

Polymer functionalized piezoelectric-FET as humidity/chemical nanosensors

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By coating one side of the surface of a ZnO nanobelt (NB) with multilayer polymers using an electrostatic self-assembling process, a humidity/chemical nanosensor based on piezoelectric field effect transistor (PE-FET) is demonstrated. The working principle of the PE-FET relies on the self-contraction/expansion of the polymer, which builds up a strain in the piezoelectric NB and induces a potential drop across the NB that serves as the gate voltage for controlling the current flowing through the NB. The response of PE-FET to the phase transition of the coating polymer was also demonstrated. The device is a component for nanopiezotronics. © 2007 American Institute of Physics. [DOI: 10.1063/1.2748097]

Devices using one dimensional nanostructure, such as nanowire (NW) and nanobelt (NB) (Ref. 1) are being extensively studied due to their supreme performance different devices. Prototype devices have been demonstrated using NWs and NBs as FET,² thermal transistor,³ field emission device,⁴ and biological sensors.⁵

Among the materials that are extensively studied in nanoscience, ZnO is perhaps one of the most important materials, and it has been applied for fabricating different electronic transistors⁶ and chemical sensors.⁷ Most recently, a research direction termed of nanopiezotronics has been coined based on the piezoelectric-semiconducting coupled properties of ZnO NWs and NBs for fabricating unique electronic components.⁸ The first application of nanopiezotronics is the piezoelectric nanogenerator based on ZnO NWs,⁹ which demonstrates a unique approach of converting nanoscale mechanical energy into electric energy and harvesting energy from the environment for self-powered nanosystems.¹⁰ PE-FET and diodes¹² that operate based on the coupling effect of piezoelectric and semiconducting properties of ZnO have been developed.

In this letter, we demonstrate a humidity/chemical sensor based on PE-FET.¹¹ The devices were based on a single-side coated ZnO NB functionalized with multilayers of polymers. Upon exposure to high humidity vapors, the polymers swell and produce an asymmetric strain across the ZnO NB. In return, the deformation of ZnO NB produces a piezoelectric field across the NB, which serves as the gate for controlling the flow of current along the NB. This is the working principle of the polymer functionalized PE-FET.

Polymers for functionalization of NB are anionically charged poly N -isopropylacrylamide (PNIPAM) and poly(diallyldimethylammonium chloride) (PDADMAC). PNIPAM is the most well known temperature sensitive polymer in aqueous solution, which exhibits a lower critical solution temperature (LCST) of around 32 °C.¹³ The volume change ratio of a cross-linked PNIPAM corresponding to its hydra-

tion and dehydration transition can reach as high as 20 times.^{14,15} In order to introduce charge groups in the polymer chain, acrylic acid sodium salt was copolymerized with NIPAM monomer at a molar ratio of 1:9.

In the experiments, our devices were fabricated with described previous method.¹⁶ During the layer-by-layer assembly experiment, ZnO was first immersed in a dilute PDADMAC solution at pH of 8. Zeta potential measurement indicated that the zeta potential of the ZnO NB in water at pH value of 7.5 is -21 mV, which means that the surface of ZnO NB was negatively charged (Fig. 1(a)). The cationically charged PDADMAC molecules were then absorbed on the ZnO surface. This ZnO NB coated with positively charged polymers on the surface was immersed in an anionically charged PNIPAM solution. By repeating this process alternatively, multilayers of polymer with controlled layer numbers can be assembled on the ZnO NB surface. This multilayer functionalization process is schematically shown in Fig. 1(b), in which the green dots represent the cationically charged PDADMAC and the orange dots represent the anionically charged PNIPAM. ZnO NBs incorporated in the device were closely attached to the substrate surface (with a distance of less than ~70 nm), so the polymer molecules (the radius of gyration in water, R_g , is 160 nm determined by SLS) will mainly adsorb only on the upper side surface to form multilayer polymers on the ZnO NB (Fig. 1(c)).

IV characteristics of these polymer functionalized ZnO NB base devices were tested. These devices are further fabricated using focused ion beam microscopy to deposit Pt to secure the contacts before polymer functionalization. Figure 2(a) is the IV characteristics of PNIPAM functionalized samples upon exposure to 85% RH water vapor (black line) and 12% RH water vapor (red curve). This current response to vapor on and off states can be repeated for many cycles and the detection limit could be very accurate according to the strong and steady response to the 12% RH water vapor in the experiment.

To explore the origin of the reduced current upon vapor exposure, we carried out a series of experiments based on different functional materials on the devices. As shown in Fig. 2(b), the current flowing through the uncoated ZnO NB

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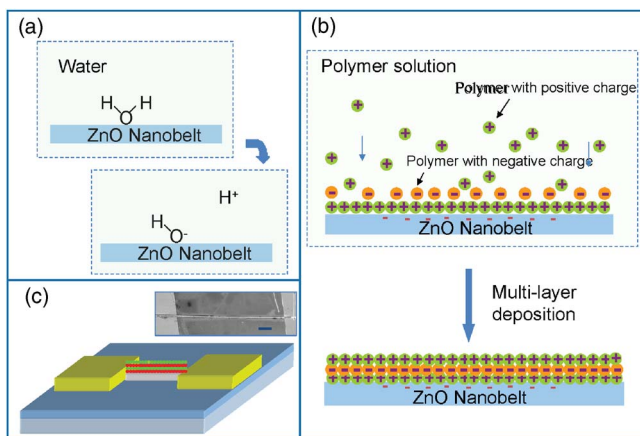


FIG. 1. (Color online) Schematic illustration of the layer-by-layer electrostatic self-assembling process. (a) Schematic illustration of ionization of H_2O molecules on the surface of ZnO NB, which results in negatively charged ZnO NBs in aqueous solutions. (b) Schematic illustration of multilayer deposition of different polymers onto the ZnO NB surface upon electrostatic attraction of the charges on polymers. The green dots represent positively charged PDADMAC. The orange dots represent the negatively charged PNIPAM. (c) Schematic illustration of the polymer functionalized device. The inset SEM image is an actual polymer functionalized device.

(black) increased from 0.005 to $0.055 \mu A$ upon 85% water vapor exposure. We suggest that, upon vapor exposure, the preadsorbed oxygen that caused the conductivity decrease was replaced by the ionic species, which might result in an increase in conductivity. Similar current increase was observed when the conducting channel contains only multilayers of polymers [Fig. 2(c) red]. This is due to the ion mobility increase in the dehydrated multiple polymer. Current responses of the multilayer polymers without ZnO NB or with ZnO NB only but without polymer are opposite to the response of polymer functionalized ZnO NBs. These experiments proved that neither ZnO NB nor multilayer polymers could produce the decreased current response upon exposing to vapor. Therefore, we suspect that the decreased current response come from the coupling effect of the coating polymer layers and the ZnO NBs.

It is believed that the reduced conductivity may come from a similar piezoelectric-semiconducting coupling properties of a bent ZnO NB, as reported previously.¹¹ The poly-

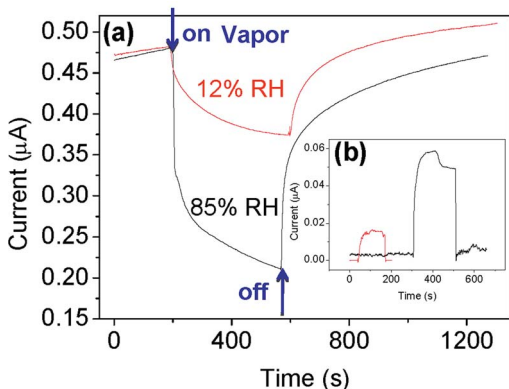


FIG. 2. (Color online) (a) I - V responses of the PNIPAM polymer functionalized devices upon exposure to 85% (black curve) and 12% (red curve) relative humidities. (b) Current response of an uncoated ZnO NB upon exposure to 85% relative humidity (black) and multilayer polymers (red) showing that neither of them individually is responsible for the reduce of current in (a).

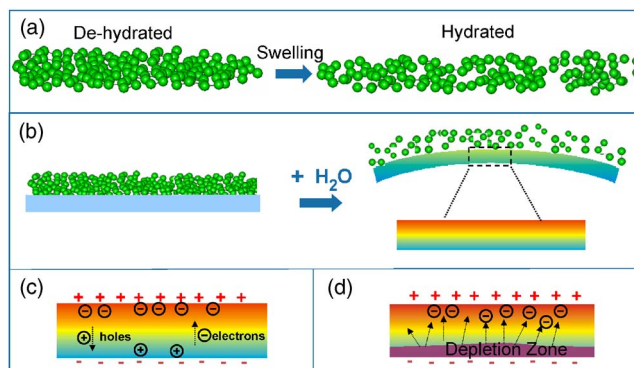


FIG. 3. (Color online) Schematic illustration of mechanisms of polymer functionalized piezoelectric field effect transistor (PE-FET). (a) The volume of the polymers increases significantly upon hydration. (b) Schematic illustration of ZnO NB deformation upon polymer swelling and the consequent generated piezoelectric fields across the ZnO NB. The inner and outer surfaces of ZnO NB are negatively and positively charged, respectively. (c) Free electrons are trapped by the positive charged surface. (d) A depletion region is formed by the repelling force of the negative charged surface.

mers used in our experiments, PNIPAM and PDADMAC, are all very sensitive to environment humidity changes. According to Ref. 17, the surface functionalization introduces surface strain on the NB. As shown in Fig. 3(a), these polymers are closely packed before vapor exposure. Upon exposure to water vapor, these polymers will undergo a hydration process. As a result, the volumes of these polymers are increased in a significant ratio. Because the polymers were coated only at one side of the ZnO NB, the swelling of polymers then generated an asymmetric tensile stress at the contact surface with ZnO NB. Consequently, ZnO NB was bent resulting in an asymmetric strain across the thickness of the NB. As demonstrated in our recent work, a bent ZnO NB could produce a piezoelectric potential across the NB due to the strain-induced piezoelectric effect. With the stretch and compression effects of a deformed ZnO NB, a positively charged and a negatively charged surfaces were produced at the outer and inner bending surfaces of a ZnO NB. Consequently, a piezoelectric field was built across the ZnO (NB Fig. 3(b)). These ionic charges are immobile on the ZnO NB surface without releasing the strain. This trapping effect lowers the available carrier densities in ZnO NBs. On the other hand, the negative charged surface of ZnO NBs acted as a back gate which repels free electrons away from the surface under the electrostatic effect. Therefore, a depletion region was formed in space close to the negative charged surface. This reduces the size of the conducting channel in the ZnO NB. This also accounts for the decrease in conductivity of the bent ZnO NB. These two mechanisms are schematically presented in Figs. 3(c) and 3(d), which together may be responsible to the observed decrease in conductivity. The depletion region formed by the negative charged surface and the consequent gating effect to the conduction channel in ZnO NB is analogous to the case of applying a gate voltage across a ZnO NB in a typical FET, e.g., PE-FET. In our experiment, bending of the ZnO NB comes from the swelling of polymers, which is a result of chemical process. When the sample was dehydrated in dry air, the strain was released and the ZnO NB returns to its original shape.

By monitoring the current changes flowing through the functionalized ZnO NB, we recorded *in situ* phase transition of PNIPAM in aqueous solutions with the increase of tem-

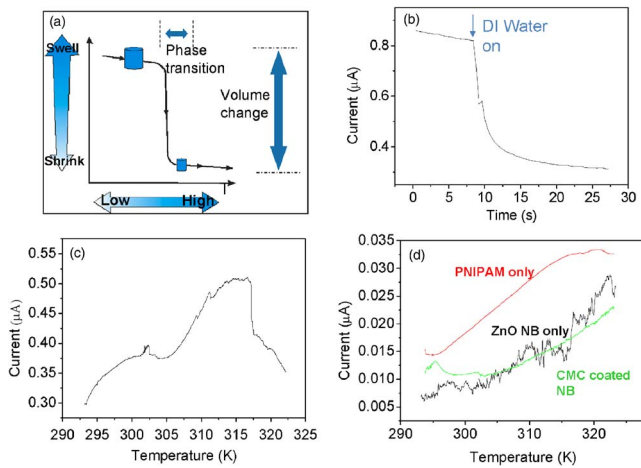


FIG. 4. (Color online) (a) Schematic illustration of the phase transition and the corresponding volume changes. (b) Current response of PNIPAM functionalized ZnO NB upon exposure to DI water. (c) Current response of the same devices with temperature increase in aquatic solution. (d) Current response of uncoated ZnO NB (black curve), PNIPAM polymer (red curve), and CMC polymer coated ZnO NB (green curve) upon temperature increase in the temperature range of 293–323 K.

perature. As mentioned before, PNIPAM has a LCST of around 32 °C (305 K). When being exposed to aqueous solution at temperature lower than 305 K, PNIPAM gels hydrate to form an expanded gel structure on NB surface. In contrast to low temperature, PNIPAM dehydrates at temperatures above 32 °C. This hydration and dehydration phase transition process results in a significant change in the polymer volume, as schematically illustrated in Fig. 4(a). As a result, the polymer produces high stress on ZnO NB at low temperature when it absorbs water moisture. However, this stress will be released at high temperature due to the dehydration of the polymer hydrogel. Therefore, it is expected that the conductivity of PNIPAM modified ZnO NB should show a temperature reversible responsibility at the PNIPAM's LCST of ~305 K.

Figure 4(b) is an *in situ* current response of the same NB upon exposure to DI water. The transport current decreased from 0.8 to 0.3 μA which was a result of the polymer swelling. By applying DI water on the polymer functionalized PE-FET, we then precisely controlled the temperature to increase from 293 to 323 K. The *in situ* current signal, is displayed in Fig. 4(c). We suspect that the abrupt change of the curve slope at the temperature of around 305 K reflects the phase transition of PNIPAM. To prove this hypothesis, the current response of different targets in aqueous solution with respect to temperature increase was tested. As shown in Fig. 4(d), an increase in temperature results in a quasilinear increase in current magnitude. This is the case for all of the tested samples, including uncoated ZnO NB (blue curve), pure PNIPAM polymer (red curve), and CMC (carboxyl me-

thyl cellulose, a polymer without the LCST phase transition effect at the temperature range tested in this study) coated ZnO NB (green curve), which shows that none of them will generate an abrupt current changes, as observed in Fig. 4(c). We can then conclude that the current signal change is a result of the stress release due to the phase transition of the PNIPAM polymer in aqueous solution with temperature increase. A tentative explanation to this effect is that, at the temperature range of 293–305 K, the current slowly increased due to the higher carrier mobility at higher temperature. At the temperature range of 305–315 K, the current underwent a faster increase. This might result from polymer contraction during the phase transition of PNIPAM in aqueous solution at this temperature range. As discussed before, when temperature increases, the volume of PNIPAM will significantly contract due to the dehydration effect of the phase transition. Contraction of polymers released the strain applied on the ZnO NB. The deformation of ZnO NB was then released. Consequently, the piezoelectric field across the ZnO NB became smaller, so are the surface charged densities and the depletion region. This results in the increase of ZnO NB conductivity. At the temperature above 315 K, phase transition and dehydration of PNIPAM were completed, so increase in temperature results in further hydration of PNIPAM and PDADMAC, which increase the bending degree of ZnO NB, and consequently, decrease the current magnitude.

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