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ZnO/anthracene based inorganic/organic nanowire heterostructure: Photoresponse and photoluminescence studies

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The effects of surface modification of vertically aligned ZnO nanowires (NWs) with anthracene for the improved photocurrent, photoresponse, and UV photoluminescence have been investigated in this work. The formation of ZnO/anthracene based inorganic/organic NWs heterostructure by surface capping with anthracene solution was confirmed from the high resolution transmission electron microscopy and Fourier transport infrared spectroscopy analyses. After the anthracene capping of ZnO NWs, despite an increase in dark current, we obtained a significant improvement in the photocurrent and photoresponse. A sixfold improvement in the UV photocurrent-to-dark current ratio is obtained with capping. Compared to the uncapped NWs, the photoresponse is significantly faster for the ZnO/anthracene system with response and reset times of 1.5 and 1.6 s, respectively. The room temperature photoluminescence spectra show threefold enhanced UV emission with large enhancement in the ratio of UV to green emission intensities. The faster photoresponse and enhanced photocurrent from the ZnO/anthracene heterostructure are explained on the basis of modification of surface defects and interfacial charge transfer process. © 2012 American Institute of Physics.

I. INTRODUCTION

The wide bandgap semiconductor ZnO has outstanding optical and electrical properties. ZnO nanowire (NW) is one of the superior candidates for the applications in optoelectronic devices, e.g., UV photodetectors,1–3 short wavelength laser,4,5 solar cells,6–8 etc. due to large surface area and a direct conduction path. Since the first report on the UV photodetection from single ZnO NWs by Kind et al.,1 many efforts have been made on ZnO NWs to improve its photodetection and photoresponse behaviors. Varieties of approaches, e.g., structural improvement, use of non-symmetrical Schottky-type contacts, surface roughening with isopropyl alcohol, surface modification with poly(vinyl alcohol) or L-lysine and surface decoration with ultra small nanoparticles (NPs) have been reported.9–15 However, photo-to-dark current ratio, i.e., photosensitivity and photoresponse time of the ZnO NWs based photodetectors still require significant improvement. Since the condition of the ZnO NWs surface strongly influence the photocurrent (PC) and photoresponse, the modification of surface by suitable material could enhance the photosensitivity as well as photoresponse time. It has been reported that ZnO NWs surface capped with organic polymer, poly(vinyl alcohol) (Ref. 12) gives rise to threefold enhancement in the photosensitivity. However, during the same time photodetector response becomes slow. In another work, when the surface of the NWs was passivated with organic monomer L-lysine, a fivefold enhancement in the photosensitivity was obtained.13

Anthracene is an organic semiconductor with wide bandgap. The crystal structure of the anthracene is monoclinic with large inter-planner spacing (d_{001} = 9.14 Å) and has a long range coherency with each (001) plane.16 Due to the lowest surface energy of (001) face, anthracene crystal grows by a periodic layer-by-layer growth process along the (001) plane.17 Efficient organic light emitting diodes (OLEDs) were fabricated by using thin films of anthracene derivatives by Huang et al.18 and Zhu et al.19 There is also a report on the use of anthracene based organic dye for the dyesensitized solar cells.20 However, there are very few reports on the fabrication of NW heterostructures with anthracene. Chen et al.21 used anthracene functionalization to the ruthenium NPs and studied the photoluminescence (PL) and electron conductivity. In another work, Das et al.22 prepared an organic capped ZnO NPs composite using anthracene derivative and studied the photoinduced quenching properties. As the photoresponse is strongly influenced by surface capping, it would be interesting to study the photoresponse behavior of the anthracene capped ZnO NWs. However, there is no study on the effect of surface modification of the ZnO NWs by anthracene on the photodetection and photoresponse behavior of the ZnO NWs. Therefore, we fabricated ZnO/anthracene based NWs heterostructure by capping ZnO NWs with the anthracene and investigated the effect of surface modification with anthracene on the PC, photoresponse, and photoluminescence behaviors. As the anthracene is a highly UV sensitive organic semiconductor, it can influence to enhance the photosensitivity of the ZnO/anthracene system. At the same time, the surface of the ZnO NWs becomes modified and it will affect the oxygen adsorption and desorption process.
II. EXPERIMENTAL DETAILS

ZnO NWs were grown by a two-step process on a Si(100) substrate by vapor-liquid-solid (VLS) method and these NWs are vertically aligned to the substrate plane, as described in detail elsewhere.\textsuperscript{23} In brief, first the ZnO seed layer was deposited on the cleaned Si(100) substrate followed by the deposition of ultrathin Au layer (of thickness \(\sim 2\) nm) by sputtering. The Si(100) substrate was pre-cleaned by standard wet chemical method followed by HF etching to remove the native oxide layer. For the growth of ZnO NWs, a mixture of commercial ZnO powder (Sigma-Aldrich, purity 99.999\%) and graphite powder (Fluka, 99.99\%) was used as a source material and placed inside a horizontal muffle furnace. The ZnO vapor was formed at 950 °C and was deposited on the ZnO/Au coated Si substrate, which was placed downstream at 750 °C. The as-prepared product was checked with field emission scanning electron microscopy (FESEM, Sigma, Zeiss) and transmission electron microscopy (TEM, JEM2100, JEOL) and it confirms the formation of ZnO NWs arrays on the Si substrate. Subsequently, ZnO/anthracene heterostructure was fabricated by dip coating of the NWs in the anthracene solution in ethanol solvent with a concentration of 3 mM for 30 min. After removing the NWs from the anthracene solution, it was dried in air and then heated at 150 °C for 15 min to remove the solvent and water moisture. The crystal structure of the NWs was characterized by a x-ray diffractometer (Seifert 3003 T/T). To confirm the surface capping with the anthracene layer, high resolution TEM and Fourier transform infrared spectroscopy (FTIR, Perkin–Elmer Spectrum BX) were employed. The PL spectra of all the samples were recorded with a 325 nm He-Cd laser excitation using a high-resolution commercial PL spectrometer (FS 920P, Edinburgh). The PL decay measurements were performed using a 375 nm laser excitation pulse of 69 ps duration, with an instrument time response of \(< 50\) ps (LifeSpecII, Edinburgh).

For the PC measurements, two circular Al contacts of diameter \(\sim 350\) \(\mu\)m and thickness 100 nm each were made on the top of the NWs by thermal evaporation process using a shadow mask. The separation between the electrodes was kept at 2.5 mm. The photocurrent was measured using a picocommimeter (Keithley, model 6487) at a bias of 3 V under the illumination of monochromated UV light (wavelength 360 nm) from a 150 W xenon lamp at an intensity of \(0.5\) mW/cm\(^2\) in ON and OFF conditions. The UV light is tightly focused onto the sample making sure that the region between the two electrodes is only illuminated. All the measurements were carried out at the room temperature and atmospheric pressure.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the FESEM image of the as-grown ZnO NWs, clearly showing the formation of vertically aligned ZnO NWs arrays on the ZnO coated Si substrate. The diameter of the NWs lies in the range of 50-80 nm and length is about a few microns. Due to the combined effect of the ZnO seed layer and Au catalyst, we obtained vertical orientation of the NWs. In a previous study, the combined effect of seed layer and Au layer on the morphology and orientation of the ZnO nanorods has been discussed in detail.\textsuperscript{23} It is observed that a few of the NWs have tapered structure, i.e., slightly lower diameter at the tip compared to the bottom end. Figure 1(b) shows the typical TEM image of a single ZnO NW with diameter 65 nm, and this is in agreement with the FESEM result. Figure 1(c) shows a high-resolution lattice image of the top end of a ZnO NW. From the high-resolution lattice fringe image, the lattice spacing of ZnO NW is found to be 0.26 nm, which indicates that the NWs are single crystalline and the growth is along the \(\langle 002 \rangle\) direction. The high resolution TEM image of the ZnO/anthracene system is shown in Fig. 1(d) and it shows a thin anthracene capping of the ZnO NW. With anthracene capping, the NW look slightly thicker due to the coverage of anthracene layer. The average thickness of the anthracene layer is found to be 15 nm.

To study the crystal structure of the ZnO NWs, x-ray diffraction measurements were carried out on the as-grown NWs and ZnO/anthracene heterostructure and the results are shown in Fig. 2. All the patterns show one intense peak corresponding to the \(\langle 002 \rangle\) plane and a weak peak corresponding to the \(\langle 103 \rangle\) plane of hexagonal ZnO lattice. The XRD analysis shows that the NWs are single crystalline and oriented along the c-axis. After the anthracene capping, the intensities of the XRD peaks were reduced due to the coverage of the anthracene layer. Although the outer anthracene layer is expected to be crystalline (monoclinic), no peak is observed for anthracene in the XRD pattern. Because of the large inter-planer spacing \((d_{001} = 9.14 \text{ Å})\) of anthracene, the
The FTIR reflectance measurements, as shown in Fig. 3. The uncapped NWs show only the intense peak comes below 10° of 2θ, where the sensitivity of the XRD detector is very low.

The presence of the anthracene layer on the surface of the NWs is further confirmed by FTIR reflectance measurements, as shown in Fig. 3. The uncapped NWs show only the peaks related to the bending and stretching modes of Zn–O, which are shown clearly in the inset of Fig. 3. On the other hand, the ZnO/anthracene heterostructure shows peaks related to the bending and stretching modes of hexagon ring and C–H bonds of anthracene, along with the bending and stretching modes of Zn–O. The observed reflectance bands at 473 and 532 cm⁻¹ correspond to the Zn–O bending modes and 580 cm⁻¹ corresponds to Zn–O stretching vibration mode of nanocrystalline ZnO. The peak at 520 cm⁻¹ is the signature of the skeletal bending (out of plane) mode of the anthracene hexagon ring. The bands observed at 810 and 1275 cm⁻¹ are due to the aromatic C–H bending modes. The skeletal vibration of the anthracene hexagon ring could be assigned to the peaks at 1620 cm⁻¹. The characteristic and strong peak at 3100 cm⁻¹ is due to the aromatic C–H stretching vibration. Therefore, the FTIR analysis confirmed the presence of the anthracene layer over the ZnO NWs surface. It is also observed that the unheated ZnO/anthracene heterostructure shows the presence of water moisture on the surface, and after the heating the water moisture is fully removed. It has been recognized that the as-grown ZnO NWs contains oxygen vacancy states on the surface, which can occur in both singly or doubly ionized states, \( V_o^+ \) or \( V_o^{++} \). The anthracene molecules are most likely to be attached on the surface of the NWs at \( V_o^+ \) or \( V_o^{++} \) sites by metal–ligand interfacial bonding interaction. This is supported by previous reports on surface functionalization of ruthenium and ZnO NPs with the anthracene derivatives.

The room temperature PL spectra of the uncapped NWs and ZnO/anthracene heterostructure are shown in Figs. 4(a) and 4(b). The as-grown NWs exhibit weak near band edge (NBE) UV emission at 378 nm and a broad green emission band. Gaussian multipeak fitting of the broad band shows the existence of two green emission bands, one at 497 nm (first green emission) and the other at 548 nm (second green emission). The observed NBE emission is due to the bound excitonic recombination; the first green emission is due to the presence of oxygen vacancies on the surface of ZnO NWs and the second green emission band is due to the presence of deep interstitial oxygen inside the NWs. The ZnO/anthracene heterostructure shows significant enhancement in the UV peak intensity, while the intensities of the green emission peaks are comparatively reduced. The intensity of the UV emission is enhanced by a factor of three, while the green emission intensity is reduced to half the value of the as-grown case. The ratio of UV-to-first green emission intensities also shows a major improvement by a factor of 7. The observed enhancement in the UV emission is likely to be due to the high absorption by the anthracene layer, and the reduction in the green emission is believed to be due to the surface modification by the anthracene. In order to understand the observed enhancement in the UV PL intensity, we need to know about the corresponding absorption and emission behaviors of the anthracene layer. The measured excitation and emission spectra for the anthracene powder are shown in Fig. 4(c). The emission spectrum show strong emission in the UV–blue region with sharp peaks at 383 and 410 nm. To better understand the absorption behavior of the anthracene, excitation scan was monitored for the emission fixed at 410 nm. The excitation spectrum of anthracene show sharp absorption peaks at 350 and 370 nm. The first one is corresponding to the emission at 383 nm and later one is for the emission at 410 nm. Therefore, in the ZnO/anthracene heterostructure when the system is excited with the 325 nm laser, both the ZnO and anthracene layers are excited and electron–hole pairs are created. It is known that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in the anthracene molecule are positioned at
−5.6 eV and −2.25 eV, i.e., LUMO is situated above the conduction band of ZnO (electron affinity ~4.65 eV). The excitation spectrum of the anthracene is in agreement with the positions of HOMO and LUMO levels. Therefore, these photoexcited electrons in the LUMO states can easily transfer to the conduction band of ZnO through interfacial interaction, and this is schematically shown in Fig. 4(d). This process will lead to the accumulation of more charge carriers at the conduction band, which will boost the electron–hole recombination probability. Simultaneously, few of the electrons at the LUMO states recombine with the holes in the HOMO states resulting in an enhancement of UV PL intensity. However, due to the transfer of most of the electrons and the presence of a very thin layer of the anthracene, this emission does not have any strong effect on the enhanced UV PL of the ZnO/anthracene heterostructure. As explained before, the anthracene molecules are likely to be attached to the surface of the NWs at the oxygen vacancy sites, which significantly reduce the concentration of oxygen vacancy states of ZnO NWs. This process results in the decrement of the green emissions in the ZnO/anthracene system. On the other hand, the transfer of photoexcited electrons from the LUMO in anthracene to the conduction band of ZnO could be the strongest possible source for the enhanced UV PL intensity.

To get more insights into the effect of capping on the green emission by surface modification, we measured the PL decay dynamics of the first green emission under the excitation of 375 nm pulsed laser. Both the decay curves in Fig. 5 (before and after capping) show bi-exponential behaviors corresponding to the components of first and second green emissions. Therefore, the PL decay results confirmed the presence of two components in the broad green emission.

FIG. 4. (Color online) Room temperature PL spectra of the: (a) uncapped ZnO NWs and (b) ZnO/anthracene based NWs heterostructure. (c) Excitation and emission spectra of the anthracene powder. Excitation scan was performed for the emission wavelength fixed at 410 nm. (d) Schematic of the energy band diagram of the ZnO/anthracene heterostructure and possible mechanism of the interfacial electron transfer.

FIG. 5. (Color online) PL decay profile of the first green emission (~500 nm) for the uncapped ZnO NWs, and (b) ZnO/anthracene based NWs heterostructure, measured under the excitation of 375 nm pulsed laser source.
The calculated decay life times are 0.7 and 7.6 ns for the as-grown ZnO NWs and 1.2 and 5.6 ns for the ZnO/anthracene system, respectively. The PL decay process becomes slow after the anthracene treatment because of the possible passivation of the vacancy defects by anthracene. Thus the anthracene capping slows down the decay rate of green emission peak, which supports the fact that anthracene molecules are attached at the oxygen vacancy sites of the ZnO NWs. This is consistent with our previous report, where we have shown the slowing down of green PL decay process from the structurally improved ZnO NWs with reduced defect states.

Figure 6(a) shows the dark current-voltage (I–V) characteristics of the uncapped ZnO NWs and ZnO/anthracene heterostructure. The I–V characteristics show nearly linear behavior with current in the range of nA. After the heterostructure formation, the dark current is increased to 12 nA from 6.0 nA at 3 V bias. The wavelength dependence of PC at a bias of 3 V under the excitation in the range 300–650 nm is shown in Fig. 6(b). The PC spectra of the uncapped NWs show a strong peak in the UV region at 369 nm and a very weak broad peak in the green region (shown as inset). The observed strong peak at 369 nm in the PC spectra is due to the band-edge absorption followed by generation of photocarriers (electron–hole pair). The other peak in the visible region is due to the generation of carriers from the oxygen vacancy related defect states. For the ZnO/anthracene system, the intensity of the PC peak in the UV region is significantly enhanced. The maximum PC is enhanced to 48.2 μA from 4 μA in the uncapped case. Photosensitivity value is also increased to ~4000, leading to a sixfold enhancement for the heterostructure as compared to the uncapped NWs. Very high photosensitivity and low dark current are very important requirements for the efficient photodetection. Therefore, the ZnO/anthracene system is very sensitive in the UV region making it an important and effective candidate for the fabrication of efficient UV photodetectors.

The enhancement in the dark current as well the photocurrent in the heterostructure can be explained as follows. Due to the presence of intrinsic oxygen vacancies on the surface of the uncapped ZnO NWs, in dark condition oxygen molecules are attached on the above defect states by adsorption process and it traps two free electrons. This process results in the decrement in conductivity by forming a depletion layer near the surface, resulting in a very low dark current. After anthracene capping, as the anthracene molecules are possibly attached at the oxygen vacancy sites with the carbon atom in the center ring of anthracene, it would trap only one electron from ZnO to stabilize the vacant defect. This accounts for the somewhat higher dark current from the ZnO/anthracene NWs heterostructure. Under the UV irradiation, electron–hole pairs are generated that increase the PC, and oxygen molecules are released by the photodesorption process. In case of ZnO/anthracene NWs heterostructure, both the ZnO and anthracene layers generate electron–hole pairs. Subsequently, the electrons at the LUMO states of anthracene are transferred to the conduction band of ZnO, as discussed before to explain the enhancement in the UV PL intensity. Under external bias, these electrons along with the photogenerated electrons (due to the band edge absorption of ZnO) contribute to the current conduction process, resulting in an enhanced PC.

The photoresponse behaviors of the uncapped and capped systems measured at 360 nm are shown in Fig. 7. The uncapped NWs have response and reset times about 7.2 and 63.2 s, respectively [Fig. 7(a)]. In contrast, the ZnO/anthracene NW heterostructure [Fig. 7(b)] shows a very fast response with response and reset times of 1.5 and 1.6 s, respectively. The response and reset time can be defined as 1-1/e, (63%) of the maximum photocurrent increased and 1/e, (37%) of the maximum photocurrent decreased, respectively. As expected, the photoresponse time for the uncapped NWs is very slow due to the presence of intrinsic defects/trap centers. Therefore, ZnO/anthracene NW heterostructure shows five times faster response and about 40 times faster reset time, which is a significant achievement for the real-time photodetection application. Figure 7(c) shows the photoresponse of the ZnO/anthracene NWs under periodic UV illumination. The saturation photocurrent in one cycle is same as that of any other cycle. Second and third cycles of photocurrent growth and decay show exactly the replica of first cycle, demonstrating a fast and reproducible PC response, which is important for the real-time application in photodetectors. It is known that anthracene molecule photodimerizes under the UV exposure. The observed
reproducible and fast photoresponse from the heterostructure indicates that this photodimerization does not affect the photoresponse behavior. However, this dimer can be reverted to anthracene by UV irradiation below 300 nm. To study the influence of environment on the performance of the ZnO/anthracene heterostructure, we measured the PC in different environmental conditions (different humidity and O2 pressure). It is found that there is no notable change in the photoresponse behavior with exposure to humidity or O2.

In general, it is known that the rates of O2 adsorption and photodesorption processes primarily control the photoresponse time. The chemisorbed O2 molecules trap the free electrons that are available on the surface of the NWs, and this results in the formation of a surface depletion layer, resulting in a upward band bending and leading to a barrier height for electrical conduction.9 During the UV illumination, i.e., the ON state, the photoexcited electron-hole pairs are generated and the holes are trapped by the adsorbed O2 through the surface electron–hole recombination, while the photoexcited unpaired electrons significantly increase the conductivity. The photocurrent gradually increases with time until desorption and readsoption of O2 reach an equilibrium state. At the end of the UV illumination, i.e., the OFF state, the hole density is much lower than electron density in the NW. Although holes recombine quickly with electrons upon turning off UV light, there are still a lot of electrons left in the NWs. With the surface readsoption of O2, the current comes to the initial value very slowly. In the present case, due to the anthracene covering on the surface of the ZnO NWs, defect states are considerably reduced due to passivation. As a result, band bending in the NW is also reduced, which results in a less effective charge separation. The ZnO/anthracene NWs show comparatively higher dark current, which supports the idea that indeed there is a reduction in the band bending. This is similar to the case when the surface of the NWs is covered with water moister.10 Due to reduced band bending, electrons and holes can easily recombine, leading to the shorter carrier lifetime. During the interfacial charge transfer from anthracene to ZnO, it is believed that sufficient amount of holes may be transferred to the valence band of ZnO. Therefore, at the end of the UV illumination, a sufficient amount of electrons and holes are available in the NW. During decay, the electrons and holes are recombining in a fast way due to the shorter carrier lifetime. This process results in a much faster photoresponse as compared to the case of uncapped ZnO NWs.

IV. CONCLUSION

In conclusion, we have investigated the effect of organic anthracene capping on the ZnO NWs and achieved a significant improvement in the photocurrent and photoresponse behavior for the ZnO/anthracene heterostructure. The PL studies show that the intensity of the UV emission is enhanced by a factor of 3, while the green emission is nearly halved to the case of uncapped NW. Although the dark current is nearly doubled after the anthracene capping, a significant improvement in the photocurrent is obtained. A sixfold improvement in the UV photosensitivity is demonstrated. Compared to the uncapped case, the photoresponse and reset times become much faster for the ZnO/anthracene system with response and reset times of 1.5 and 1.6 s, respectively. Therefore, the ZnO/anthracene system is an important and effective candidate for the fabrication of efficient UV photodetectors.
