

Impact of a polystyrene-based passivating interlayer on hybrid polymer/ZnO nanowire heterojunctions

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Abstract. To improve the quality of hybrid p-polymer/n-zinc oxide (ZnO) nanowire heterojunctions a thin polystyrene (PS)-based passivating interlayer is deposited on plain aqueous-chemically grown ZnO nanowires by spin coating. The structural investigation of the PS-coated nanowires via scanning electron microscopy shows that the concentration of PS in the solution affects the thickness of the PS layer. For vertically aligned nanowires a concentration of 0.125 g in 10 ml toluene is needed to get thin homogeneous passivating layers. Photoluminescence measurements of the PS-coated nanowires show a decrease of the deep-level emission depending on the PS concentration which indicates a passivation on the nanowire surface without affecting the general optical properties of the ZnO. Current-voltage characteristics of these samples show a decreased hysteresis and an increased current with decreasing PS concentration/PS layer thickness. However, a reasonably thin layer reduces the tunnelling through trap states of the ZnO nanowires.

1. Introduction

Developing low-cost and efficient optoelectronic devices for applications as light emitting diodes or energy harvesting devices like solar cells is presently of huge interest.

Hybrid inorganic-organic core-shell structures, especially hybrid inorganic ZnO/organic polymer core-shell nanowires, have recently attracted considerable attention since they provide new functionalities that cannot be achieved with either the organic or inorganic part alone. ZnO is a low-cost II-VI material with a direct band gap of 3.37 eV (room temperature), high electron mobility and high absorbance in the UV spectral range [1]. In particular, ZnO nanowires show that surface-dependent optical and electrical properties are dominant due to the large surface-to-volume ratio which can be systematically tailored by surface-functionalization.

For p-doping of ZnO no reliable and reproducible procedure exists. However, the coating of n-doped ZnO nanowires with p-conductive polymers can result in p-n heterojunctions for diodes and solar cells. Polymers like poly(3,4-ethylenedioxythiophene-polystyrene sulfonate) (PEDOT:PSS) and poly({4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl}{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl}) (PTB7) are well suited for such structures. Both p-type polymers are well-known for their flexibility, high conductivity, stability and highly absorbent properties, respectively [2]. A controlled deposition of the polymer shell with a thickness control in the nm range is required to form an efficient p-n heterojunction. The polymer deposition via spin coating is a suitable method to provide conformal coating of the nanowires in the nanometer range [3].



However, wet-chemical methods lead to defects at the interface. The quality of the interface has a huge impact on the recombination processes occurring in the heterojunctions. Defects at the interface can act as trap states leading to recombination of charge carriers that lowers the quality of a diode [4]. To decrease the number of defects at the interface, a thin insulating passivation layer with high transparency is necessary. Polystyrene (PS) is a promising candidate which shows a high transparency in the visible spectral range [5].

In this work aqueous-chemically grown (ACG), vertically aligned ZnO nanowires are coated with a PS layer by spin coating to study the impact of this passivating interlayer on the hybrid p-n heterojunctions. The concentration of the PS solution is systematically modified to study its impact on the layer thickness and accordingly on the defect state passivation of the heterojunction interface. Scanning electron microscopy (SEM) images serve to investigate the structural PS layer properties on the nanowire surface. The optical properties (especially the deep level emission) of the PS-coated ZnO nanowires are studied by photoluminescence spectroscopy. Electrical measurements show the I-V-characteristics of the passivated heterojunctions.

2. Experimental section

2.1. ZnO NW

The vertically aligned nanowires (diameter range 50 - 300 nm, length $\sim 2 \mu\text{m}$) were grown by a hydrothermal method [6] at 80 °C for 3 h on a ZnO seed layer on top of a conductive ITO (indium doped tin oxide) glass as substrate.

2.2. PS deposition via spin coating

For the polystyrene solution two different PS concentrations were used. 0.5 g and 0.125 g of polystyrene were dissolved in 10 ml toluene at 80 °C for 2 h.

The spin coater model WS-650-MZ-23NPP from Laurell was used with an acceleration rate of 1200 rpm/s, a rotation speed of 5000 rpm and a deposition time of 40 sec. Afterwards, the samples were annealed for ~ 5 min to evaporate toluene residuals.

2.3. Structural, optical and electrical characterization

Structural characterization was performed by the FIB/SEM dual system Nova 200 (FEI, acceleration voltage 5 kV, FIB – focused ion beam).

Optical studies of the core-shell nanowires were performed using a HeCd cw-laser IK3552R-G (Kimmon, output power 60 mW, excitation wavelength 325 nm) at room temperature. The overview spectra were recorded using a fiber-coupled spectrometer (AvaSpec-ULS3648TEC, Avantes, spatial resolution ~ 2 nm).

The electrical characterization of the structures was done using a potentiostat-galvanostat Autolab PGSTAT302N and obtained by contacting the coated ZnO NWs and their respective ITO substrates with gold plated round probe tips. A bias voltage of ± 5 V was used.

3. Results and Discussion

3.1. Structural analysis

Figure 1 shows SEM images of uncoated ZnO NWs (figure 1(a), reference sample, PS-coated ZnO NWs obtained from a solution of 0.5 g polystyrene dissolved in 10 ml toluene (figure 1(b)) and PS-coated ZnO NWs from a solution of 0.125 g polystyrene dissolved in 10 ml toluene (figure 1(c)).

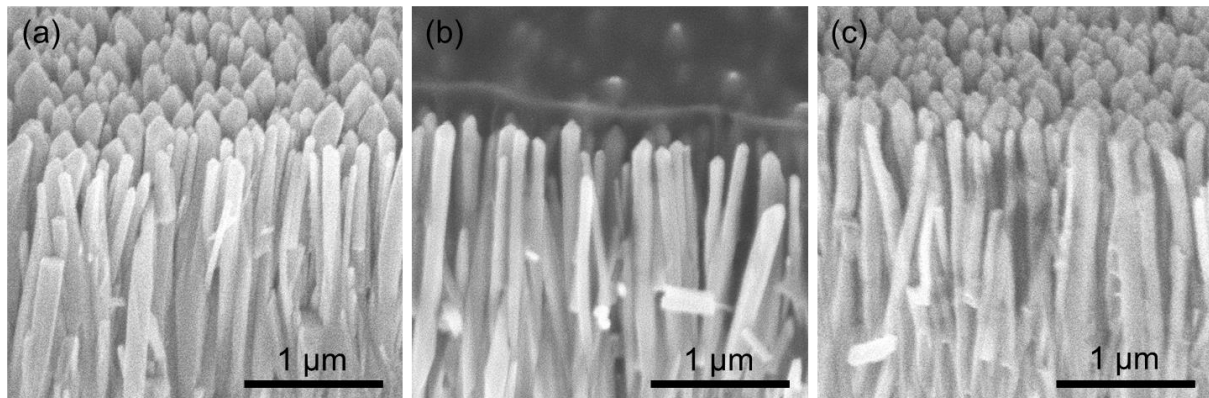


Figure 1: SEM images of (a) uncoated ZnO NWs, (b) PS-coated ZnO NWs (0.5 g PS in solution, see text) and (c) PS-coated ZnO NWs (0.125 g PS).

The PS layer obtained by using the highest PS amount in solution is as a result thick enough to act like an insulating capping layer on the NW tips. It seems that it is unable to cover the nanowires entirely. This may hinder the charge carrier transport in the p-n heterojunction.

However, the coated ZnO NWs obtained by using the lowest PS amount in solution show a very thin and homogenous coating in the small nm range, covering the nanowires completely as observed in figure 1(c).

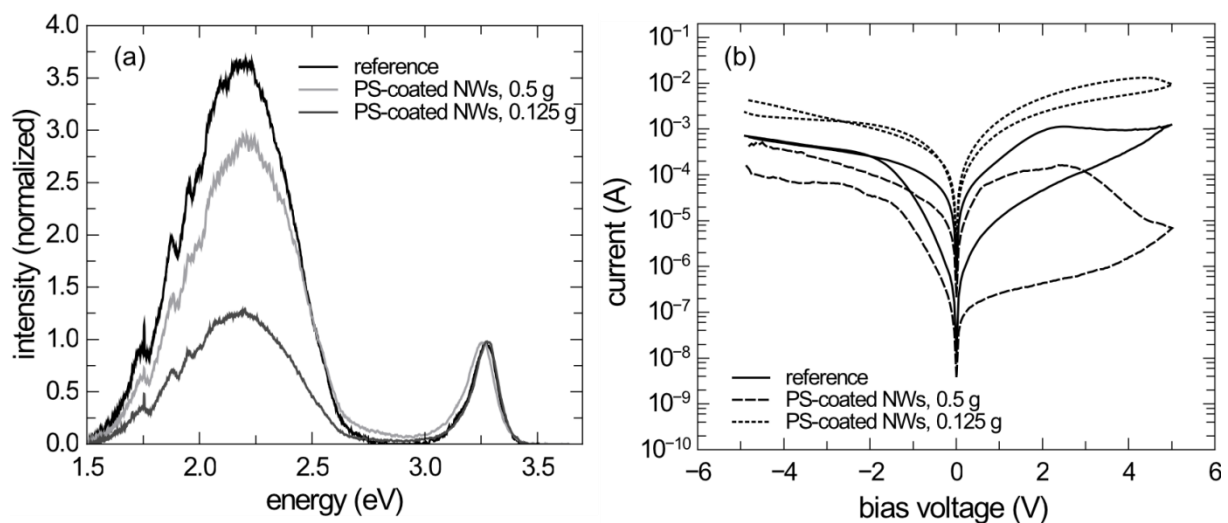


Figure 2: Overview PL spectra (a) and I-V curves (b) of uncoated ZnO NWs, PS-coated ZnO NWs (0.5 g PS amount) and PS-coated ZnO NWs (0.125 g PS amount).

3.2. Optical analysis

In figure 2(a) the PL overview spectra of the uncoated and coated ZnO NWs are depicted. All spectra are normalized with regard to the band of the near-band-edge emission (NBE) at about 3.3 eV to allow for a direct comparison of the relative intensities of the deep-level emission (DLE) which corresponds to the defect luminescence of the ZnO NWs.

In general, the overall optical properties of the nanowires are not significantly affected by the different PS coatings. However, the relative intensities of the observed bands strongly differ for various coating approaches. The black line shows the PL intensity of the uncoated nanowires. Compared to that of the NBE band, the DLE intensity is much higher which is attributed to a large

number of defects. The gray curve belongs to the PS-coated NWs with an amount of 0.5 g PS in solution. The DLE band intensity is only slightly reduced. The dark gray line corresponds to the spectrum of the PS-coated NWs with an amount of 0.125 g PS in solution. Compared to the reference the DLE band intensity is strongly reduced by a factor of about 3.

This strong reduction of the DLE band is related to the passivation of the nanowire surface being achieved by an appropriate PS layer. Because of its high transparency, the absorption properties of the polystyrene should not seriously affect the luminescence in this spectral range. For thick PS layers no significant decrease of the DLE band is visible. The thick layer in combination with the wet chemical deposition method may even induce new surface defects on the nanowires.

3.3. Electrical analysis

The I-V curves of the uncoated and coated ZnO NWs are displayed in figure 2(b). The samples were scanned from negative to positive voltage and back to observe the hysteresis effects.

The black curve shows the I-V characteristics of the uncoated reference sample. The relatively low current and the hysteresis indicate that the carrier transport is hindered by surface defects in the ZnO NWs. The black dashed I-V curve belongs to the PS-coated NWs obtained for 0.5 g polystyrene. In comparison to the reference, the current is decreased and the hysteresis increased. The thick polystyrene layer is obviously forming an additional dielectric layer that hinders the carrier transport. The I-V characteristic of the PS-coated NWs obtained for 0.125 g polystyrene is shown as a dotted line. The current is increased and the hysteresis is strongly reduced.

In accordance with the interpretation of the optical measurements, the thin polystyrene layer is passivating the surface which leads to a reduction of surface defects that act as trap states for electrons and therefore, the carrier transport is enhanced.

4. Conclusions

In conclusion, the structural, optical, and electrical properties of PS-coated ZnO nanowire structures have been investigated by SEM, PL and electrical measurements. The achieved results confirm a successful passivation of the interface of ZnO/polymer core-shell heterostructures by deposition of an ultra-thin PS interlayer. The amount of the polystyrene in the solution strongly influences the thickness of the PS layer. The use of small amounts of polystyrene leads to smooth interfaces and an improved carrier transport in the hybrid devices.

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References

- [1] Bunn C W 1935 *Proc. Phys. Soc.* **47**(5) 835
Mead C A 1955 *Phys. Lett.* **18**(3) 218
Janotti A and Van de Walle C G 2009 *Rep. Prog. Phys.* **72**(12) 126501
- [2] Lövenich W 2014 *Polym. Sci. Ser. C* **56** 135
Lu L, and Yu L. 2014 *Advanced Materials* **26**(26) 4413-4430
- [3] Hall D B, Underhill P and Torkelson J M 1998 *Polymer Engineering & Science* **38**(12) 2039-2045
- [4] Milnes A G and Feucht D L 1972 *Heterojunctions and metal-semiconductor junctions* (Academic Press, New York)
- [5] Vala Jr. M T, Haebig J and Rice S A 1965 *The Journal of Chemical Physics* **43** 886-897.
Ishii T, Handa T and Matsunaga S 1977 *Makromol. Chem.* **178**(8) 2351-2366
- [6] Ma T, Guo M, Zhang M, Zhang Y and Wang X 2007 *Nanotechnology*, **18**(3), 035605