in this work.

References

[1] Levchenko, Igor, et al. "Novel biomaterials: plasma-enabled nanostructures and functions." Journal of Physics D: Applied Physics 49.27 (2016): 273001.

[2] Beckers, Job, et al. "Particle contamination control by application of plasma." Extreme Ultraviolet (EUV) Lithography XI. Vol. 11323. International Society for Optics and Photonics, 2020.

[3] van Minderhout, Boy, et al. "Charge neutralisation of microparticles by pulsing a low-pressure shielded spatial plasma afterglow." Plasma Sources Science and Technology 30.4 (2021): 045016.

[4] Heijmans, L. C. J., et al. "Dust on a surface in a plasma: A charge simulation." Physics of Plasmas 23.4 (2016): 043703.

[5] Marvi, Zahra, et al. "Quantum dot photoluminescence as a versatile probe to visualize the interaction between plasma and nanoparticles on a surface." Applied Physics Letters 119.25 (2021): 254104.

[6] Pustylnik, M. Y., et al. "On the optical measurement of microparticle charge using quantum dots." Journal of Physics D: Applied Physics 55.9 (2021): 095202.