

## Maskless electrodeposited contact for conducting polymer nanowires

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This letter reports a simple and scalable method to create mechanical joints and electrical contacts of conducting polymer nanowires to electrodes by selective maskless metal electrodeposition on electrodes. This is an attractive route for contacting nanowires as it bypasses harsh processing conditions of conventional methods. The electrodeposition conditions and initial resistance of the nanowires were found to have a significant impact on the selective maskless deposition. Different dopants were also investigated to understand the polymer reduction during cathodic deposition of metal. A single dodecyl sulfate doped polypyrrole nanowire with maskless electrodeposited nickel contacts was shown to have improved sensitivity toward ammonia gas. © 2008 American Institute of Physics. [DOI: 10.1063/1.2883923]

One-dimensional conducting polymer nanostructures provide significant promise for miniaturized devices. The inherent properties of polymeric nanostructures are particularly suited for sensors because their mechanical flexibility, chemical sensitivity, room temperature operation, and potential for high density arrays are ideal for compact portable platforms.<sup>1</sup> Although, various methods including lithography,<sup>2</sup> nanoscale solder,<sup>3</sup> focused ion beam (FIB),<sup>4</sup> and annealing<sup>5</sup> have been investigated to contact inorganic nanostructures to electrodes, and processing incompatibilities have excluded applying those methods to conducting polymer nanowires. For example, post-assembly contact of conducting polymer nanowires by lithography requires complex alignment procedures and exposure to harsh processing conditions, subjecting the nanowires to high intensity ultraviolet light, and organic solvents that may permanently degrade, stress, or dissolve organic nanowire surfaces.<sup>6,7</sup> The photoresist may also permeate the porous nature of some organic materials leaving difficult to remove residuals. Alternative serial patterning techniques such as FIB are costly with low-throughput and localized heating that may sever contact rather than promote it. Similarly, the high operating temperature for nanoscale solder may ultimately decompose these organics and does not provide the necessary palette of materials for ohmic contact with organics. Lastly, nanowires deposited on top of prefabricated electrodes are not exposed to extreme environments but are loosely bound with minimal contact area.

In this letter, we present selective maskless metal electrodeposition to electrodes to contact and embed the ends of polymer nanowires. This approach is amenable to high throughput processing as electrodeposition is an easily scaled process compatible with the microelectronics industry.<sup>8</sup> Several high-work function materials, Cu, Ni, and Au, were investigated to achieve ohmic contact for p-type polymer semiconductors, such as the polypyrrole (PPy) nanowires. The applied deposition potential, initial resistance of loosely bound interconnects, and electrodeposition bath compositions were found to be crucial parameters in controlling the

deposition selectivity. Scanning electron microscopy (SEM) images and current-voltage (*I-V*) responses confirmed the nature of the selective electrodeposition of metal on the electrodes to completely embed the nanowire. The applied potential and dopant of polymer were also shown to impact reduction of the nanowire during cathodic electrodeposition of metals. Preliminary sensing of gaseous NH<sub>3</sub> using a single dodecyl-sulfate doped PPy (DS-PPy) nanowire was also demonstrated.

The PPy nanowires were synthesized by template-directed electrodeposition in alumina templates (Anodisc®, Whatman, Inc.) with a nominal pore diameter of 200 nm. The electrolytes consisted of 0.1M pyrrole and 1% sodium dodecyl sulfate or 0.5M pyrrole and 0.2M LiClO<sub>4</sub> in aqueous media. DS was selected as a dopant for its size and structure which has been demonstrated to have a relatively low mobility<sup>9</sup> compared to smaller spherical dopants (i.e., chloride and perchlorate) and greater response to small polar molecules.<sup>10</sup> A three electrode configuration was used in a single cell with a Pt counter electrode under ambient condition. The electrolytes were purged with N<sub>2</sub> (99.999%) for 30 min prior to electrodeposition. DS-PPy nanowires were galvanostatically deposited at 1 mA cm<sup>-2</sup> and ClO<sub>4</sub><sup>-</sup> doped PPy nanowires were potentiostatically deposited at 0.9 V (versus Ag/AgCl). After suspending the PPy nanowires in water or isopropyl alcohol, they were drop cast on prefabricated 5 μm gap gold microelectrodes containing peripherally positioned contact pads, which were electrically interfaced with copper tape and silver paint.<sup>11</sup>

The maskless contacts were potentiostatically electrodeposited in a three electrode configuration by submerging the microelectrodes with loosely bound nanowires (i.e., working electrode) in an electrolyte and applying constant deposition potential against a Ag/AgCl reference electrode. Counter electrodes were nickel for nickel plating or platinum coated titanium for gold and copper plating. Nickel sulfamate baths were used to embed DS-PPy nanowires and nickel sulfamate baths, gold sulfite baths, and copper sulfate baths were used for contacting perchlorate doped PPy (ClO<sub>4</sub>-PPy) nanowires. Nickel was electrodeposited from 0.91M Ni(SO<sub>3</sub>NH<sub>2</sub>)<sub>2</sub> + 0.2M NiCl<sub>2</sub> + 0.4M H<sub>3</sub>BO<sub>3</sub> by varying the deposition potential from -0.7 to -1.1 V. Gold was electrodeposited from

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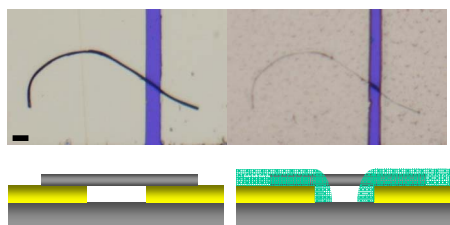


FIG. 1. (Color online) (Top) Optical images of a single PPy nanowire on gold electrodes before (left) and after (right) maskless electrodeposition of nickel: scale bar represents  $3 \mu\text{m}$ . (Bottom, left) Corresponding schematic of loosely bound nanowire crossing two gold microelectrodes. (Right) Selective maskless electrodeposition of metal (green) on electrodes to embed the nanowire for better electrical and mechanical contact.

40 mM NaAuSO<sub>3</sub> electrolytes purchased from Technic Inc., by varying the deposition potential from  $-0.5$  and  $-0.7$  V. Copper was electrodeposited from 0.5M CuSO<sub>4</sub> and 0.5M NaSO<sub>4</sub> with an applied potential of  $-0.025$  V.

Maskless electrodeposition of nickel on the DS-PPy nanowires was studied to determine the effects of applied deposition potential and initial resistance on selectivity of the deposit, reduction of the nanowires, and contact improvement. Selectivity is a measurement of electrodeposited material to discriminate between the desired deposition on the electrodes and nonpreferential deposition on the nanowire, ideally depicted in Fig. 1. The electrodeposited nickel displayed tunable selectivity for the PPy nanowire with the applied potential. At  $-0.7$  V, the nanowire was coated with nickel particles while higher cathodic potentials were used to embed the nanowire ends in Ni with no observable deposition on the bridging portion of the nanowire. Particles size and density was greatest at low deposition potentials (i.e.,  $-0.7$  V), with 7.45 particles/ $\mu\text{m}^2$  and an average diameter of 204 nm to being not visible with SEM at  $-1.1$  V for a constant charge density of 3.53 C/cm<sup>2</sup> (Fig. 2). This trend was facilitated by very low deposition rates on the electrodes at lower cathodic potentials (e.g.,  $E = -0.7$  V) and, hence, longer deposition times which permitted more nucleation sites and subsequent particle growth for kinetically limited deposition on the conducting polymer without closing the

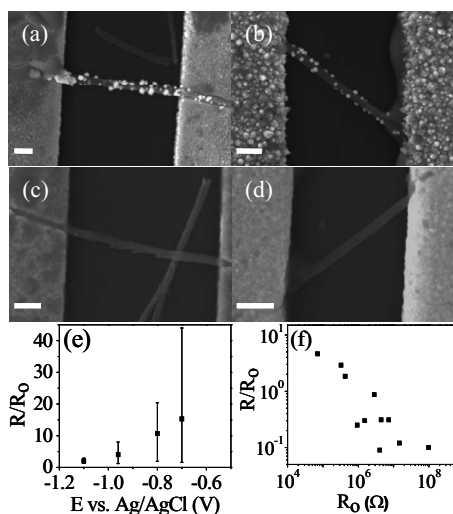


FIG. 2. SEM micrographs of DS-PPy nanowires on electrodes after maskless nickel electrodeposition at (a)  $-0.7$  V, (b)  $-0.8$  V, (c)  $-0.96$  V, and (d)  $-1.1$  V at a constant charge density of 3.53 C/cm<sup>2</sup> (scale bars represents 1  $\mu\text{m}$ ). The  $R/R_0$  ratio (e) as a function of applied deposition potentials and (f) initial resistance for contacts deposited at  $-0.96$  V.

electrode gap. The selective metal deposition on electrodes, particularly in the case of Ni, is also a consequence of the nanowire reduction, which acts as a barrier preventing deposition on the PPy nanowire. Particle deposition on the nanowire is detrimental to its electrical properties as charge tunneling may occur between the PPy and Ni nanoparticles, resulting in unstable electrical behavior when the particles consist of various sizes.<sup>12</sup> On the other hand, metallic nanoparticles can enhance sensitivity to some gas analytes through catalytic activity.

More notably, the initial resistance had a profound impact on the efficacy of the apparent contact improvement  $R/R_0$  ( $R_0$  and  $R$  are the resistances before and after electrodeposited contact, respectively), as the process was counterbalanced by reduction of the polymer. The reduction is dependent on the applied potential and is a strong function of the polymer redox state,<sup>13</sup> increasing with increased resistance.<sup>14</sup> Nanowires in the megaohm range experienced a decrease in resistance down to hundreds of kilo-ohms, while nanowires of initially 300 k $\Omega$  or less increased in resistance of up to threefold for an applied potential of  $-0.96$  V. This procedure was also shown to contact nanowires short of bridging the electrode gap with post-electrodeposition resistances in the low megaohm or high kilo-ohm range. This is a consequence of isotropic growth for the electrodeposited metal which closes the electrode gap, enabling contact of partially bridging nanowires. This behavior can be interpreted as a complex response to increased interfacial area between the nanowire and the electrodeposited contacts with simultaneous reduction of the electrode gap and declination of the nanowire conductivity. The reduction of these nanowires occurs by ingress of cations during the cathodic electrodeposition of metal contact because of the relative immobility for the larger DS dopant.<sup>6,9,14,15</sup>

In the case of ClO<sub>4</sub><sup>-</sup>-PPy nanowires, the level of reduction increased dramatically, typically an order of magnitude. The increased reduction can be rationalized by dedoping of PPy nanowire because of an egress of the smaller spherical perchlorate anions. This increased reduction and higher resistance also inhibited metal deposition on the nanowire as the Ni was selectively deposited on the electrode surface wrapping around the conducting polymer nanowire even at  $-0.96$  V. The electrodeposited gold contacts were less selective than nickel with particle formation on the nanowire and normalized resistance ( $R/R_0$ ) changes of  $0.67 \pm 0.46$  and  $7.14 \pm 1.52$  at  $-0.5$  and  $-0.7$  V, respectively. Lastly, the copper showed no preferential deposition, with complete coating of the nanowire and electrodes, shorting the nanowire device. Thus, the choice of electrolyte served as another approach to tune this technique with different potential windows for electrodeposition. The lower applied cathodic potential of  $-0.5$  V with the gold electrolyte also resulted in minimal nanowire reduction and contact improvement. In the case of Ni, the lower deposition potentials resulted in an order of magnitude drop in current density, requiring much greater times for the same quantity of Ni deposition on the electrodes. This extended time period, during which the cathodic deposition potential was continually applied to the nanowire, created a deeply reduced state in the polymer resulting in the trend shown in Fig. 2(e). Thus, our method is able to create mechanical joints and electrical contacts of conducting polymer nanowires to electrodes but may be limited to conducting polymer and large band gap semiconduct-

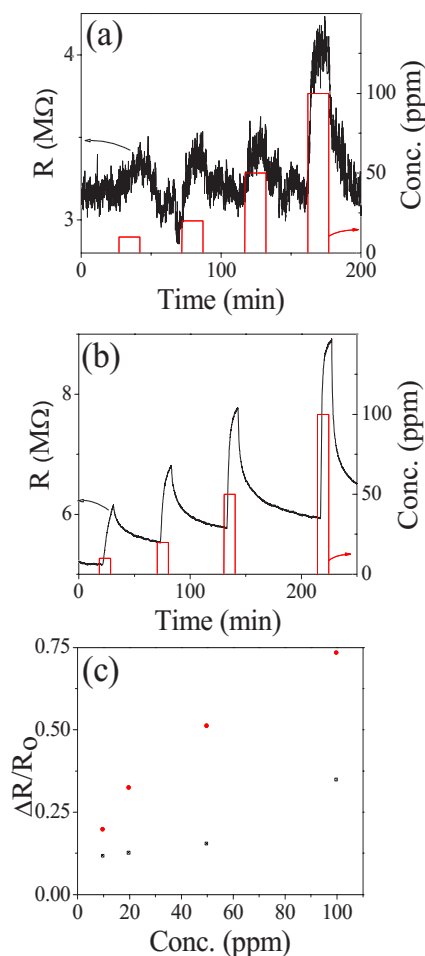


FIG. 3. (Color online) Sensor response of a loosely bound (a) and an embedded (b) single DS-PPy nanowire as a function of different  $\text{NH}_3$  concentrations in air. (c) The sensitivity of a loosely bound (■) and embedded nanowire (●).

ing nanowires since metallic and low band gap semiconductor nanowires could promote nonpreferential deposition on the nanowire.<sup>8</sup>

The sensing performance of a single DS-PPy nanowire of pre- and post-electrodeposited contacts was investigated by exposing the nanowire to ammonia gas in air. Adsorbed ammonia donates an electron to the PPy nanowire, reducing the backbone and the conductivity until the electron is transferred back to the donating ionic counterpart.<sup>16</sup> The sensing behavior of the nanowire with electrodeposited contacts (Fig. 3) shows a drastic increase in sensitivity as well as an order of magnitude decrease in noise, from 0.1 to 0.01  $M\Omega$ . The noise reduction can arise from the increased contact area, the solid mechanical joints that prevent disturbances of electrical contact, and the reduction of charge traps. In disordered materials, such as polypyrrole, the noise can be related to the traps which concomitantly contribute to the conductivity in an intermittent fashion due to their spectrum of relaxation times.<sup>17</sup> The electrodeposited contact procedure is believed to electrochemically reduce many of these charge traps

which arise from branching and disordered chain termination. The sensitivity increase may also be attributed to a decrease in contact resistance and operation in a bulk limited regime or possibly to Ni ion inclusions.<sup>18</sup> The combined effect is a significant improvement of sensing performance (lower detection limit, greater signal-to-noise ratio).

In summary, a facile technique to create good electrical and mechanical contacts for single conducting polymer nanowires has been described. Electrodeposition has been shown to provide maximum contact area for reduced contact resistance. The nucleation of metal particles on the PPy nanowire has been shown to be tunable by adjusting the deposition potential and electrolyte compositions. In the case of conducting polymers, a complex interplay between contact resistances, redox state of nanowires was presented. Preliminary gas sensing results have indicated significant noise reduction and improved sensitivity.

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