



## Hybrid structures of porous silicon and conjugated polymers for photovoltaic Applications

Journal:	<i>physica status solidi</i>
Manuscript ID:	pssc.201000203.R1
Wiley - Manuscript type:	Contributed Article
Date Submitted by the Author:	n/a
Complete List of Authors:	Sa'ar, Amir; Hebrew University of Jerusalem, Physics
Keywords:	Porous silicon, conjugated polymers, photovoltaics



view

pss-Header will be provided by the publisher

Review copy – not for distribution

(pss-logo will be inserted here  
by the publisher)

# Hybrid structures of porous silicon and conjugated polymers for photovoltaic Applications

Amit Nahor<sup>1</sup>, Oren Berger<sup>1</sup>, Yosef Bardavid<sup>2</sup>, Gil Toker<sup>2</sup>, Yair Tamar<sup>2</sup>, Leah Reiss<sup>2</sup>, Micha Asscher<sup>2</sup>, Shlomo Yitzchaik<sup>2</sup> and Amir Sa'ar<sup>\*,1</sup>

<sup>1</sup> Racah Institute of Physics and the Harvey M. Krueger Family Center for Nanoscience and Nanotechnology, the Hebrew University of Jerusalem, Jerusalem 91904, Israel

<sup>2</sup> The Chemistry Institute and the Harvey M. Krueger Family Center for Nanoscience and Nanotechnology, the Hebrew University of Jerusalem, Jerusalem 91904, Israel

Received ZZZ, revised ZZZ, accepted ZZZ

Published online ZZZ (Dates will be provided by the publisher.)

**Keywords:** Porous silicon, conjugated polymers, photovoltaics

\* Corresponding author: Email saar@vms.huji.ac.il

We report on a novel approach to synthesize hybrid nanostructures of meso porous silicon and conjugated organic polymers that are suitable for solar cell applications. Meso-porous silicon substrates with relatively large pores (~ 100 nm) have been exploited for electrochemical polymerization of organic monomers, which were intro-

duced into the porous silicon matrices and electro-polymerized to create poly-vinyl-carbazole (PVK). We present electrical characteristics of a device having relatively thin films of the hybrid medium, which exhibits a photovoltaic mode of operation.

Copyright line will be provided by the publisher

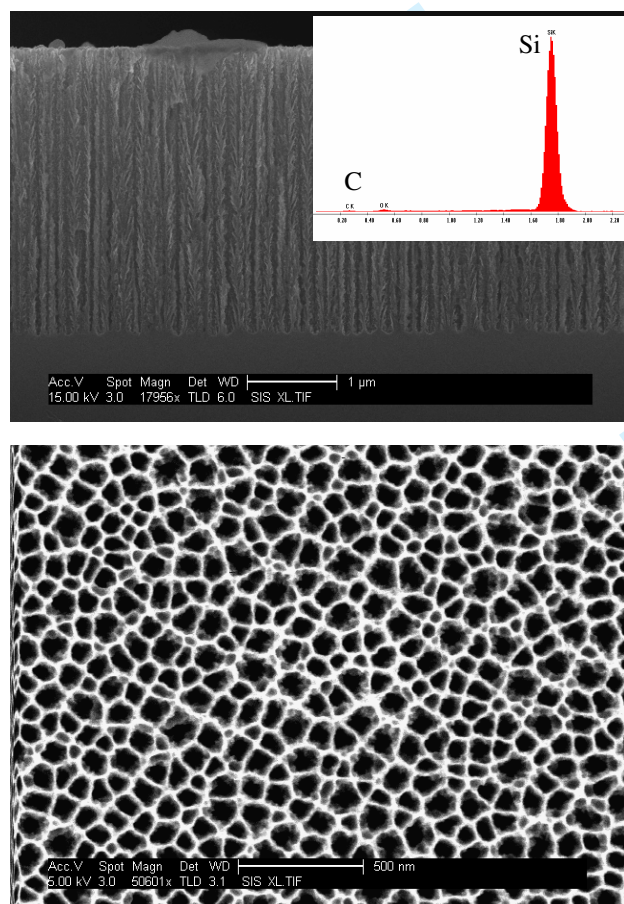
**1 Introduction** Developing renewable energy sources that are secured for long term supply at affordable cost and do not depend on hydrocarbon fossil fuels, is one of the most challenging research topics of the 21st century [1-2]. Solar energy in general and particularly photovoltaic (PV) energy conversion is expected to play a major role in this area. Currently, the dominant PV technology is based on crystalline silicon with bulky silicon wafers used to create photovoltaic p-n diode junctions [3]. However, silicon based solar cells suffer from a poor efficiency-to-cost ratio (usually defined in units of \$ per kW/h) and there is an urgent need for alternative PV technologies, with improved efficiency-to-cost ratio. One of the most promising approaches is using other photo-active compounds such as semiconductor quantum dots [4-6], metallic nanoparticles [7], organic polymers or dye molecules for light harvesting [8-10]. In this case, due to the considerably larger light absorption coefficient of these compounds (relative to silicon), one needs a much thinner film for absorbing the solar energy. On the other hand, thin film compounds require interfacing with other semiconductors to create hybrid, thin

film solar cells (sometime called "third generation solar cells [11]). A porous matrix, particularly a porous silicon (PS) matrix [12-15], seems to be an ideal matrix for this purpose. The ability to control the size of the pores, their morphology and the conductivity of the PS layers [16-17] make PS a very promising candidate for PV applications [18-21].

Here, we report on the extension of our previous investigation, aimed at developing hybrid structures of PS and conjugated polymers [22-23], for PV applications. To achieve this objective, it is necessary to develop a method to uniformly infiltrate conjugated polymers that are characterized by long chains of monomers, into relatively deep and narrow pores (20-100 nm in diameter and few microns in depth; see Fig.1). Hence, most electroless polymerization techniques (such as chemical [24-25] and thermal polymerization [26]) seem to be less appropriate for this purpose, particularly since the formation of a polymer layer at the entrance to the pores can block the polymerization process and prevents a uniform coverage of the entire

Copyright line will be provided by the publisher

pore's volume. Another electrochemical polymerization technique that seems to be more suitable for PV applications is the cyclic voltammetry (CV) method [27-29]. In this technique, monomers are introduced into the PS matrix followed by cyclic scan of the voltage applied between the silicon substrate (the working electrode) and upper Pt and Ag wire electrodes, used as the counter and the reference electrodes respectively. We have chosen to work with poly-vinyl-carbazole (PVK) as a test polymer medium due to its excellent photoconductivity [30-32], and to demonstrate the concept of the PV device in general, and particularly the suitability of the CV polymerization process for creating hybrid PS-polymer structures.



**Figure 1:** (top) Cross-section and (bottom) top view SEM images of the meso-PS matrix revealing a typical columnar structure of large pores (~100 nm in diameter), about 15-30 nm thick silicon walls and a depth of ~ 3 μm. The inset shows the EDS spectrum, measured along the cross-section of the PS matrix, prior to polymerization.

## 2 Experimental

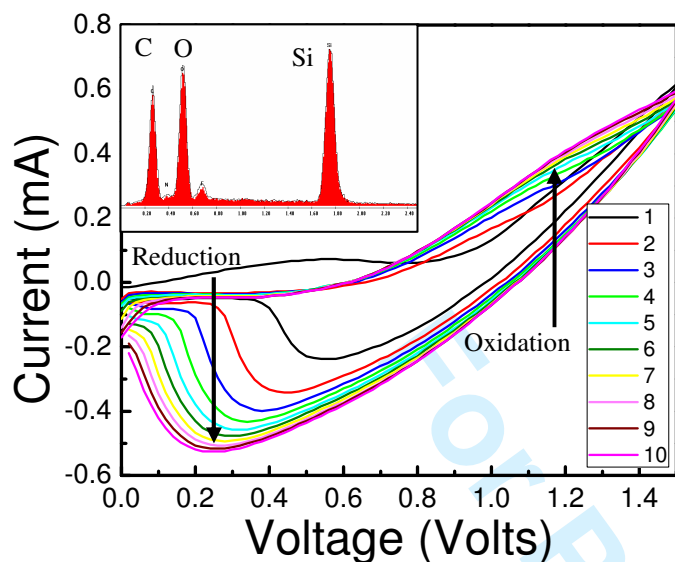
**2.1 Meso porous silicon fabrication** In order to allow the introduction of long polymer chains into the PS matrix we have applied the following procedure. Heavily doped, (100) n-type silicon substrates (10-20 mΩ·cm) have

been used to create meso-PS matrices by electrochemical anodic etching. An aquatic solution containing hydrofluoric acid, HF (4 w%),  $KMnO_4$  (8 mM) and a surfactant (byk-348) [33] has been used for etching at galvanostatic current densities of 25 mA/cm<sup>2</sup> under dark conditions (using the Keithley 238 source-measure-unit). This process has been carried out for 300 seconds to yield a PS matrix of about 3 μm in thickness, a porosity of ~ 70 % with average pore diameter of ~ 100 nm. The above etching process, which provides relatively large pore diameters, has been utilized for improving the penetration of the monomers into the PS matrix. In addition, the samples have been kept in ambient conditions for 48 hours to create a native oxide layer on the pore's walls. Figure 1 shows cross-section and top view SEM images (using the Sirion model, high-resolution SEM from FEI) of the meso-PS structure with a typical columnar structure [34].

**2.2 Polymer's infiltration** The following CV technique has been exploited for infiltrating polymers into the PS matrix. We have used an Acetonitrile based solution containing vinyl-carbazole monomers (0.1M) and  $NaClO_4$  (0.1M) for the CV process while the applied voltage has been scanned periodically over the 0 - 1.5 V voltage range; see figure 2. Two peaks, marked by arrows in the CV current-voltage characteristics of figure 2, appear at about 0.25 V and at 1.15 V, and are related to reduction and oxidation of the polymer respectively. The gradual increase of the oxidation-reduction peaks with the number of cycles until a saturation is accomplished (after about 7-8 cycles), indicates that PVK is formed inside the pores. Saturation is accomplished after the entire volume of monomers inside pores have been polymerized into PVK.

In order to verify that the entire volume of the porous matrix has uniformly been infiltrated with polymers we have carried out the following experiment. At first, the hybrid PS-PVK structure has been cleaved and a cross-section SEM image has been measured; see figure 3. Next, energy-dispersive X-ray spectroscopy (EDS) and mapping has been exploited to identify the various chemical elements inside the hybrid matrix and to obtain a depth profile of the polymer inside the pores. The results, presented in figure 3, reveal a columnar structure of the PS-PVK matrix quite similar to the original PS matrix (e.g., figure 1). This indicates that the CV process does not alter the porous structure. On the other hand, the polymerization process has caused a substantial change in the EDS spectrum as presented at the insets to figures 1 (prior to polymerization) and figure 2 (after polymerization). In particular, the appearance of Carbon (C) and Oxygen (O) after polymerization is a direct manifestation of the PVK growth inside the pores. Therefore, we have used the Carbon-to-Silicon ratio as a marker for the presence of a polymer (PVK) inside the pores, and map this ratio (C/Si) along the depth of the hybrid matrix. Results of the EDS depth mapping are shown in figure 3, indicating that the amount of carbon along the

depth of the pores varies by less than 10%, thus confirming that the polymer penetrates all the way to the bottom of the pores (about 2.5  $\mu\text{m}$  below the surface of the structure).



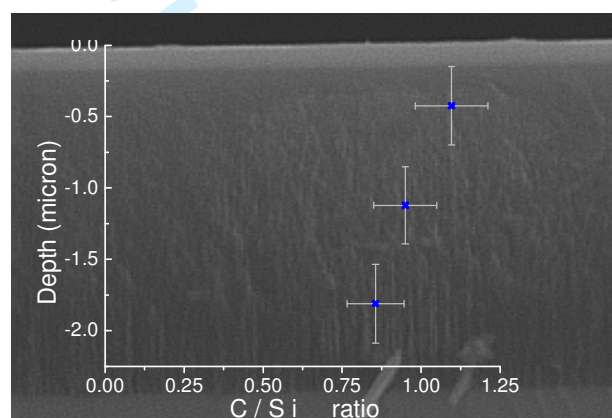
**Figure 2:** The cyclic voltammetry (CV) process for polymerizing vinyl-carbazole monomers inside the porous matrix. Each curve represents a different cycle with the arrows indicate the oxidation (1.15V) and the reduction (0.25V) peaks. Both peaks consistently increases with the increasing number of cycles indicating the formation of more polymer (PVK) inside the pores. The inset presents the EDS spectrum after polymerization.

**2.3 Photovoltaic Diode** In order to create electrical junction between the polymer and the n-type meso-PS we applied the following procedure. After completion of the CV polymerization stage, we have performed an additional oxidation cycle, which has been terminated in the doped state of the polymer (e.g., at a voltage of 1.15 V, see figure 2). This oxidized state of the polymer is known to be a good photoconductive state of the polymer, with the conductivity being dominated by holes transport [35-36] (in this respect, it is equivalent to a formation of a "p-type" semiconductor). Finally, a top thin film of Au, about 20 nm in thickness, was evaporated on the top polymer layer to create a top contact electrode to the polymer. The thickness of the Au layer has been chosen so that about 50% of the visible light will be transmitted through the film, as verified in a control experiment where the transmission of a similar Au layer, deposited on a glass, has been measured. In addition, a standard Al backside electrode has been defined and alloyed to the silicon substrate. Finally, the device was annealed at 100°C for two hours for releasing the stress and improving the polymer's conductivity [37-39].

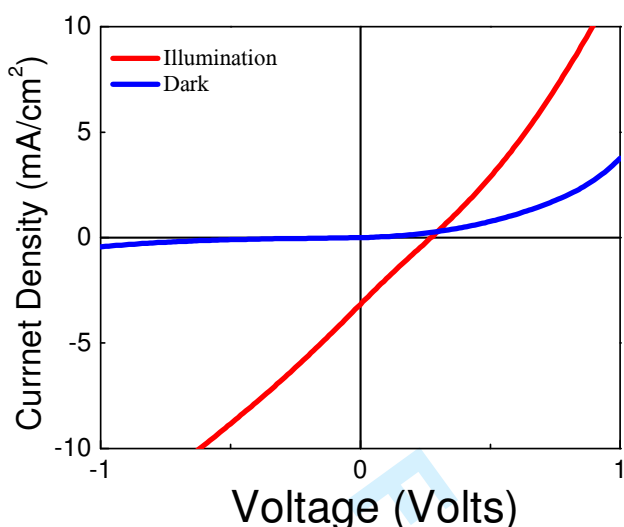
The current voltage (I-V) characteristics of the PS-PVK diode were measured under dark conditions and under illumination using a probe station (Karl Suss model EP4) connected to a Kiethley system 4200 electrical characterizations station. The illumination source was a solar

simulator (Newport model 96000) having a power density of one suns (100  $\text{mW}/\text{cm}^2$ ) and a solar spectrum of AM 1.5. Figure 4 presents the I-V characteristics of the device under dark conditions (blue line) and under illumination (red line). Noticeably, the dark I-V characteristics demonstrate a diode like behavior of the PS-PVK junction with the forward voltage direction being defined for a positive voltage connected to the top gold electrode (and therefore, to the PVK polymer), while the backside Al electrode (connected to the silicon substrate) is at a negative voltage relative to the top polymer electrode. In comparison to an ideal diode the PS-PVK diode has an ideality factor of 30. The quite large deviation from an ideal diode can be explained by the relatively high resistance (or poor conductivity) of PVK in the dark. From this model for the dark current of the diode we can also extract the turn-on voltage to be, (1.3 $\pm$ 0.1) V. For backward voltages, the dark current density of the device is fairly low, of the order of  $\sim 10^{-3}$   $\text{mA}/\text{cm}^2$ , as can be expected for a junction-like, "quasi" p-n diode structure (with the PS being the "n-side" and the PVK acting as the "p-side" of the junction). Under illumination, the PS-PVK device exhibits a pronounced photovoltaic effect (red line in figure 4) with the open circuit voltage,  $V_{OC}$ , and the short circuit current density,  $J_{SC}$ , given by:  $V_{OC} \cong 280$  meV and  $J_{SC} \cong 3.2$   $\text{mA}/\text{cm}^2$  respectively.

**3 Discussion** The most significant result of our research is the diode-like behavior and the appearance of photovoltaic characteristics for the PS-PVK junction, as presented in figure 4. Notice that we have previously reported about a similar polymer-PS junction, of polyaniline (PAN) and PS, where the polymer behaves as a "quasi" p-type



**Figure 3:** Cross-section SEM image of the hybrid PS-PVK structure after 10 periods of CV polymerization cycles. The inset shows the EDS depth mapping of the carbon-to-silicon ratio versus the depth of the hybrid structure. The corresponding EDS spectrum is shown at the inset to figure 2.



**Figure 4:** The current-voltage characteristics of the PS-PVK device. The blue line presents the current-voltage characteristics under dark conditions while the red line shows the current-voltage characteristics under one sun AM 1.5 solar simulator illumination. The measured short circuit current density is about  $3.2 \text{ mA/cm}^2$  while the open circuit voltage is about 280 mV. The fill factor has been estimated to be 25%.

semiconductor (e.g., hole's dominated transport) that creates semi-ideal ohmic contacts to p-type silicon and a junction-like contact to n-type silicon [21]. A similar behaviour has been found here for the PVK-PS device, indicating that hole's dominated transport is also the dominant mechanism for PVK.

However, as opposed to ordinary semiconductor p-n junctions, the diffusion length for excitons in organic conjugated polymers is significantly shorter than in silicon (of the order of 5-20 nm for most conjugated polymers [40]). Therefore, the hybrid structure is basically limited to average pore's size that should be comparable to the excitons diffusion length. On the other hand, the smaller are the pores, the more challenging is the demand to uniformly infiltrate the polymers into the porous matrix, particularly for structures with relatively deep pores. Equivalently, one can interpret the results in terms of type II band alignment between the n-type silicon (more precisely, porous silicon) and the polymer to create charge separation between the polymer (holes) and the silicon (electrons) over distances comparable to the pore's size.

The creation of good metallic contacts to the device is another major issue that has to be addressed for any PV device, particularly for our PVK-PS junction. Of particular importance is the creation of good ohmic contacts to the polymer. The method we have developed is based on thin, semi-transparent metal (Au) film deposition to create ohmic contacts to the polymer. While this method still require further investigation, improvement and comparison with other methods to deposit transparent conductors, it

seems to be a fairly promising method particularly for the conjugated polymers discussed here.

Finally, let us discuss the PV performance of the PS-PVK devices. For the measured open circuit voltage (280 mV) and short circuit current ( $3.2 \text{ mA/cm}^2$ ), we can estimate the device power conversion efficiency to be in the range of 0.2-0.5 %, and the filling factor to be about 25%. Here again, the non-ideal characteristics of the diode under dark conditions seems to be quite significant, apparently due to the substantially smaller hole's mobility of the polymer (relative to that of silicon), which results in high resistivity of the device and, presumably non-ideal electrical characteristics.

**4 Conclusions** In summary, we reported about the fabrication and the characterization of novel hybrid PS-conjugated polymer structures for photovoltaic applications. We have demonstrated the suitability of the cyclic voltammetry technique for electro-polymerizing monomers inside relatively narrow and deep silicon pores. Finally, we have demonstrated the fabrication of a PS-PVK photovoltaic junction, particularly the formation of good ohmic contacts to the polymer using thin, semi-transparent Au films. The power conversion efficiency of the device has been estimated to be about 0.2-0.5%.

**Acknowledgements** This work has been partially supported by grants from the MAGNET program of the Israeli ministry of Industry, the Israeli ministry of Energy and Infrastructure and by a grant from the "CleanTech" fund of the Hebrew University of Jerusalem.

## References

- [1] J. A. Turner, *Science* **285**, 687 (1999).
- [2] R. Gross, M. Leach, and A. Bauen, *Environ. Int.* **29**, 105 (2003).
- [3] H. Tsubomura, and H. Kobayashi, *Crit. Rev. Solid State Mat. Sci.* **18**, 261 (1993).
- [4] L. Tsakalagos, *Mater. Sci. Eng. R-Rep.* **62**, 175 (2008).
- [5] A. Marti, N. Lopez, E. Antolin, E. Canovas, C. Stanley, C. Farmer, L. Cuadra, and A. Luque, *Thin Solid Films* **511**, 638 (2006).
- [6] A. J. Nozik, *Physica E* **14**, 115 (2002).
- [7] S. Pillai, K. R. Catchpole, T. Trupke, and M. A. Green, *J. Appl. Phys.* **101**, 8 (2007).
- [8] H. Hoppe, and N. S. Sariciftci, in *Photoresponsive Polymers II* (Springer-Verlag Berlin, Berlin, 2008), pp. 1.
- [9] B. Oregan, and M. Gratzel, *Nature* **353**, 737 (1991).
- [10] S. Guenes, and N. S. Sariciftci, *Inorg. Chim. Acta* **361**, 581 (2008).
- [11] M. A. Green, *"Third Generation Photovoltaics"* (Springer-Verlag, Berlin 2003).
- [12] . A. G. Cullis, L. T. Canham and P. D. J. Calcott, *J. Appl. Phys.* **82**, 909 (1997).

- [13] A. G. Nassiopoulou, in "Encyclopedia of Nanoscience and Nanotechnology", Ed. H. S. Nalwa (American Scientific, CA 2004), Vol. **9**, p.793
- [14] For a collection of reviews see, "Light Emission in Silicon: From Physics to Devices", ed. D. J. Lockwood (Academic, NY, 1998); W. Theiß, Surface Science Reports **29**, 91 (1997); O. Bisi, S. Ossicini and L. Pavesi, Surface Science Reports **38**, 1 (2000). L. Pavesi, L. Dal Negro, C. Mazzoleni, G. Franzo and F. Priolo, Nature (London) **408**, 440 (2000)
- [15] P. L. Ong, and I. A. Levitsky, Energies **3**, 313.
- [16] H. Foll, M. Christophersen, J. Carstensen, and G. Hasse, Mater. Sci. Eng. R-Rep. **39**, 93 (2002).
- [17] B. Urbach, E. Axelrod and A. Sa'ar, Phys. Rev. B **75**, 205330 (2007).
- [18] I. A. Levitsky, W. B. Euler, N. Tokranova, B. Xu, and J. Castracane, Appl. Phys. Lett. **85**, 6245 (2004).
- [19] Priyanka, S. N. Sharma, S. Salam, M. Husain, and M. Lal, Sol. Energy Mater. Sol. Cells **91**, 1510 (2007).
- [20] M. Rajabi, and R. S. Dariani, J. Porous Mat. **16**, 513 (2009).
- [21] J. R. Maiolo, H. A. Atwater, and N. S. Lewis, J. Phys. Chem. C **112**, 6194 (2008).
- [22] B. Urbach, N. Korbakov, Y. Bar-David, S. Yitzchaik, and A. Sa'ar, J. Phys. Chem. C **111**, 16586 (2007).
- [23] B. Urbach, E. Axelrod, and A. Sa'ar, Phys. Status Solidi A-Appl. Mat. **204**, 1480 (2007).
- [24] D. A. Shipp, J. Macromol. Sci.-Polym. Rev **C45**, 171 (2005).
- [25] M. K. Mishra, J. Macromol. Sci.-Rev. Macromol. Chem. Phys. **C20**, 149 (1981).
- [26] S. Tazuke, and S. Okamura, **6**, 2907 (1968).
- [27] M. Baibarac, P. Gomez-Romero, M. Lira-Cantu, N. Casan-Pastor, N. Mestres, and S. Lefrant, Eur. Polym. J. **42**, 2302 (2006).
- [28] S. Patil, M. A. More, and P. P. Patil, J. Appl. Polym. Sci. **74**, 3009 (1999).
- [29] A. A. Syed, and M. K. Dinesan, Talanta **38**, 815 (1991).
- [30] H. Block, M. A. Cowd, and S. M. Walker, Polymer **18**, 781 (1977).
- [31] J. E. Carnes, and P. J. Warter, **5**, 1557 (1972).
- [32] H. Jin, Y. B. Hou, X. G. Meng, and F. Teng, Chin. J. Polym. Sci. **24**, 553 (2006).
- [33] Y. H. Ogata, A. Koyama, F. A. Harraz, M. S. Salem, and T. Sakka, Electrochemistry **75**, 270 (2007).
- [34] V. Lehmann, "Electrochemistry of Silicon" (Wiley-VCH Verlag GmbH, Weinheim, 2002)
- [35] J. V. Grazulevicius, P. Strohriegl, J. Pielichowski, and K. Pielichowski, Prog. Polym. Sci. **28**, 1297 (2003).
- [36] J. F. Morin, M. Leclerc, D. Ades, and A. Siove, Macromol. Rapid Commun. **26**, 761 (2005).
- [37] B. Friedel, P. E. Keivanidis, T. J. K. Brenner, A. Abrusci, C. R. McNeill, R. H. Friend, and N. C. Greenham, Macromolecules **42**, 6741 (2009).
- [38] W. N. Wang, and E. A. Schiff, Appl. Phys. Lett. **91**, 3 (2007).
- [39] Y. C. Huang, Y. C. Liao, S. S. Li, M. C. Wu, C. W. Chen, and W. F. Su, Sol. Energy Mater. Sol. Cells **93**, 888 (2009).
- [40] H. Z. Lin, R. Camacho, Y. X. Tian, T. E. Kaiser, F. Wurthner, and I. G. Scheblykin, Nano Lett. **10**, 620.