

## STUDY OF PHOTOVOLTAGE STABILITY ON NANODIAMOND-POLYPYRROLE COMPOSITES BY KELVIN PROBE METHOD

<sup>1,2</sup>Yen-Chen CHANG, <sup>1,2</sup>Daria MILIAIEVA, <sup>1,2</sup>Bohuslav REZEK

<sup>1</sup>*Institute of Physics of the Czech Academy of Science, Prague, Czech Republic, EU,*  
[changyen@fzu.cz](mailto:changyen@fzu.cz)

<sup>2</sup>*Faculty of Electrical Engineering, Czech Technical University, Prague, Czech Republic, EU*

### Abstract

Diamond thin films and nanodiamond particles are considered promising for addressing the long-term challenge of organic photovoltaics: efficiency and stability. In this work, we characterize stability of surface potential and photovoltage on polyfunctional detonation nanodiamonds merged with polypyrrole oligomers. The polyfunctional-detonation nanodiamond (poly-DND), polypyrrole (PPy), and poly-DND/PPy composites were prepared on p-type silicon wafer substrates. In order to investigate illumination induced effects, surface potential and photovoltage of the samples were characterized by macroscopic Kelvin Probe method as a function of time. The poly-DND/PPy composite exhibits better stability of surface potential and surface photovoltage in short-term as well as in long-term (up to 8 weeks) compared to individual materials. The nanodiamond composites thus appear advantageous for use in organic photovoltaics.

**Keywords:** Diamond, nanoparticles, polypyrrole, scanning Kelvin probe

### 1. INTRODUCTION

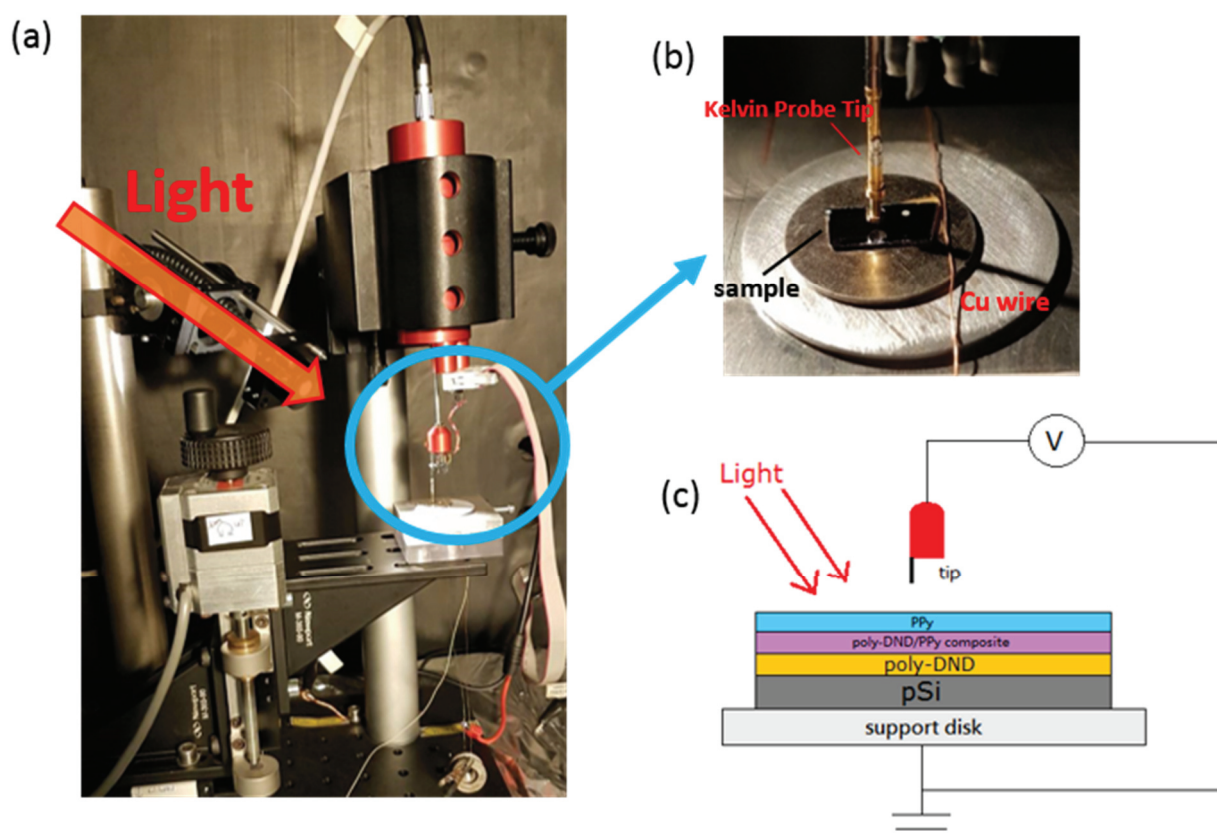
Organic-based photovoltaic (OPV) devices are not so much limited in output under low-light or diffuse light conditions compared with silicon PV modules. OPV production and installation is also easy on large areas and in various shapes as they can be made on polymer foils. However, the main drawback of OPV is their long-term instability due to various chemical degradation processes and susceptibility to humidity. Many solutions including non-fullerene inorganic acceptors are being investigated. Diamond may provide interesting properties in this respect. The diamond interface with polypyrrole (PPy) was already shown to promote exciton generation and dissociation [1]. This property of the hybrid diamond/PPy composite may be thus beneficial to generate free charge. For this purpose it may be beneficial to use diamond in form of nanoparticles, so called nanodiamonds, which are commercially available in large quantities. Similarly as bulk diamond, nanodiamonds are reported as non-toxic [2,3] and generally chemically stable [4]. Synthesis process and structural interactions in nanodiamond/PPy composite were recently reported in our previous article [5]. In this work, opto-electronic properties of such composite are studied by Kelvin Probe. We present time-resolved measurements [6] of surface potential in dark and under illumination and we assess how stable the photovoltage of the nanodiamond-dye composite is compared with individual materials.

### 2. MATERIALS AND METHODS

We employed commercially available polyfunctional detonation nanodiamonds (NanoAmando) with oxygen and hydrogen surface chemical groups (poly-DND). The poly-DND particles, polypyrrole (PPy), or poly-DND/PPy composite were deposited on p-type silicon wafers according to the established protocol [5]. Briefly, the substrates were covered with poly-DND particles using 1 hour ultrasonication in aqueous colloidal poly-DND solution with concentration of 20 mg/mL [7] and then rinsed with deionized water. The process leads to a dense coverage by poly-DND [5]. The substrate with poly-DND layer was immersed in Py monomer solution (98 %) for 1 hour in dark to adsorb Py monomers on the nanodiamonds. The substrate with adsorbed Py was

immersed into HCl acid (0.3 M) for 16 hours under indoor illumination to induce polymerization. Finally, the sample was taken out, rinsed with deionized water, and blown dry with nitrogen.

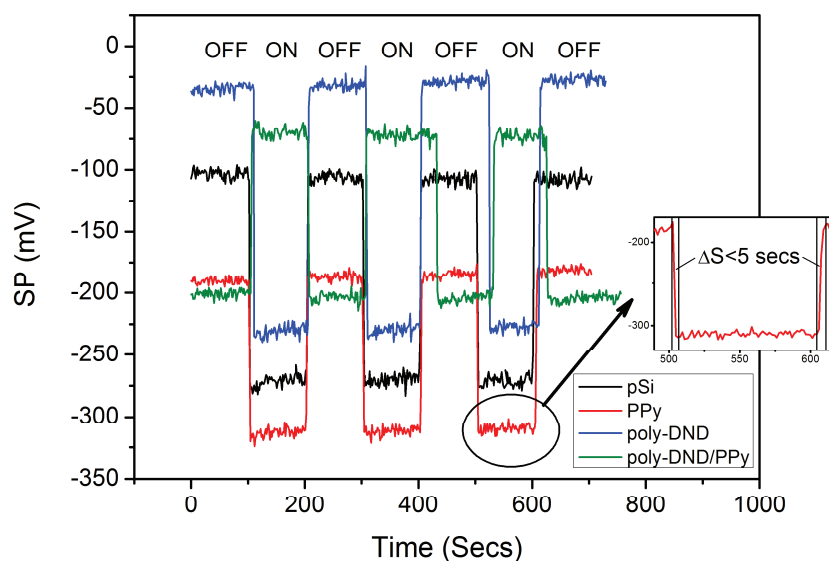
Scanning Kelvin probe (SKP) method was used to determine the surface potentials [6,8] of the samples in dark and under illumination with light intensity of about 200 W/m<sup>2</sup> (white cold light source with halogen lamp). SKP setup is shown in **Figure 1 (a)**. **Figure 1 (b)** is the detailed photograph of the sample in Kelvin probe setup. Measurement of each sample was conducted with a gold-plated tip electrode of 2 mm in diameter. The surface potential was detected at similar location on the sample in each measurement. At first, we measured surface potential in dark and waiting till it was stable for 100 seconds. Then we turned the light on quickly within 5 seconds and kept measuring the potential for 100 seconds. The procedure was continuously repeated during 12 min. Finally the measurement was stopped in the dark. Then the surface photovoltage was calculated from the surface potential data.



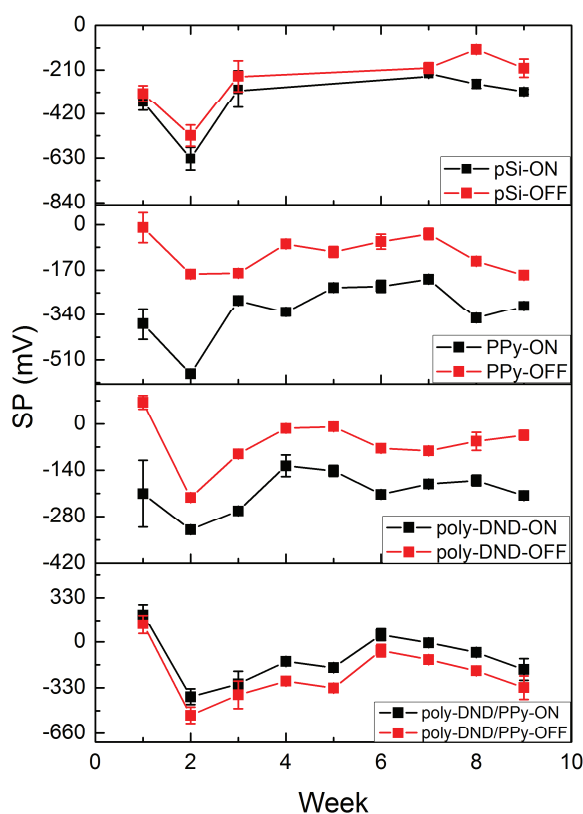
**Figure 1** (a) Photograph of Scanning Kelvin probe setup. (b) Detailed photograph of the sample in Kelvin probe setup. (c) The scheme of macroscopic Scanning Kelvin Probe measurement with poly-DND/PPy composite.

### 3. RESULTS AND DISCUSSION

**Figure 2** shows the results of surface potential (SP) measurement in the short-term. We can see that all surface potentials are stable (within 6 mV of standard deviation) and regularly reproducible during light switching in each measurement. Thus we averaged the whole surface potential measurement data in dark and under illumination for each material. The averaged surface potential with standard deviation in dark and under illumination was: pSi ( $-101 \pm 6$  mV and  $-272 \pm 5$  mV), PPy ( $-189 \pm 3$  mV and  $-311 \pm 5$  mV), poly-DND ( $-34 \pm 4$  mV and  $-230 \pm 6$  mV), and poly-DND/PPy composite ( $-202 \pm 4$  mV and  $-69 \pm 3$  mV).



**Figure 2** Surface potential of pSi, PPy, poly-DND, poly-DND/PPy as a function of time and visible light illumination in the short-term (0 - 12 min). The potential profiles correspond to measurements after 7 weeks. The inset shows that the rise and fall edges when illumination changes.



**Figure 3** Average value of surface potential in dark and under illumination plotted as a function of time for the long-term stability evaluation

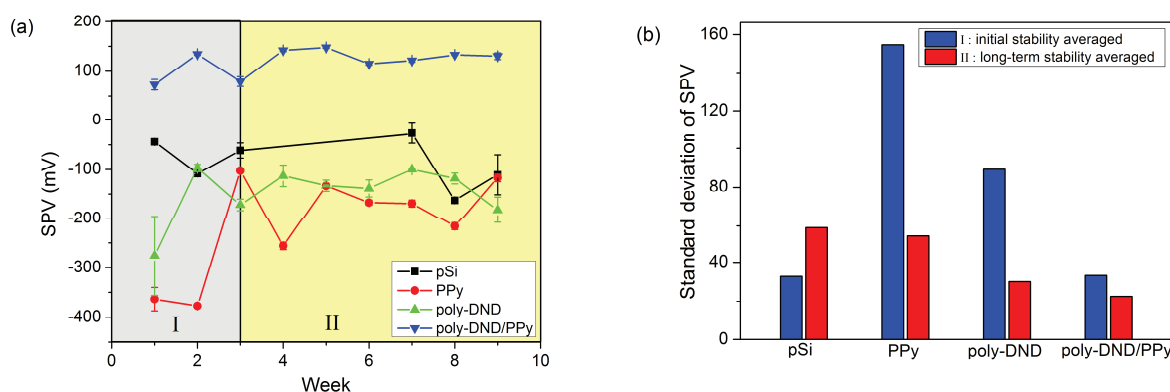
Then we repeated the short-term measurements every week for 8 subsequent weeks to investigate the long-term stability. Shape of the short-term profiles with the fast rise and fall edges was the same for the whole 8 weeks. Thus we averaged Kelvin Probe data in dark and under illumination each week. The averaged potential

in dark and under illumination is plotted in **Figure 3**. Standard deviation of the average value is used as the error bar. We can see that in the long-term (during 8 weeks), the potentials in dark and under illumination are slowly fluctuating. The potential fluctuations are qualitatively very similar for all the studied materials, hence they are most likely related with some external factors.

The surface potentials exhibit similar fluctuation in dark and under illumination. Evaluation of surface photovoltage was thus used to observe actual material (in)stability in spite of the overall potential fluctuations. In **Figure 4 (a)** presents surface photovoltage (SPV) that was calculated as ( $SP_{\text{illumination}} - SP_{\text{dark}}$ ) each week for 8 weeks.

SPV exhibits the most pronounced changes during the first 3 weeks (area I), than during the remaining 6 weeks it seems fluctuating around a stabilized value (area II). To characterize this (in)stability, we calculated average SPV and its standard deviation in each area (values at the boundary were accounted for in both areas). The averaged SPV values with standard deviation in area I and area II are: pSi ( $-85 \pm 33$  mV and  $-91 \pm 59$  mV), PPy ( $-281 \pm 155$  mV and  $-166 \pm 55$  mV), poly-DND ( $-182 \pm 90$  mV and  $-137 \pm 30$  mV), and poly-DND/PPy ( $95 \pm 33$  mV and  $124 \pm 22$  mV).

**Figure 4 (b)** shows in the form of bar graph the standard deviation as a measure of SPV (in)stability. We can see the standard deviation difference of the averaged SPV between area I and area II on pSi (33 mV and 59 mV), PPy (155 mV and 55 mV), poly-DND (90 mV and 30 mV), and poly-DND/PPy (33 mV and 22 mV). The minimum standard deviation is observed on poly-DND/PPy composite during the whole 8 weeks.



**Figure 4** (a) Surface photovoltage (SPV) of all the materials for 8 weeks. Area I is defined as initial stability and area II as long-term stability. (b) The standard deviation of the averaged SPV value.

Thus the SPV of the poly-DND/PPy composite was the most stable from the very beginning after fabrication till the last measurement after 8 weeks. The material interaction in poly-DND/PPy composites thus contributes to photovoltage stability [6,9]. Note in this respect that surface photovoltage of poly-DND/PPy composite has opposite (positive) sign compared the SP of pSi, PPy and poly-DND. Such positive charging of the surface, i.e. polypyrrole, is in agreement with theoretical atomic scale calculations [10] and indicates role of nanodiamonds as electron acceptors. This effect together with polypyrrole tight binding to nanodiamond may explain the improved stability of the composite.

#### 4. CONCLUSION

In the range of minutes, surface potential (SP) under dark and illumination was stable and well reproducible for all the materials. In the long-term (weeks), the surface potentials of all materials were slowly fluctuating in similar way, most likely due to external factors. The generated photovoltage revealed actual material stability. The photovoltage was the most stable in the case of the poly-DND/PPy composite compared with individual materials. The improved stability is most likely due to the tight material interaction in poly-DND/PPy composites

and nanodiamond acting as an electron acceptor. Nanodiamond composites may be thus advantageous for improving organic photovoltaics.

## ACKNOWLEDGEMENTS

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