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Communication

Room-Temperature Sensing Achieved by GaAs Nanowires and oCVD Polymer Coating[a]

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Novel structures comprised of GaAs nanowire arrays conformally coated with conducting polymers (poly(3,4-ethylenedioxythiophene) (PEDOT) or poly(3,4-ethylenedioxythiophene-*co*-3-thiophene acetic acid) (poly(EDOT-*co*-TAA))) display both sensitivity and selectivity to a variety of volatile organic chemicals (VOCs). A key feature is room temperature operation, so that neither a heater, nor the power it would consume, is required. It is a distinct difference from traditional metal oxide sensors, which typically require elevated operational temperature. The GaAs nanowires are prepared directly via self-seeded metal organic chemical deposition, and conducting polymers are deposited on GaAs nanowires using oxidative chemical vapor deposition (oCVD). The range of thickness for the oCVD layer is between 100 nm to 200 nm, which is controlled by changing the deposition time. X-ray diffraction analysis indicates an edge-on alignment of the crystalline structure of the PEDOT coating layer on GaAs nanowires. In addition, the positive correlation between the improvement of sensitivity and the increasing nanowire density is demonstrated. Furthermore, the effect of different oCVD coating materials is studied. The sensing mechanism is also discussed with studies considering both nanowire density and polymer types. Overall the novel structure exhibits good sensitivity and selectivity in gas sensing, and provides a promising platform for future sensor design.

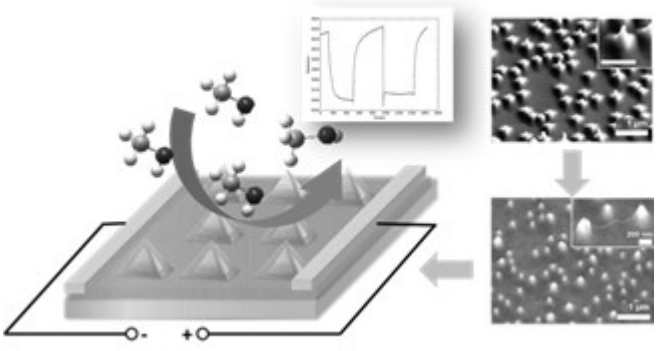


FIGURE FOR ToC_ABSTRACT

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1. Introduction

Ever since the discovery of conducting polymers, such as polyacetylene and polythiophenes, researchers have been exploring their applications in chemical sensing based on their unique electronic[1-4], optical[1, 5, 6] and chemical properties[4, 7]. Among the conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most investigated sensing materials because of its high conductivity and stability[2, 8]. The nanostructured PEDOT, such as PEDOT nanowires or nanorods, is especially important as the surface area is greatly increased compared to PEDOT thin films, and the required diffusion length for the analyte is remarkably decreased as well[2, 9-11]. Many researchers have been dedicated to developing gas detectors based on PEDOT nanowires. For example, Jang et al[11] synthesized PEDOT nanorods and demonstrated the sensitivity towards ammonia and hydrochloric acid vapor. Yoon et al[2] reported 1D PEDOT nanowires as alcohol sensing materials, Cao et al[10] developed PEDOT nanowire alcohol sensor with mechanism studying showing the correlation between the charge transport regime and the resistive signal. These studies support PEDOT as a great candidate for an economic and efficient sensor.

Typically the 1D PEDOT nanowire synthesis utilizes solution-based processes, such as lithographically patterned electrodeposition[12, 13], template directed electrodeposition[14], or interfacial polymerization[11]. Because of their low modulus and solution driven capillary effects, these PEDOT nanowires typically do not extend as straight vertical posts from the substrate but appear as randomly oriented nanowire clusters which may touch neighboring structures[11, 14]. Additionally, the nanowires are usually used to fabricate single nanowire devices, which may increase the complexity of the fabrication process [10, 14, 15].

To date, the PEDOT nanowire sensing research has primarily concentrated on redox active analytes such as NH_3 [11, 16, 17], NO_2 [16, 18], CO[19], or NO[17]. The mechanism of sensing is due to the

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modulation of the work function in the conducting polymers. Fewer researchers have investigated the sensitivity and selectivity of PEDOT nanowires towards organic vapors as the basis for a resistive chemical sensor. [2, 13-15].

Here we demonstrate a novel hybrid sensor based on GaAs nanostructure arrays combined with two types of polymer coatings (PEDOT or poly(EDOT-*co*-TAA)) (Figure 1) deposited using oxidative chemical vapor deposition (oCVD). The GaAs nanowires are fabricated via self-seeded growth using metal-organic chemical vapor deposition (MOCVD) method[20], and the conducting polymer coating is synthesized with oCVD directly on the GaAs arrays. oCVD is a very effective way to synthesize conformal conducting polymer coatings[21]. It has the merits of being solvent-free, enabling facile patterning, low cost, and having good compatibility with substrates [21-23]. The highly uniform GaAs nanowire arrays are utilized as a scaffold in gas sensors as they provide high surface-to-volume ratio and are aligned on a substrate *via* an epitaxial relationship. The nanowire morphology addresses some of the challenges of gas sensor applications including increased sensitivity and signal to noise ratio with increased surface area. Similar concept has been demonstrated using carbon nanotube arrays, where increased surface area was essential for sensitivity and response of gas sensors[24]. In this case, however, the conformal coating of polymer on the carbon nanotube scaffold can be challenging due to aggregation of carbon nanotubes. In contrast, we demonstrate good conformal coating on GaAs nanowire resulting in enhanced gas sensing response for nanowire/polymer chemical sensors.

The hybrid structure of GaAs/PEDOT has superior mechanical characteristics as compared to PEDOT nanowires alone. In addition, with an array structure consisting of multiple GaAs nanowires coated with PEDOT, this work demonstrates that the overall response signal is larger than that of the single PEDOT nanowire sensors when tested at room temperature under the same concentrations of

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analyte[10]. Another outstanding merit of this GaAs/PEDOT hybrid structure is that the density of nanowires can be easily adjusted by the deposition condition of GaAs nanowire arrays[20], and the thickness of the PEDOT layer can be easily adjusted by the duration time of deposition. Therefore, there is remarkable degree of freedom to optimize the device for different applications. It is also worthwhile to note the coating material can be easily customized for a specific analyte by substituting any oCVD conducting polymers from our material library[22]; hence our structure provides a great platform for fabrication sensors for different classes of analytes. Additionally, the measurement method of the resistive change is simpler compared to the single PEDOT nanowire sensors, providing a good opportunity to be integrated into a readily sensor circuit board. In this communication, we demonstrate the sensitivity and selectivity of this proposed structure with varying nanowire density, PEDOT coating thickness, and conducting polymer types.

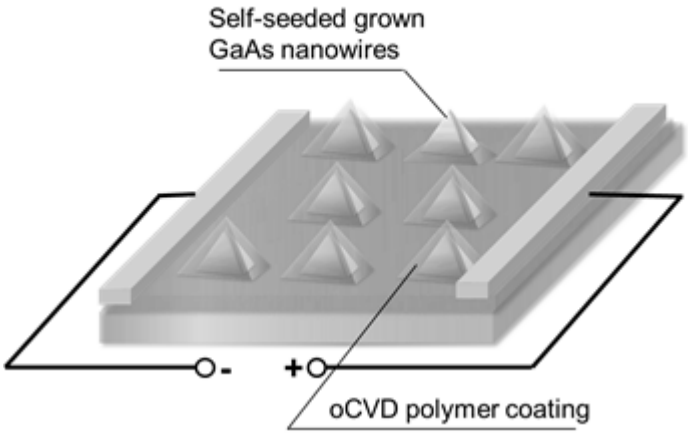


Figure 1 A schematic representation of the hybrid structure of GaAs nanowire arrays and oCVD polymer coatings.

2. Experimental Section

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2.1. GaAs nanowire array growth via self-seeded metal-organic chemical vapor deposition (MOCVD)

MOCVD growth of GaAs nanowires on GaAs (110) and (111)A substrates started with annealing the substrates at 600°C for 10 min under H_2 flow. Following annealing, Ga seed deposition was performed by flowing Trimethylgallium (TMGa) for one minute at 600°C with an effective flow rate of 1.67 sccm (standard cubic centimeters per minute). After Ga seed deposition, substrates were cooled to the growth temperature under hydrogen, and the nanowire growth was performed by flowing TMGa and AsH_3 at 435°C. Effective flow rates of precursors during growth were 1.67 sccm for TMGa and 8.49 sccm for AsH_3. At the end of the growth, TMGa was turned off and the chamber was cooled under H_2 and AsH_3 ambient until 350°C. The MOCVD process was conducted under atmospheric pressure. Details of self-seeded nanowire growth and density-diameter control by surface orientation of the substrate is explained elsewhere[20].

2.2. PEDOT and poly(EDOT-*co*-TAA) coating via oCVD

PEDOT and poly (EDOT-*co*-TAA) coating layers were grown directly on GaAs nanowires via oCVD. The process of oCVD has been reported elsewhere[21, 23]. The monomers, 3,4-ethylenedioxythiophene (EDOT) and 3-thiophene acetic acid (TAA), were heated to 140 ℃ and 200 ℃ respectively, and were introduced into a vacuum chamber in vapor phase. For PEDOT homopolymer films, only the EDOT monomer was used. The flowrate of EDOT is approximately 3sccm, similar to the work reported by Im et al[25]. The copolymer, poly (EDOT-*co*-TAA), was synthesized by introducing 1:1 EDOT and TAA vapors into the vacuum chamber. Simultaneous with the monomer introduction, iron (III) chloride ($FeCl_3$) was sublimed at 350 ℃ in the same chamber as the oxidant. The monomer(s) and the iron chloride adsorbed on the substrate (GaAs nanowires) which was heated to 100 ℃. The pressure of the chamber was controlled at 20 mTorr. The material characterization of the copolymer can be found in previous papers from our group [26, 27]. All the chemicals were purchased from Sigma Aldrich and used as received without further purification.

2.3. Material characterization

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The X-ray diffraction (XRD) data was collected with a Rigaku Smartlab diffractometer operated at 45 kV and 200 mA with CuKα1 (0.154 nm) radiation. JEOL 6700 (under10 kV) and Zeiss Merlin high-resolution scanning electron microscope (SEM, under 5kV) were used to get the SEM images.

2.4. Measurement of sensing signal

The signal collecting system was introduced in previous publications[24, 26]. Nitrogen was used as the carrier gas. Initially, the device was stabilized under pure nitrogen gas flow in a stainless steel chamber. After the stabilization, the analyte vapor was mixed with certain amount of nitrogen to achieve the target concentration, and was later introduced into the chamber. After the electrical resistance of the device reached another steady state, the flow of the mixture (analyte vapor and nitrogen) was substituted with pure nitrogen flow, in which the device was stabilized again. During the test cycle, the resistive change was measured with a Keithley 4000 multimeter. The resistive response is defined as $Response\ (\%) = \frac{R-R_0}{R_0} \times 100$, where R_0 represents the original resistance before introducing the analyte gas and R

represents the resistance of the device. Methanol, toluene and acetone were purchased from Sigma Aldrich, and nitrogen gas was purchased from Airgas.

3. Results and Discussion

3.1. SEM images showing the hybrid structure

Figure 2 shows the SEM images of the more sparsely distributed GaAs nanowire I (~0.4 wires /μm^2), grown on GaAs (110) substrates (a), the more densely distributed GaAs nanowire II (~3.3 wires/μm^2), grown on GaAs (111)A substrates (b), and the PEDOT coated GaAs nanowire I (c) and II (d). Both GaAs nanowire I and GaAs nanowire II show a very sharp tip, which is most easily seen from Figure 2 (a) inset. With the coated PEDOT layer, the tips are much blunter in (c) and (d) compared to (a) and (b) respectively. By taking a cross sectional image (insets of (c) and (d)), the polymer coating thickness on the flat substrate can be extracted. The thickness of PEDOT coating can be easily

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modulated by controlling the duration time of deposition. In this study, the GaAs nanowire I/II are always deposited within one batch to make sure the consistency of coating thickness on both substrates.

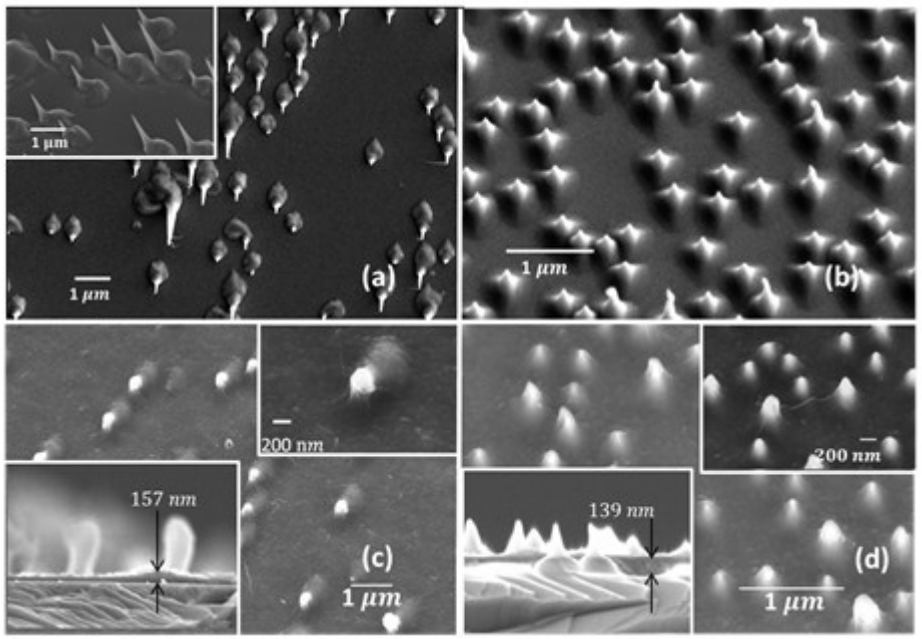


Figure 2 the SEM images of (a) sparser GaAs nanowire I, grown on GaAs (110) substrate, the main image is taken from the top and the inset image is taken with 45° tilt; (b) 45° tilt image of denser GaAs nanowire II, grown on GaAs (111)A substrate; (c) main image: the PEDOT coated GaAs nanowire I, taken from the top; top right corner: one signal coated GaAs nanowire with higher magnification; bottom left corner: cross sectional image showing the coating thickness; (d) main image: the PEDOT coated GaAs nanowire II; top right corner: image with a larger magnification; bottom left corner: cross sectional image showing the coating thickness

3.2. XRD

We also characterized the hybrid GaAs nanowire/PEDOT polymer structure using XRD (Figure 3). Figure 3 compares the PEDOT film coated on flat Si wafer and PEDOT coating layer on GaAs nanowire I with thickness of 200 nm as thicker coating layer provides stronger signal. The peak at 6.4° corresponds to the edge-on configuration (as shown in Figure 3) with a d-spacing of 1.38 nm[8, 28], while the peak at 26° corresponds to a face-on configuration (as shown in Figure 3) with a d-

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spacing of 0.34 nm[8, 28]. Other peaks are mainly generated by FeO_x from the oCVD process. Both PEDOT films on GaAs and Si shows strong face-on crystallinity. However, the edge-on configuration is only observed on the PEDOT films coated on GaAs nanowires, indicating a great enhancement of the unique crystalline orientation of the conducting polymer layer. The vertically aligned nanowire structure may act as seeds for the polymer crystallization, and thus provide the enhanced edge-on structure.

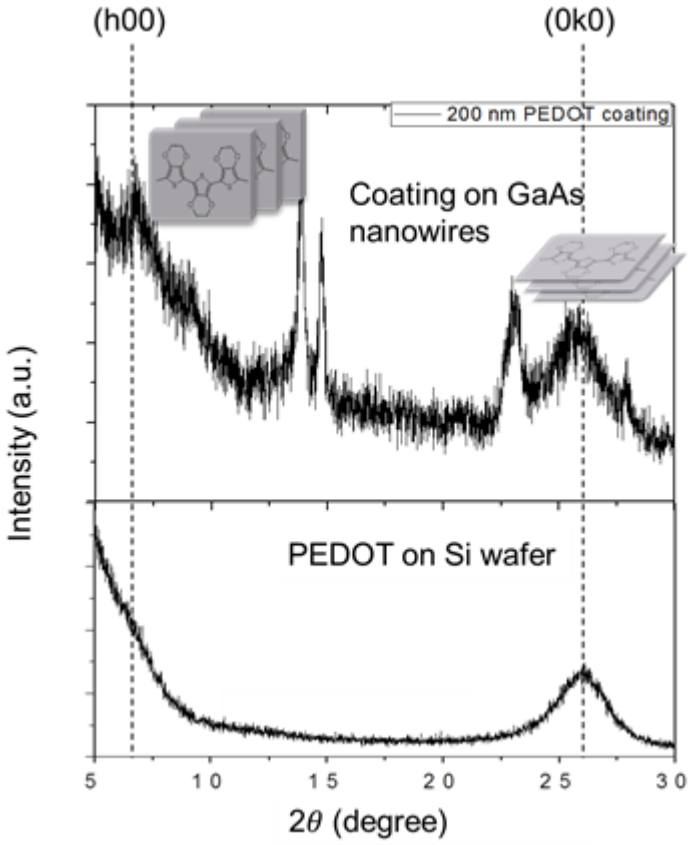


Figure 3 XRD results comparing the PEDOT with 200 nm thickness coated on GaAs I samples, and PEDOT thin film deposited on Si wafer.

3.3. Resistive response and selectivity

Figure 4 summarizes the results of the resistive response measurements to various organic vapors. In Figure 4 (a), the response of GaAs nanowire I coated with ~ 100 nm PEDOT layer over the exposure of methanol and toluene vapor is plotted. Both the responses are negative, showing that the resistance of the device decreases during exposure to the analyte vapors. With a more negative response to methanol vapors, the hybrid structure showed great sensitivity and selectivity of

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methanol over toluene. In addition, as shown in Figure S1 in the supporting information, the hybrid structure does not respond to acetone vapors at all, and hence demonstrates a strong selectivity in favor of methanol or toluene over acetone. Same phenomena can be observed in GaAs nanowire II (more densely distributed) coated with the same PEDOT layers (Figure 4 (b), same oCVD batch as in GaAs I/ PEDOT). The lowest concentrations tested on the devices are 236 ppm for methanol and 91 ppm for toluene, which are comparable to the detection limits of metal nanoparticle based gas sensors[27, 29], and are far below the industrial requirement of 10% of the lowest explosive limit (LEL)[30] (for methanol, LEL~60,000 ppm[31] and for toluene, LEL~11,000 ppm[31]). In addition, the magnitude of the signal here is much greater than the vertically aligned carbon nanotube (VA-CNT)/PEDOT sensor previously reported[24]. For example, the response of GaAs II/PEDOT device to 406 ppm methanol is -1.37%, while the response of the VA-CNT based device to the same concentration of methanol vapor is only ~ -0.05%[24]. This phenomenon may due to the much larger amount of PEDOT material coated on the vertical skeletons (100 nm thickness on GaAs nanowires vs. 8-17 nm PEDOT coating on CNTs limited by the inter-tube space in the CNT forest) and much better vertical alignment (the VA-CNTs are wavy and touching each other[24], potentially causing short circuit bypassing the actual sensing material PEDOT). Additionally, the performance of the GaAs/PEDOT device is comparable to the single PEDOT nanowire devices. For example, the magnitude of the response of GaAs II/PEDOT device shown in Figure 4 (b) to 406 ppm methanol vapor (response ~ -1.37%) is already larger than the response of the single PEDOT wire device to 700 ppm methanol vapor (response ~ -0.35 %)[10]. We suspect that the improvement in performance may due to the array structure consisting of multiple GaAs nanowires coated with PEDOT, and thus collectively providing larger signals. There are many factors which can influence the overall resistive response of all the aforementioned sensor types; therefore the performance can be tuned accordingly. However, at least, the comparison above showed that our GaAs/PEDOT sensing device is able to provide comparable results with the designs based on CNT and single PEDOT wires.

As shown in Figure 4 insets, the reversibility of the devices is also excellent. In the inset of Figure 4 (b), the responding time is ~100 s and the resistance can recover within ~ 500 s. Compared with GaAs I/PEDOT, GaAs II/PEDOT shows more negative resistive response with the same concentration of methanol or toluene, which indicates that the density of GaAs nanowires plays an important role in the gas sensing behavior. GaAs II, as shown in the SEM images in Figure 2, has denser distribution of GaAs nanowires (~3.3 wires/μm^2) compared to GaAs I (~0.4 wires/μm^2). In addition, GaAs II has a pyramid shaped base with vertical nanowires, while GaAs I has a round base with inclined

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nanowires. The shape and the density of the GaAs nanowires can influence the effective surface area that analyte vapor molecules can adsorb on. Hence, the signal generated by GaAs II/PEDOT is significantly larger than GaAs I/PEDOT (Figure S2 plotted the response over methanol and toluene vapors generated by GaAs I/PEDOT and GaAs II/ PEDOT together for a clearer comparison). The effect of coating thickness is also studied (Figure S7). With thicker PEDOT layer, the resistive response to methanol vapors is more negative compared with the response generated by thinner PEDOT layer. This is potentially due to the larger load of the sensing material (PEDOT) in the thicker PEDOT coating layers than the thinner layers.

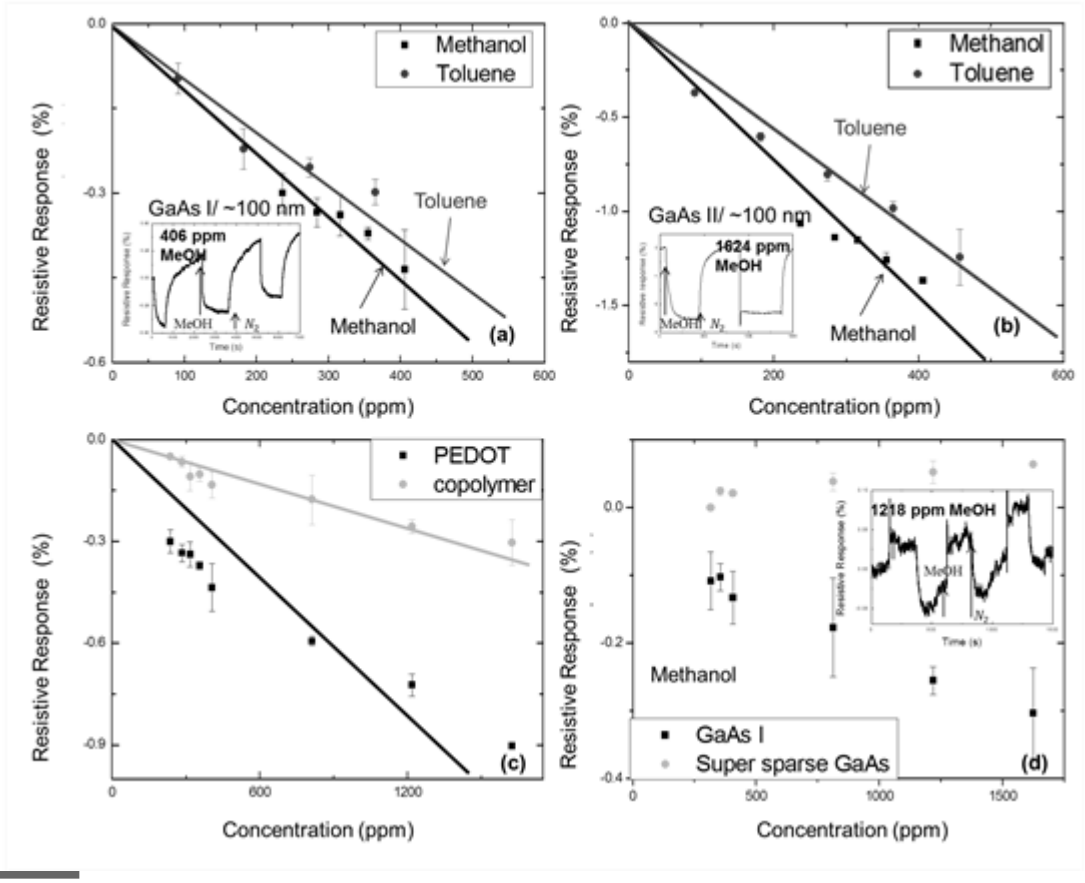


Figure 4 Resistive response of (a) GaAs nanowire I with ~ 100 nm PEDOT coating to methanol and toluene vapors: main figure is resistive response vs. the concentration of analyte; inset is the time dependent signal (resistive response vs. time) of the device to 406 ppm methanol vapor; (b) GaAs nanowire II with ~ 100 nm PEDOT coating to methanol and toluene vapors, inset: the time dependent signal to 1624 ppm methanol vapor; (c) GaAs I coated with PEDOT and poly(EDOT-co-TAA) to methanol; (d) GaAs I and super sparse GaAs nanowires coated with poly(EDOT-co-TAA) responding to methanol vapors; inset: the positive time dependent response of the super sparse GaAs nanowire array coated with poly(EDOT-co-TAA).

The type of oCVD coating on GaAs nanowires also influences the sensitivity to analyte vapors. Figure 4 (c) compares the resistive response generated by PEDOT and poly(EDOT-co-TAA) coatings on GaAs

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nanowires I to methanol vapors. The copolymer coatings generated a much smaller response than the PEDOT coating. One potential explanation of this phenomenon is that copolymer has much less doping level compared with the pure PEDOT coatings since the TAA part tend to dedope in the environment (UV-vis spectra of oCVD PTAA and PEDOT can be found in Figure S3, showing a bleach of PTAA in the polaron region, indicating dedoping and lack of polarons[32], while oCVD PEDOT shows well doped state). Similar dedoping phenomena are commonly seen in oCVD polythiophene[33] and poly(EDOT-co-3-thiophene ethanol)[34]. The doping level of conducting polymers is essential to their sensing behavior. Analytes such as methanol will undergo a partial charge transfer from the p-doped conducting polymer, causing a decrease in the electrical resistance, and thus generating a negative response[10, 15]. The introduction of other monomers in the copolymer chain significantly decreased the p-doping level[34]. With less doping level, the polymer property would move to the insulating region, and the effect of partial charge transfer from the polymer to the methanol will be less significant compared to the highly doped metallic PEDOT coating layer, which is supported by previous research[10]. In addition, with the distortion introduced by the TAA monomers in the polymer chain, the crystallinity of the copolymer is significantly reduced compared to the homopolymer PEDOT films (XRD plot see Figure S4). Therefore, the charge transport regime is moved towards the insulator side for the copolymer further, which is less favorable to methanol detection[10].

While the partial charge transfer mechanism induces negative resistive response for metallic conducting polymers when detecting methanol vapor, a competing mechanism that involves the hindering of interchain electron hopping by the adsorption of analyte molecules may contribute to the increase of the electrical resistance of the conducting polymers[10, 28], and further a positive resistive response when it overtakes the partial charge transfer mechanism[10]. That phenomenon may occur when the polymer is less metallic and the surface area is not large enough to have a fully contact with the analyte molecules. In order to study this possibility, we compared the performance of copolymer coated GaAs nanowire I and a super sparse GaAs nanowire in Figure 4(d) (SEM image of the super sparse GaAs: see Figure S5). The new type of GaAs nanowire[20] (~3.94×10^{-3} wires/μm^2) is much more sparsely distributed than GaAs I nanowires. Therefore, the surface area of the hybrid structure of the new GaAs nanowire and copolymer is remarkably smaller than the GaAs I/ copolymer structure. That explains the much worse performance of the super sparse GaAs/copolymer nanowire arrays in detecting methanol. Also the doping level of copolymer is small enough to allow the super sparse GaAs nanowire/copolymer structure to generate a small

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positive (consistent with Cao et al[10]), instead of negative, response after exposure to methanol. It is worthy to note that after exposure to saturated methanol vapor ($\sim 1.2 \times 10^5\ ppm$), super sparse GaAs nanowire/ copolymer generates a negative response (Figure S6), which indicates that with a p-type polymer coating, the overall effect at large concentration condition is still partial charge transfer dominating.

4. Conclusions

We have successfully demonstrated a novel structure of various GaAs nanowires and oCVD coatings. The XRD result indicates a better edge-on crystalline configuration compared to the oCVD PEDOT film directly coated on flat Si wafers. In addition, we demonstrated the sensitivity of detecting methanol and toluene with great selectivity over acetone vapors. The density and the shape of the GaAs nanowires play an important role in modulating the resistive response signal. In addition, the type of the oCVD coating also modulates the signal mainly by different doping level and crystallinity. With a low doping level and a much sparser nanowire distribution, the super sparse GaAs nanowire/copolymer hybrid structure shows interesting sensing behavior to methanol vapors: at low concentrations, it will generate a small and positive signal, while with large concentrations, the partial charge transfer mechanism dominates, and it will generate a negative signal. Our results demonstrate the possibility to modulate the sensing behavior by varying the nanowire density and the type of the polymer coating. This versatile structure provides a useful platform for future researchers to integrate other skeleton material and other polymer coatings in order to achieve different sensing performances.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author

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Appendix/Nomenclature/Abbreviations

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Table of Contents

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In this work, we report a room temperature operating, sensitive and selective chemiresistor based on GaAs nanowire arrays with conformal conductive polymer coatings. The GaAs nanowires are grown via metal organic chemical deposition (MOCVD). Conducting polymers, poly(3,4-ethylenedioxythiophene) (PEDOT) and poly(3,4-ethylenedioxythiophene-*co*-3-thiophene acetic acid) (poly(EDOT-*co*-TAA)), are synthesized directly via oxidative chemical vapor deposition (oCVD) on top of the GaAs nanowire arrays. High sensitivity of the nanostructure to detect various organic vapors is demonstrated and the selectivity is also studied. Overall, the novel structure exhibits good sensitivity and selectivity in gas sensing, and provides a promising platform for future sensor design.

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