Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Energy Band Structure of Device-Grade Silicon Nanocrystals

Manuel Macias-Montero, Sadegh Askari, Somak Mitra, Conor Rocks, Chengsheng Ni, Vladimir Svrcek, Paul Connor, Paul Maguire, John T. S. Irvine, and Davide Mariotti*

S1. Experimental device for Mott-Schottky measurements.

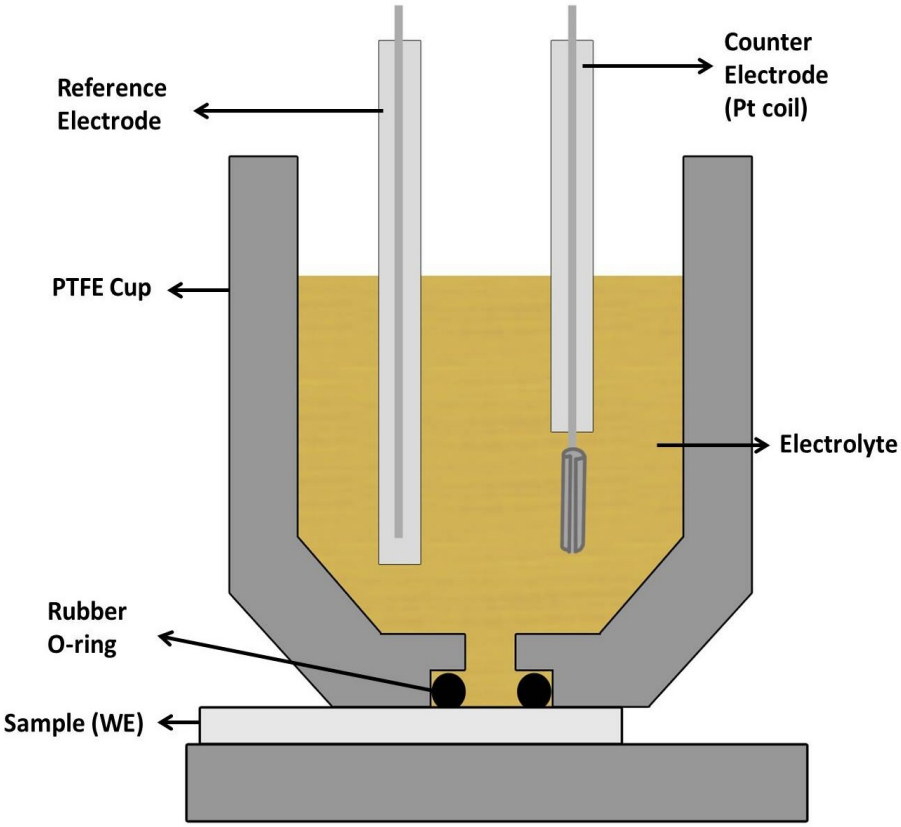

Figure S1: Schematics of the testing setup for Mott-Schottky measurements (WE stands for working electrode).

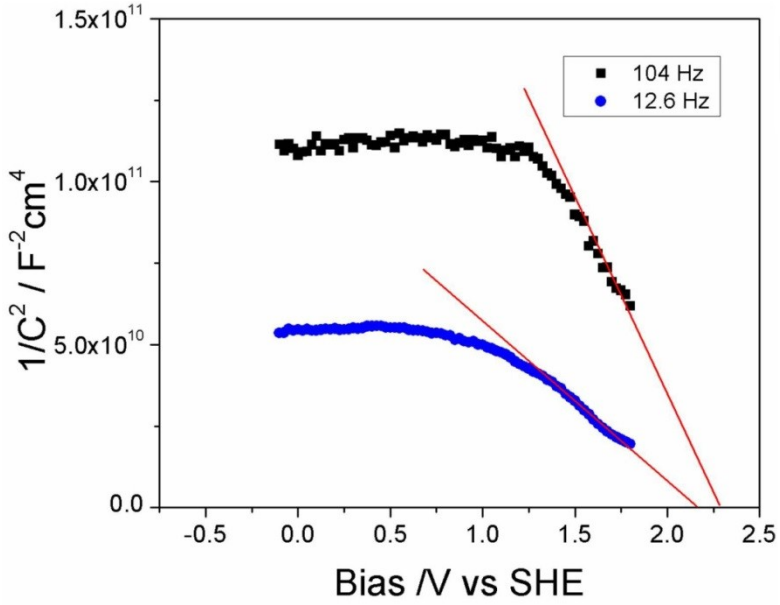

Figure S2: Mott–Schottky plots for Si nanocrystals in LiClO4 (1 M) solution in propylene carbonate according to impedance measurements. The flat-band potentials are obtained from the intercepts of the extrapolated lines.

S2. Si nanocrystals thin films.

An important feature needed to integrate Si nanocrystals (NCs) in different systems such as photonic or photovoltaic devices is the possibility to deposit them on a substrate forming a thin film. Our plasma system allows the direct deposition of layers of Si NCs onto any type of material at room temperature and atmospheric pressure. Macroscopically, the deposited films present a homogeneous coverage of the substrate at the naked eye. In order to characterize the samples at a microscopic scale, we used scanning electron microscopy (SEM) analysis. An example of a film analyzed using this technique is displayed in Figure S3. In the normal view micrograph (Figure S3a) it is possible to observe that the substrate is homogeneously covered with a Si NCs layer with a porous structure. The cross section micrograph (Figure S3b) provides an insight of the Si NCs thin film and allows estimating its thickness. In this case, the layer thickness is of 1.5 µm and corresponds to a deposition of 30 s over an area of 18 mm^2. In order to obtain the mass deposition rate of NCs, NCs were deposited for longer times and subsequently weighed. The results show a throughput of 300 µg/h. Additionally, combining the obtained thickness value with the deposited

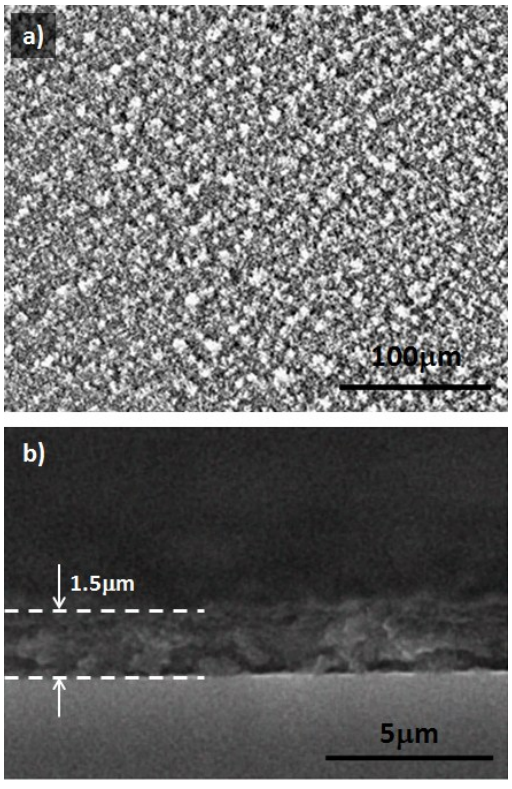

Figure S3: Normal (a) and cross section (b) scanning electron microscopy micrographs of a Si nanocrystals layer.

area it is possible to calculate the total volume occupied by the Si NCs and then, based on the 300 µg/h throughput, estimate the porosity, which resulted to be 30%.

The deposition of 300 µg/h is a relatively low throughput when compared with other techniques at a lab-scale.[S1] However, large scale nanomanufacturing is still a challenge for most synthesis methods with respect to Si-based NCs. In this context, atmospheric pressure plasmas present great scale-up potential. Particularly, the plasma system described in this work presents an interesting feature as the use of flat electrodes that allows the scalability of the process. This system is designed in a configuration where the plasma width and length can be extended maintaining constant the distance between the electrodes. Increasing these dimensions would allow an increment of the total throughput of Si NCs, maintaining a device-grade quality, and the simultaneous deposition of Si NCs layers over larger areas. If this is taken into account, the throughput of Si NCs can easily reach that of other technique and offer great room for improvements.[S1]

S3. Evaluation of the absorption coefficient of Si nanocrystals.

Combining the information of the growing process (production rate, layer porosity, etc.) with the ultra-violet/visible (UV-Vis) absorption, it is possible to calculate an important parameter such as the absorption coefficient. Thus, the absorption coefficient can be calculated as:

$$\mu_a = -\frac{1-(T+R)}{1-T}\frac{\ln T}{L}$$

where T stands for the transmittance, R represents the specular reflection and the scattered light by the sample that can be directly measured, and L is the photon's pathlength of travel through the medium. The latter parameter depends on the thickness of the film and in our case also on the film morphology and NCs distribution.

Thin films made of plasma Si NCs present a non-uniform thickness along the sample area due to its high roughness and the gradient from the centre to the edges. To calculate the absorption coefficient correctly it is necessary to estimate the Si NCs layer thickness accurately. To do this, we have used a model in which we consider spherical particles of equal diameter in a cubic lattice. Inputs required for this model would be the total mass of Si NCs deposited and the coated area. Figure S4 presents a scheme of the distribution of the particles together with the geometrical parameters of the model.

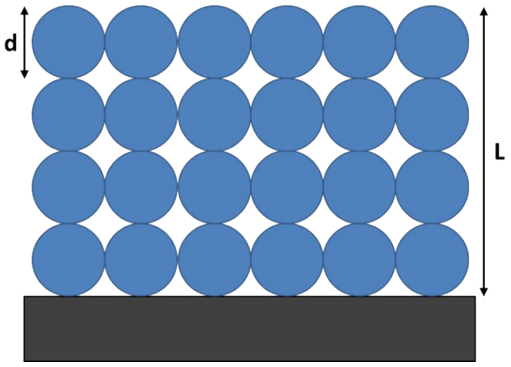

Figure S4: Scheme of the nanocrystals distribution in the cubic model.

Using this model, the optical thickness L would be the total number of nanocrystals layers (N_L) times the particle diameter (d):

$$L = N_L \cdot d$$

N_L can be calculated as a function of the total number of particles in the layer:

$$N_L = \frac{p}{p_m}$$

where p is the total number of particles and p_m is the number of particles in a monolayer. In turn, p can be estimated as the ratio between the total mass deposited and the mass of a single QD:

$$p = \frac{m}{m_{QD}} = \frac{m}{\rho_{Si}\, V_{QD}}$$

where m is the total mass of Si NCs deposited, ρ_{Si} is the mass density of silicon and V_{QD} is the volume of a spherical QD of diameter d, which is equal to $4/3\pi(d/2)^3$.

On the other hand, the number of NCs in a monolayer depends on the total area coated (a) and the area occupied by a QD (a_{QD}):

$$p_m = \frac{a}{a_{QD}} = \frac{a}{d^2}$$

In summary, the value of the total thickness is given by:

$$L = N_L \cdot d = \frac{p}{p_m} \cdot d = \frac{m\, d^2}{\rho_{Si}\, V_{QD}\, a} \cdot d = \frac{6}{\pi} \frac{m}{\rho_{Si}\, a}$$

In the particular case of the sample employed to measure the UV-Vis absorbance, plasma deposition of Si NCs lasted 10 minutes yielding approximately 50 µg over a surface of 100 mm^2. Hence, the thickness calculated is 0.41 µm. Hence, using this value it is now possible to calculate the absorption coefficient of the plasma-produced Si NCs.

Figure S5 displays the absorption coefficient of Si NCs as a function of the wavelength. For comparison we have included a standard solar spectrum (ASTM E-490) and the absorption coefficient of bulk silicon,[S2] where Si NCs exhibit a slightly higher absorption coefficient in the visible range at wavelengths below 480 nm. Values obtained show that Si NCs have an absorption coefficient comparable with bulk silicon along the visible range, being slightly larger in the 400-550 nm rage, which coincides with the maximum of the solar spectral irradiance.

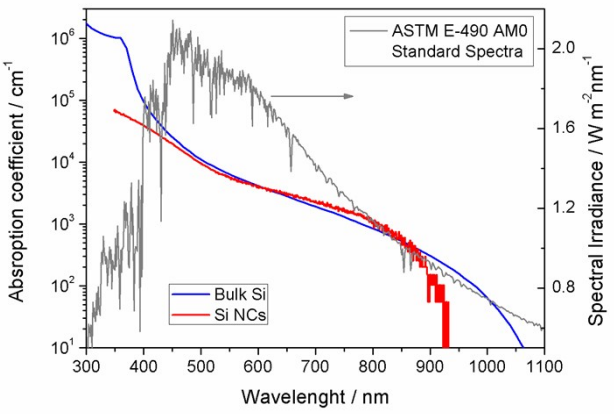

Figure S5: Absorption coefficient of Si nanocrystals (red) and bulk silicon (blue) on the left edge, and standard solar spectral irradiance (grey) on the right edge.

References

[S1] S. Askari, M. Macias-Montero, T. Velusamy, P. Maguire, V. Svrcek, D. Mariotti Journal of Physics D: Applied Physics in press.

[S2] M. A. Green, M. J. Keevers, Prog. Photovolt: Res. Appl. 1995, 3, 189.