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Progressive multi-layer drop-casting of CdSe nanoparticles for photocurrent down shifting monitoring

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We investigated the spectroscopic photocurrent response of photovoltaic devices versus an increasing number of drop-casted CdSe nanoparticles onto planar and nanocones silicon p-i-n junctions. For all samples, a strong enhancement of the photocurrent in the UV range was detected as well as a constant increase of the photocurrent up to 20% (16%) for a planar (nanocones) junction in the range 600–800 nm. The analysis of the photocurrent versus the number of drop casted nanoparticles layers allows us to evidence a down-shifting mechanism in the U-V range and an adaptative index effect below the threshold of absorption. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4816956>]

In order to increase the energy conversion efficiency of semiconductor solar cells, many improvements have been studied (see Ref. 1 for a recent review) such as (i) hot carrier collection which reduces thermalization losses, (ii) multi-junction cell which allows absorption of a wider range of wavelengths in the solar spectrum, (iii) multi-exciton generation which promises the generation of a few excitons for one absorbed photon, (iv) intermediate band collection in which low-energy photons can be absorbed in a two-photon process, (v) up-conversion layers which convert two IR photons into one UV photon, and finally (vi) absorbing layers which convert one high UV energy photon into one low energy IR photon (down shifting) or one UV photon into more than one IR photons (down-conversion). This paper is focussed on down-shifting CdSe nanoparticle (NP) layers drop-casted on silicon junction.

Down-conversion was first proposed by Dexter² in 1957. Detailed analyses of the possible performance enhancement have been published^{3,4} and experimental evidences were obtained in 1974 using rare earths⁵ and are still of interest today.^{1,6} Another promising way for down-conversion layers is the use of NPs which exhibit a series of advantages: their gap can be tuned by their size, they have high brightness, stability, and quantum efficiency.⁷ Efficient light harvesting was demonstrated in planar or nanostructured junctions by adding various NPs layers such as ZnS,^{8–10} PbS,¹¹ ZnSe,¹² CdS,¹³ or Si¹⁴ ones. Since their down-shifting effect evidenced by Lysen *et al.*,¹⁵ the most used nanoparticles are CdSe ones,¹⁶ with observations of non-radiative energy transfer (Förster effect),¹⁷ simulated by Govorov *et al.*¹⁸

Generally, the NPs are deposited using one shot, i.e., with one thick layer of nanoparticles, excepted in the case of ZnS NPs⁸ deposited using four different liquid concentrations. In this work, we have measured the photocurrent of n+-i-p planar junctions and nanostructured ones with

nanocones versus the number of CdSe drop-casted nanoparticle layers. This analysis allows us to distinguish a down shifting effect observed with an excitation in the UV band and a dielectric effect observed even for a few layers of deposited NPs.

The planar junctions were obtained by LPCVD deposition of 20 nm intrinsic silicon layer followed by 70 nm n+doped silicon layer (typically 2×10^{19} As cm⁻³) on a planar p doped silicon substrate (typically 5×10^{18} B cm⁻³). Aluminium (200 nm) was deposited as back contact. Ti (100 nm)–Au (200 nm) electrodes with a U shape were evaporated on the top of the structures. The technological process for nanostructured junctions was the same except that starting from bulk silicon; nanocones were obtained by Reactive Ion Etching with SiO₂ used as mask. The typical dimensions of the nanocones are: 700 nm at the bottom, 165 nm at the top, 440 nm for the height, and with an average density of 1.5×10^8 nanocones cm⁻². The CdSe NPs were obtained by a classical method developed by Kim *et al.* with minor modifications¹⁹ and a target 3 nm mean size. At the end of the growth, precipitated NPs were redispersed into hexane. Additional washing (by adding methanol and using centrifugation) was needed for four more times to remove extra unreacted organics. At least, three cycles of dispersion in chloroform and drying under azote gas flow and then redispersion in chloroform were done. The photoconductivity measurements were performed using a monochromator source (ORIEL), with a 100 W Xenon light, allowing a spectroscopic analysis from 300 nm to 1100 nm. The photon flux was calibrated using a thermopile detector with a broad flat spectral response from 200 nm to 50 μm. All the photocurrent curves were therefore normalized. In order to increase the signal/noise ratio, the light flux was chopped at a frequency of 30 Hz and a lock-in detection²⁰ was used. In order to correlate the morphology of the drop-casted NPs layers with their absorption spectra, AFM (Atomic Force Microscopy) measurements were performed, as illustrated in Figure 1. The large scale view shows different layers of NPs

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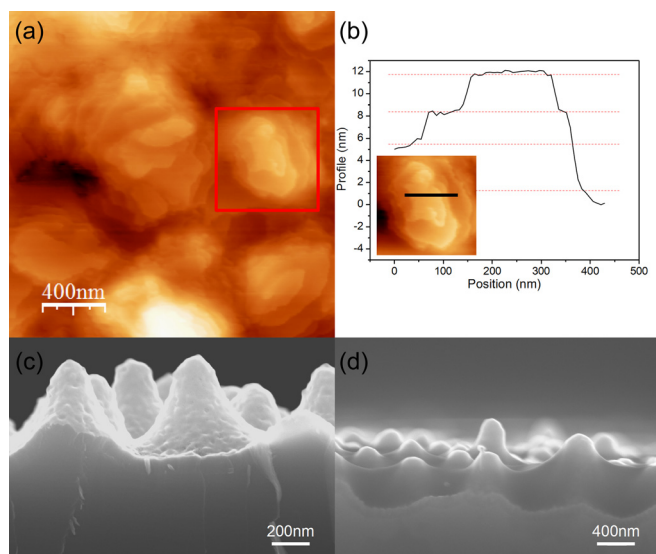


FIG. 1. (a) AFM image ($5\ \mu\text{m} \times 5\ \mu\text{m}$) of drop-casted CdSe NPs on the silicon substrate; (b) enlarged image ($0.5\ \mu\text{m} \times 0.5\ \mu\text{m}$) with height cross section showing steps associated with CdSe compact layers; cross sectional SEM images of a sample with nanocones and (c) without and (d) with drop casted CdSe nanoparticles.

with partially filled top layers (Fig. 1(a)). On the enlarged view (Fig. 1(b)), compact plateaux are clearly observed along a height cross section with step height of typically $3.4 \pm 0.1\ \text{nm}$. Figure 1(c) is a SEM image of a cleaved sample with nanocones, without NPs and Figure 1(d) is the same sample after drop casting of CdSe nanoparticles (black contrast between the nanocones). We observed that the NPs are mainly deposited between the nanocones and not on their top. Moreover, the CdSe layer does not exhibit visible stacking defects, i.e., the drop casted layer has a good homogeneous stacking.

The absorption spectra of the CdSe NPs is maximum at 550 nm. According to the equation proposed by Yu *et al.*,²¹ the preferential diameter size of the NPs should be 3 nm. For the same absorption peak, de Freitas *et al.*,²² measured a diameter ranging from 2.6 to 4.8 nm with high-resolution transmission electron microscopy technique. So, the values we measured are well associated with typically one layer of CdSe NPS with an average diameter of 3–3.5 nm. This is in agreement with their absorption spectrum. It was also observed (Figure 2) in the photoconductivity spectrum of a thick layer of CdSe NPs dropcasted on silicon, where the variation of the photocurrent is perfectly superimposed to the optical absorption spectrum of the CdSe NPs. (The insert in Fig. 2 shows the photoluminescence of CdSe NPs in solution.)

In the following, we present photoconductivity measurements recorded versus the number of drop-casted NPs layers.

The photocurrent measured on planar junctions versus the number of drops (Figure 3) shows a dramatic increase up to 550% for an excitation around 350 nm. This spectrum is obtained as follows: at each wavelength, we calculate the ratio $(I_1 - I_0)/I_0$ where I_1 is the photocurrent measured after the deposition of NPs and I_0 is the photocurrent measured without any NPs.

In order to account for this effect, the following mechanisms are discussed. First, down conversion is ruled out

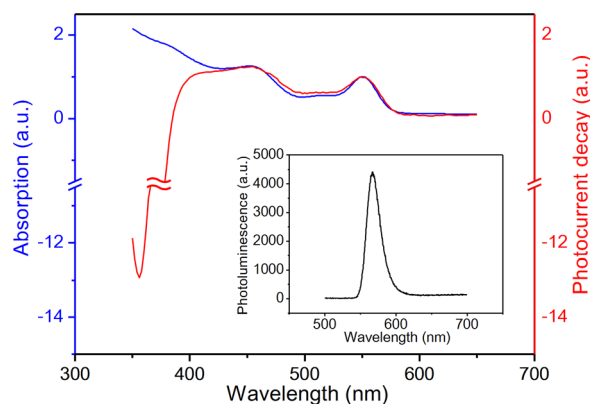


FIG. 2. Comparison of the photocurrent variation according to the CdSe NPs absorption spectrum for 6 drops (insert: PL of a solution of CdSe nanoparticles).

because it is associated with the absorption of one UV photon transformed to two IR photons. In our case, the absorption is maximum at 354 nm (3.50 eV) and the photoluminescence emission of the CdSe NPs is at 560 nm (2.21 eV). So, a photon at 3.50 eV cannot be transformed into two photons at 2.21 eV. Second, a Förster effect needs Coulombic transfer between nanoparticles with a nanoparticle size larger and larger as the transfert of the exciton is made at energy lower and lower. As the lifetime of an exciton in CdSe is of the order of a few ns and as the transfer time for the Förster effect is of the order of 100 ps,²³ a typical series of ten transfers is possible through the CdSe nanoparticles layer. But, the observed effect increases with the thickness of dropcasted nanoparticles and the Förster effect should decrease accordingly because it is more and more difficult to achieve an increasing number of bonds, with an efficacy of the transfert which varies as $1/d$,⁶ where d is the distance between two neighboring particles. Förster effect is improbable.

So, we propose that a down shifting effect is observed. Indeed, this effect should be proportional to the volume of the NPs, as observed in the insert of Figure 3. Moreover, the saturation of the photocurrent is explained as the absorption

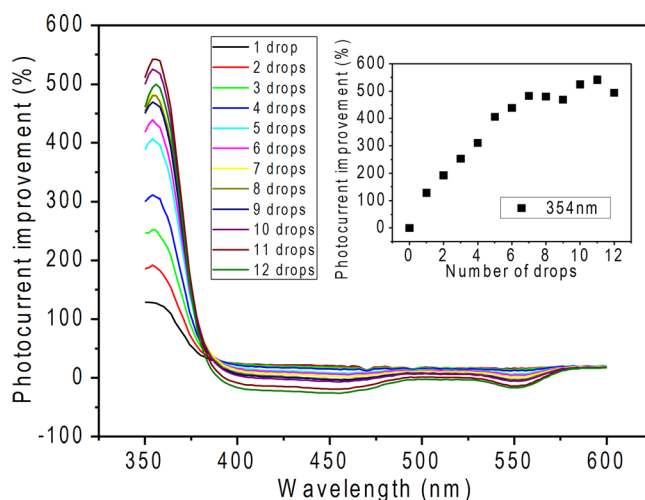


FIG. 3. Relative increase of the photocurrent versus the number of drops of CdSe NPs layers for an optical excitation ranging from 350 to 600 nm; Insert: Relative increase of the photocurrent versus the number of drops of CdSe NPs layers measured for an optical excitation of 354 nm.

of a high energy photon by the down-shifting layer can only result in the generation of one electron-hole pair in the junction, i.e., this mechanism cannot overcome the Shockley-Queisser efficiency limit.

As shown in Figure 4, the same effects have been observed in nanocones n+i-p junction.

However, a decrease of the photocurrent is observed at 366 nm. A simulation using the Finite Difference Time Domain (FDTD) method shows a different behavior of the reflectance between a planar and a NCs structure. At 366 nm (maximum of the n index of silicon), a peak is observed for reflectance. Relatively, this peak (amplitude of 10%) has more importance for NCs (average reflectance of 20%) than for planar structure (average reflectance of 45%) and, therefore, it is easily detected. As the NPs can be considered as resonators coupled to the structure, they “feel” the global behavior of the structure. Moreover, simulations show a decrease of the electric field near the surface for excitation at 366 nm, compared to the one obtained at 354 nm. So, the absorption of the NPs is less enhanced at 366 nm, leading to a lowering of the down shift effect, i.e., a decrease of the photocurrent.

Another increase of the photocurrent correlated with the number of dropcasted NPs is also observed in the range 600 to 800 nm, below the threshold of the absorption in the NPs.

Figure 5 shows the relative increase of the photocurrent measured at 650 nm and versus the number of drops (layers) on planar junctions (filled squares). As soon as one or two drops are deposited, i.e., for a few ten monolayers of NPs, a relative increase of the photocurrent ranging from 18% to 20% is observed.

We attribute this increase to a dielectric adaptation effect. The photocurrent is directly bound to the transmission coefficient $t_{\text{air-silicon}}$ between air ($n_{\text{air}} = 1$) and silicon ($n_{\text{Si}} = 3.43$) or $t_{\text{air-CdSe-silicon}}$ when CdSe nanoparticles are dropcasted. This coefficient, between two materials 1 and 2, is equal to $4n_1n_2/(n_1 + n_2)^2$ where n is the optical index equal to the square root of the dielectric constant of the material. For three materials (i.e., air, CdSe, and silicon), the transmission coefficient is equal to the product between the one

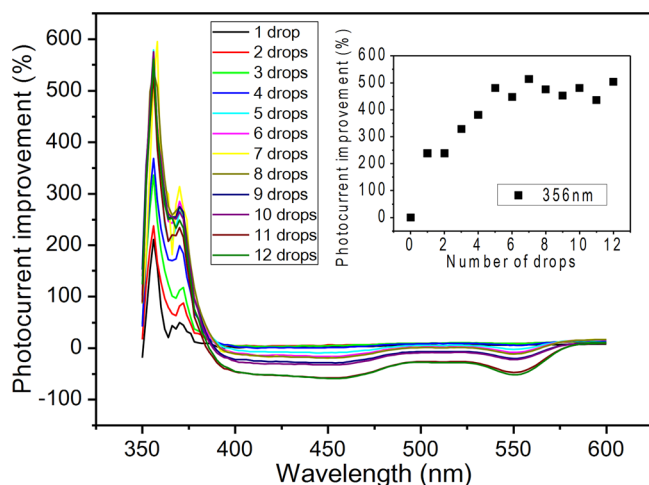


FIG. 4. Relative increase of the photocurrent versus the number of drops of CdSe NPs layers for an optical excitation ranging from 350 to 600 nm in a nanocone junction; Insert: Relative increase of the photocurrent versus the number of drops of CdSe NPs layers measured for an optical excitation of 354 nm.

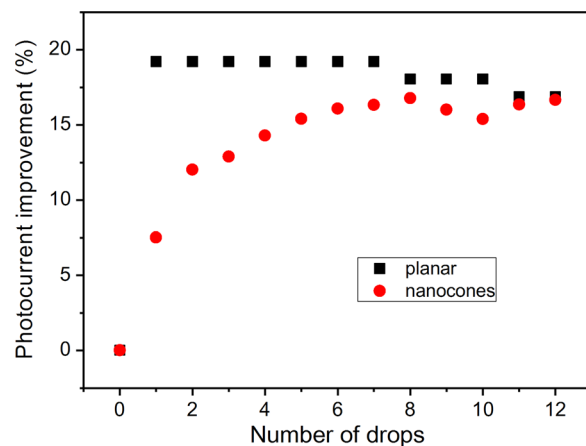


FIG. 5. Relative increase of the photocurrent versus the number drop-casted CdSe NPs layer measured for an optical excitation at 650 nm for a planar junction (squares) or a nanocones based junction (filled circles).

calculated at the air-CdSe interface by the one calculated at the CdSe silicon interface. We find $t_{\text{air-silicon}} = 0.70$ and $t_{\text{air-CdSe-silicon}} = 0.832$, i.e., a relative increase of 19%, in good agreement with the experimental value. For the dielectric constant of CdSe (equal to 7 for bulk material), we have taken into account the filling factor of a compact network of spherical nanoparticles (see Figure 1), equal to 0.48, i.e., the effective dielectric constant of the nanoparticles layer is equal to 7×0.48 . Another correction can be taken into account: the top layers are not filled at 100% as shown in Figure 1(a). But, as only a few top layers are concerned, compared to a great number of underlayers, the effect on the total filling factor is less than 5%, i.e., a final impact on the transmission coefficient of 1 or 2% (because the transmission function versus the n index is a smooth function around its maximum, which is our experimental case), always in agreement with the experimental results.

The same effect is observed on nanocones based junctions, as shown in Figure 5 (filled circles). In that case, the relative increase of the photocurrent associated with the graded dielectric effect is a little lower compared to the precedent one, i.e., of the order of 16%. This is logical since there is already a dielectric effect associated with the nanocones (the dielectric constant associated with the silicon nanocones is lower than the bulk silicon one because their silicon filling factor is less than one). So, the CdSe layer dielectric effect is just an additional effect. Moreover, for the first drops, as shown in Figure 1(d), the NPs are preferentially between the nanocones and therefore the associated dielectric effect is lower compared to the effect observed on the planar junction.

In conclusion, we have evidenced an increase of photocurrent of a planar silicon junction or of nanocones based silicon junction associated with a progressive number of CdSe dropcasted nanoparticles layers. This original progressive approach allows to unambiguously separate an efficient down-shifting effect and a graded dielectric effect.

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- ¹X. Huang, S. Han, W. Huang, and X. Liu, *Chem. Soc. Rev.* **42**, 173 (2013).
- ²D. Dexter, *Phys. Rev.* **108**, 630 (1957).
- ³B. S. Richards, *Sol. Energy Mater. Sol. Cells* **90**, 1189 (2006).
- ⁴W. G. J. H. M. van Sark, *Thin Solid Films* **516**, 6808 (2008).
- ⁵W. Piper, J. deLuca, and F. Ham, *J. Lumin.* **8**, 344 (1974).
- ⁶R. Rothmund, S. Kreuzer, T. Umundum, G. Meinhardt, T. Fromherz, and W. Jantsch, *Energy Procedia* **10**, 83 (2011).
- ⁷P. V. Kamat, *J. Phys. Chem. C* **112**, 18737 (2008).
- ⁸C.-Y. Huang, D.-Y. Wang, C.-H. Wang, Y.-T. Chen, Y.-T. Wang, Y.-T. Jiang, C.-C. Chen, and Y.-F. Chen, *ACS Nano* **4**(10), 5849 (2010).
- ⁹M. Ahmad, K. Rasool, M. A. Rafiq, and M. M. Hasan, *Appl. Phys. Lett.* **101**, 223103 (2012).
- ¹⁰A. Le Donne, S. K. Jana, S. Banerjee, S. Basu, and S. Binetti, *J. Appl. Phys.* **113**, 014903 (2013).
- ¹¹C.-Y. Huang, D.-Y. Wang, C.-H. Wang, Y.-T. Chen, Y.-T. Wang, Y.-T. Jiang, Y.-J. Wang, C.-C. Chen, and Y.-F. Chen, *J. Phys. D: Appl. Phys.* **44**, 085103 (2011).
- ¹²J.-Y. Jung, K. Zhou, J.-H. Bang, and J.-H. Lee, *J. Phys. Chem. C* **116**, 12409 (2012).
- ¹³H.-C. Chen, C.-C. Lin, H.-V. Han, K.-J. Chen, Y.-L. Tsai, Y.-An. Chang, M.-H. Shih, H.-C. Kuo, and P. Yu, *Sol. Energy Mater. Sol. Cells* **104**, 92 (2012).
- ¹⁴X. Pi, L. Zhang, and D. Yang, *J. Phys. Chem. C* **116**, 21240 (2012).
- ¹⁵W. G. J. H. M. van Sark, A. Meijerink, R. E. I. Schropp, J. A. M. van Roosmalen, and E. H. Lysen, *Sol. Energy Mater. Sol. Cells* **87**, 395 (2005).
- ¹⁶S. Chanyawadee, R. T. Harley, M. Henini, D. V. Talapin, and P. G. Lagoudakis, *Phys. Rev. Lett.* **102**, 077402 (2009); B. Güzelürk, E. Mutlugün, X. Wang, K. L. Pey, and H. V. Demir, *Appl. Phys. Lett.* **97**, 093111 (2010); H. M. Nguyen, O. Seitz, D. Aureau, A. Sra, N. Nijem, Y. N. Gartstein, Y. J. Chabal, and A. V. Malko, *ibid.* **98**, 161904 (2011); J. Choi, B. Parida, H. Y. Li, S. Park, and K. Kim, *J. Nanosci. Nanotechnol.* **12**(7), 5619 (2012); O. Seitz, L. Caillard, H. M. Nguyen, C. Chiles, Y. J. Chabal, and A. V. Malko, *Appl. Phys. Lett.* **100**, 021902 (2012).
- ¹⁷T. Förster, *Ann. Phys. Leipzig* **437**, 55 (1948).
- ¹⁸P. L. Hernandez-Martinez and A. O. Govorov, *Phys. Rev. B* **78**, 035314 (2008).
- ¹⁹J. I. Kim and J. K. Lee, *Adv. Funct. Mater.* **16**, 2077 (2006).
- ²⁰T. Xu, Y. Lambert, B. Grandidier, D. Stiévenard, A. Akjouj, Y. Pennec, and B. Djafari-Rouhani, *J. Appl. Phys.* **112**, 033506 (2012).
- ²¹W. W. Yu, L. H. Qu, W. Z. Guo, and X. G. Peng, *Chem. Mater.* **15**, 2854 (2003).
- ²²J. N. de Freitas, I. R. Grova, L. C. Akcelrud, E. Arici, N. S. Sariciftci, and A. F. Nogueira, *J. Mater. Chem.* **20**, 4845 (2010).
- ²³S. Lu, Z. Lingley, T. Assano, D. Harris, T. Barwicz, S. Guha, and A. Madhukar, *Nano Lett.* **9**, 4548 (2009).