

Principles and mechanisms of gas sensing by GaN nanowires functionalized with gold nanoparticles

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Electrical properties of a chemical sensor constructed from mats of GaN nanowires decorated with gold nanoparticles as a function of exposure to Ar, N₂, and methane are presented. The Au nanoparticle decorated nanowires exhibited chemically selective electrical responses. The sensor exhibits a nominal response to Ar and slightly greater response for N₂. Upon exposure to methane the conductivity is suppressed by 50% relative to vacuum. The effect is fully reversible and is independent of exposure history. We offer a model by which the change in the current is caused by a change in the depletion depth of the nanowires, the change in the depletion depth being due to an adsorbate induced change in the potential on the gold nanoparticles on the surface of the nanowires.

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INTRODUCTION

The interaction of gases with surfaces is an ongoing area of interest to the scientific community. This interest has peaked significantly over the past decade with the advent of nanoscale materials with high surface to volume ratios and concomitant higher sensitivity to surface interactions. This enhanced sensitivity of nanomaterials has garnished industrial interest with the hopes of developing a class of chemical sensors with greater sensitivity and range of operation. As such, much work is ongoing to develop sensors using nanoparticles, nanotubes, and nanowires.¹⁻³ When the term “nanosensors” is used one typically thinks of sensors that are themselves nanometers in scale. However, this is not necessarily the best approach to using nanomaterials for sensing. First, a nanosensor constructed from a single nanoparticle or nanowire will suffer from poor signal to noise ratio which would require excessive signal processing. Second, the process of separating and localizing an individual nanowire between metallic electrodes for electrical transport characterization is extremely time consuming and requires the use of tools such as electron beam lithography or atomic force microscopy facilities, which would make sensor fabrication prohibitively expensive. Sensor fouling is another concern. A single nanoparticle or nanowire sensor could fail under conditions where micron and submicron particulates are present. One solution to potential fouling would be to construct an array of single particle or nanowire devices. This is an impractical solution given the difficulties of indexing a large

number of individual nanoparticles or nanowires with sufficient reliability so that the process would be compatible with lithography techniques.

The solution to the difficulties of using nanomaterials as sensors requires a paradigm shift in sensor design. A nanosensor does not have to be nanoscale in dimensions to take advantage of the unique properties of nanomaterials. In this paper we present the experimental results of a design for a nanosensor utilizing a hybrid structure constructed with GaN nanowires decorated with Au nanoparticles which is capable of detecting methane and nitrogen. The sensor is macroscopic in size, but its sensitivity derives from the sensitivity of the Au nanoparticles and the subsequent response of the GaN nanowires. Furthermore, by using chemically stable materials such as Au and GaN, it is demonstrated that the sensor is self-refreshing. In the majority of the sensors constructed with Au nanoparticles the chemical response was measured by monitoring the intensity of the Au surface plasmons.^{4,5} However, sensors based purely on electrical current-voltage (*I-V*) measurements can be much more compact and can be integrated with other electronic circuits, as well as can provide much more accurate quantitative data. The goals of this work have been to design sensitive and reversible gas-detecting devices, which at the same time are compact, inexpensive to construct, and readily commercialized, as well as to develop a theoretical model of their electrical transport properties as a function of gas adsorption.

DEVICE FABRICATION

The GaN nanowires were grown in a standard tubular flow furnace^{6,7} at atmospheric pressure. The substrates were *c*-axis oriented sapphire coated with a Ni seed layer approxi-

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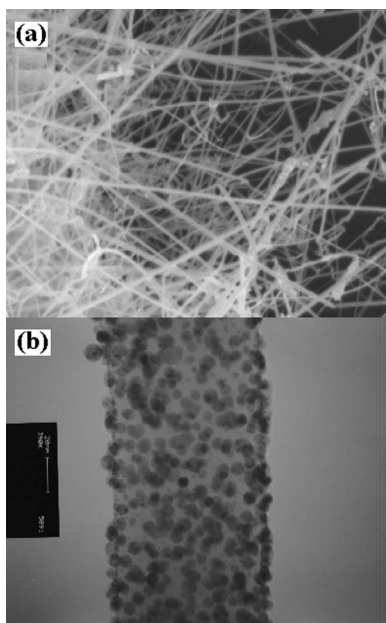


FIG. 1. (a) A SEM image of a mat of GaN nanowires and (b) a TEM image of a GaN nanowire decorated with Au nanoparticles.

mately 50 nm thick. The nitrogen source was ammonia and the Ga source consisted of a pellet of Ga. The growth temperature was 950 °C. The sapphire substrate was placed approximately 2.5 cm from the Ga source and 100% ammonia flow was used during nanowire growth. Comparison of the electrical measurements of the Ni coated sapphire substrates before and after GaN nanowire growth indicated that the Ni seed layer is discontinuous after nanowire synthesis and therefore does not contribute to the electrical response of the chemical sensors. A scanning electron microscope (SEM) image of a typical GaN nanowire mat is displayed in Fig. 1(a). The mats are typically 10–20 μm thick. Gold nanoparticles were grown onto the nanowires by plasma enhanced chemical vapor deposition (PECVD), which has been described in detail elsewhere.⁸ The average size of the Au nanoparticles was approximately 5 nm. A transmission electron microscope image of a Au nanoparticle coated GaN nanowire is displayed in Fig. 1(b).

A schematic of the nanosensor is shown in Fig. 2. The sensor is a standard four terminal design, where the terminals

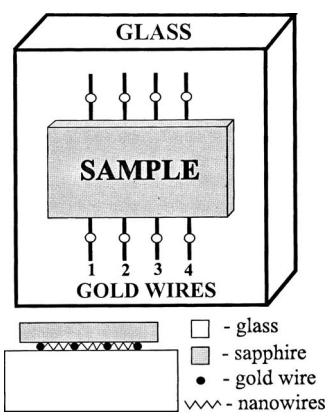


FIG. 2. A schematic of the gas sensor.

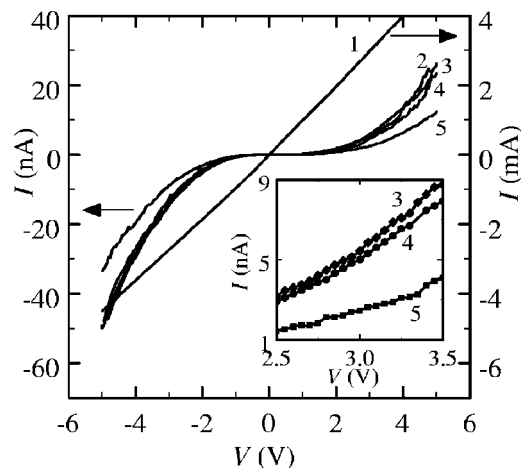


FIG. 3. Current-voltage curves of a sensor constructed from a mat of bare GaN nanowires (1) (right-hand vertical axis) and a sensor constructed from a mat of gold nanoparticle-decorated GaN nanowires (curves 2–5) (left-hand scale) for in vacuum (2), and atmospheres of Ar (3), N_2 (4), and methane (5). The inset is an expanded view of the I - V data in the first quadrant (\diamond —vacuum, \bullet — N_2 , and \blacksquare —methane).

consist of 25 μm diameter gold wires that are placed parallel to one another and separated by a 1 mm gap. For the I - V measurements electrodes 1 and 4 were used as the input and output current terminals and electrodes 2 and 3 sensed the voltage. To improve the electrical contact between the gold wires and the sample, the system was sandwiched between two 10 mm square glass plates. This design is optimal for electrical characterization, but at the expense of accurate time dependent response to gas exposure. Since one of the focal points of this work is the development of a theoretical model of the transport properties of the sensor, this was considered an acceptable trade off. The I - V measurements were conducted in a high vacuum chamber capable with a base pressure of 10^{-7} Torr. The system is equipped with a gas manifold with argon (99.95%), nitrogen (99.95%), and extra-purity methane (100.0%) gas sources. A needle valve was used to regulate gas flow and pressure in the vacuum chamber. The I - V curves were acquired with a Keithley-236 source-measure unit over the range of 0– ± 5 V using a step interval of 0.05 V. A 10 s dwell time between each voltage step was used to allow the sensor to reach an equilibrium electrical state between measurements of the current.

EXPERIMENTAL RESULTS

A typical I - V curve for a bare GaN nanowire device is shown in Fig. 3 (curve 1). The Ohmic behavior at room temperature is consistent with a previous report of their transport properties.⁹ The current through the bare GaN nanowire mesh is in the milliamper range, which is quite high and when taken in conjunction with the Ohmic behavior, indicates good contact between the Au wire leads and the nanowire mat. The shape of the I - V curve and the magnitude of the current were found to be independent of the chemical environment. Based on this result it is concluded that the GaN nanowires alone are not suitable for chemical sensing.

This behavior is not unexpected since GaN is considered to be relatively chemically inert as is evidenced by its extremely low reactive-ion etch rates.¹⁰

We hypothesized that the chemical sensitivity of GaN nanowires could be enhanced by functionalizing their surface with gold nanoparticles. It is well known that Au nanoparticles with a diameter <10 nm are extremely good catalysts.^{11,12} Desorption can be induced thermally or by a change in pressure which makes gold nanoparticle-based chemical sensors highly reversible.^{4,13,14} The I - V curve for a mat of nanoparticle coated GaN nanowires in vacuum is displayed in Fig. 3 (curve 2), where it now exhibits nonlinear behavior. The current through this device in vacuum, relative to the uncoated GaN nanowire device, has decreased by five orders of magnitude. This indicates that the primary transport channel in this device is not through the Au nanoparticles on the surface of the nanowires. The I - V curves in vacuum (curve 2) and Ar at atmospheric pressure (curve 3) are nearly indistinguishable. The I - V curve for N_2 at atmospheric pressure (curve 4) deviates slightly from the I - V curves for vacuum and Ar (see inset in Fig. 3). This response to N_2 is consistently observed under repeated conditions, where the conductivity either increases or decreases. Note that, compared to the vacuum I - V characteristic, with forward bias the conductivity is increased and is decreased with reverse bias. In some cases the response was reversed to that in Fig. 3. However, in all cases an increase in the conductivity in the first (third) quadrant was always accompanied by a decrease in the third (first) quadrant. Since in our experiments industrial-grade argon and nitrogen (99.95% purity) were used, the most likely explanation for this response is that contaminants weakly physisorbed onto either the bare regions of the GaN nanowire or to the Au nanoparticles and that reversing of the bias causes desorption.

The most reactive of the three gases used in this study is methane (curve 5, Fig. 3) and as expected, produced the greatest response. Under forward or reverse bias the conductivity always decreased by about 50% relative to vacuum. Furthermore, the I - V curve always returned to that of vacuum once the methane pressure decreased to below 10^{-6} Torr. This demonstrates that the sensor can be refreshed, i.e., it is reversible.

DISCUSSION

The chemical sensing capabilities of the device were only achieved once the GaN nanowires were coated with Au nanoparticles. To explain the sensitivity, we examined two possible mechanisms by which the decoration of the nanowires by the metal nanoparticles could be responsible for the observed behavior.

First we consider how conduction through a nanoparticle that has grown between two nanowires would contribute to the sensing abilities of the nanowire mat. If two nanowires were close together (~ 5 nm apart) a nanoparticle could grow at the point of closest approach between them forming a semiconductor-metal-semiconductor symmetric Schottky junction. Because of carrier depletion in the semiconductor beneath the nanoparticle, junctions of this type would have a

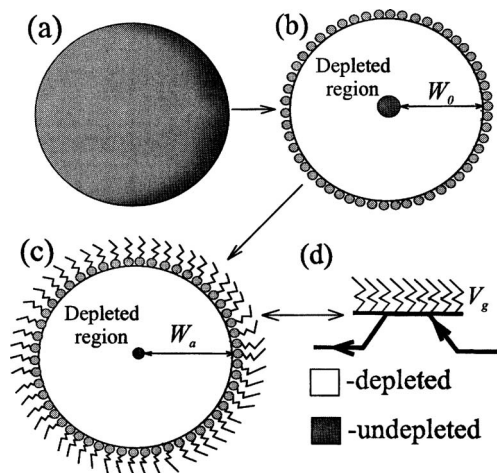


FIG. 4. A cross-section view of a nanowire showing the size of the conducting region (grey) with no gold nanoparticles on the surface (a), with a layer of nanoparticles on the surface in vacuum (b), with gas physisorbed on the surface of the nanoparticles (c) and an equivalent circuit diagram representative of the operation of the nanowire as a gas-sensitive field effect transistor with V_g representing the induced potential by the adsorbed molecules. W_0 is the depletion depth due to just metal on the surface and W_a is the depletion depth when gas molecules have been physisorbed onto the gold nanoparticles.

characteristic conductance much smaller than semiconductor-semiconductor contacts formed where nanowires had been touching directly before decoration with nanoparticles. The high conductivity of the nondecorated nanowire mat (Fig. 3, curve 1) compared to the nanoparticle-decorated mat (Fig. 3, curves 2–5) is evidence that conduction through nanowire-nanowire junctions is quite high. Being in parallel, little current will flow through the low-conductivity nanowire-nanoparticle-nanowire junctions compared to the preexisting high conductivity nanowire-nanowire junctions. Consequently, the low-conductivity junctions are not expected to contribute to the I - V characteristics of the nanowire mat. Furthermore, if the I - V characteristics are analyzed under the assumptions of current flow through Schottky barriers,¹⁵ one does not obtain physical values for the ideality parameter or the barrier height for GaN-gold Schottky contacts.^{15,16} For these reasons we conclude that the change in the I - V curves with Au nanoparticle metallization cannot be explained in terms of the formation of a Schottky barrier between nanowires bridged by a nanoparticle.

A more likely explanation for the reduction in the conductivity of the sensor with Au nanoparticle metallization is the reduction in the size of the conducting channel within the nanowires due to the formation of a depletion layer by the nanoparticles. This explanation has been used previously to explain the transport properties of sensors constructed from SnO_2 nanowires coated with Pd nanoparticles.¹⁷ We begin by considering a bare GaN nanowire with no depletion [Fig. 4(a)]. After the GaN nanowire is decorated with Au nanoparticles a depletion layer of depth W_0 forms below the surface. For a high enough nanoparticle density the depletion layer can be considered homogeneous. The amount of depletion is determined by the boundary condition at the Au nanoparticle-GaN nanowire interface, where the Fermi level

of the nanoparticle must equate with the Fermi level of the nanowire. An increase in the depth of the depletion layer from 0 to W_0 decreases the cross-sectional area of the conducting region (r_c), or channel, within the nanowires [Fig. 4(b)], which produces a drop in conductivity of the metallized nanowires relative to the bare nanowires [Fig. 4(a)]. The effect of physisorption of gases onto the surface of the Au nanoparticles is to induce a potential (V_g) on the nanoparticles that causes a change in the depletion depth from W_0 to W_a , which changes the diameter of the conduction channel of the nanowire [Fig. 4(c)]. Schematically the metallized nanowire can be treated as a field effect transistor [Fig. 4(d)], where the physisorbed induced potential on the nanoparticles can be viewed as the gating voltage.

This model is similar to that invoked to explain the operation of GaN nanowire field-effect transistors. Whereas for transistor devices, an external potential is applied to change the size of the conducting channel, in our model the change in potential originates from charge redistribution in the nanoparticle when a gas molecule physisorbs onto it. The observed reduction in the current when exposed to the gases (Fig. 3) indicates that the conduction channel is reduced in size, signifying an increase in the depletion in the nanowires. Undoped GaN being a wide band-gap intrinsic n -type semiconductor, an increase in the depletion indicates that a negative potential is induced by the physisorption and is responsible for the drop in the conductivity and increase in the nonlinearity of the device,^{9,18} exactly as observed.

In order to quantify the phenomena observed in Fig. 3 we considered a geometrical configuration that can be used for computational modeling of the interaction between the nanowire and nanoparticle coating and the effect of molecular physisorption. Due to the high density of nanoparticles on the surface of the nanowires [Fig. 1(b)] it can be assumed that the depletion layer below the particles overlap and therefore the coating can be approximated as a continuous metal film, as opposed to discrete particles.

Historically, studies of metal-semiconductor Schottky contacts have been restricted to planar structures.^{19,20} For the case of a nanowire covered by the layer of gold nanoparticles such a model can only be used as a guideline. For nanowires, cylindrical boundary conditions must be used. The depletion approximation assumes that the space charge is composed only of ionized doping impurities, and the contribution of free carriers to the local charge is negligible. The expression, which connects the depletion depth W and applied bias V_g , can be derived from the Poisson equation in cylindrical coordinates.²¹ By treating the nanowire as infinitely long the potential Φ will depend only on the radial coordinate r and is therefore independent of ϕ and z . Because the GaN nanowires are undoped and intrinsically n -type, at room temperature we can assume the donor concentration to be approximately equals to the electron density $N_d \approx N$.^{19,20}

The Poisson equation for the depleted region can be written (in cylindrical coordinates) in the following form:

$$\frac{\partial^2 \Phi}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi}{\partial r} = \frac{-qN}{\epsilon_0 \epsilon_{sc}}, \quad (1)$$

where q is the charge of the carrier, ϵ_0 is the permittivity of free space, and ϵ_{sc} is the dielectric constant of the semiconductor. The general solution of this equation can be written in the form

$$\Phi(r) = -\frac{qNr^2}{4\epsilon_0\epsilon_{sc}} + C_1 \ln(r) + C_2. \quad (2)$$

The boundary conditions that determine the constants C_1 and C_2 are that the potential Φ and electric field E are equal to zero in the quasineutral part of the nanowire, i.e.,

$$\Phi(R_{nw} - W) = 0,$$

$$\frac{\partial \Phi}{\partial r}(R_{nw} - W) = 0, \quad (3)$$

where R_{nw} is the physical radius of the nanowire. Applying the boundary conditions (3) to the expression for the potential (2) we find

$$\Phi(r) = -\frac{qNr^2}{4\epsilon_0\epsilon_{sc}} + \frac{qN(R_{nw} - W)^2}{2\epsilon_0\epsilon_{sc}} \ln(r) + \frac{qN(R_{nw} - W)^2}{2\epsilon_0\epsilon_{sc}} \left[\frac{1}{2} - \ln(R_{nw} - W) \right]. \quad (4)$$

At the metal-semiconductor boundary ($r=R_{nw}$) the potential has the value $\Phi(R_{nw})=V_i-V_g$, where V_i is the height of unbiased Schottky barrier in the semiconductor (the built-in potential)^{15,19,20} and V_g is the contact bias voltage. Finally, the equation that connects the depletion depth W and the applied bias V_g can be written in the form

$$V_i - V_g = -\frac{qNR_{nw}^2}{4\epsilon_0\epsilon_{sc}} + \frac{qNr_c^2}{2\epsilon_0\epsilon_{sc}} \ln(R_{nw}) + \frac{qNr_c^2}{2\epsilon_0\epsilon_{sc}} \times \left[\frac{1}{2} - \ln(r_c) \right], \quad (5)$$

where $r_c=R_{nw}-W$ is the radius of the conducting region of the nanowire, $\epsilon_0=8.8541 \times 10^{-14}$ F/cm, $\epsilon_{sc}=10.4$ is the dielectric constant of GaN, and $q=-1.6022 \times 10^{-19}$ C is the charge of carrier. The value of the built-in potential (V_i) is taken to be 0.822 V, based on experimental studies of planar Au-GaN Schottky contacts by Khan *et al.*¹⁵

Equation (5) is transcendental with respect to r_c and can only be solved numerically. The numerical solution of Eq. (5) for $V_g=0$ gives us the radius of the conducting region of the nanowire for an unbiased metallic shell. When a negative voltage is applied to the metallic shell, the radius r_c of the conducting region of the nanowire decreases. The current through the conducting region of radius r_c can be written as $I=qN\pi r_c^2 v_d$, where v_d is a drift velocity. We observe that the physisorption of gases onto the surface of the metallized nanowire induces a decrease in the current through the nanowire which we believe to be caused by a negative gate voltage which had increased the depletion depth W causing a

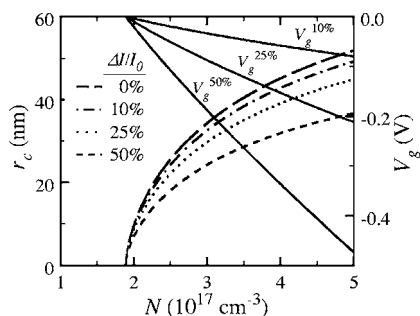


FIG. 5. The conducting channel radius r_c and the induced potential V_g of a nanowire of radius $R_{\text{nw}}=100$ nm as a function of the carrier concentration (N). The curves for r_c and V_g are shown for four different cases: unbiased nanowire shell $\Delta I/I_0=0\%$ (bias $V_g=0$) and biased nanowire shells corresponding to the relative current drops of $\Delta I/I_0=10\%$ (bias $V_g^{10\%}$), $\Delta I/I_0=25\%$ (bias $V_g^{25\%}$), and $\Delta I/I_0=0.50\%$ (bias $V_g^{50\%}$).

reduction in the conducting channel size. The ratio of the current with physisorption to vacuum is given by the following relationship:

$$\frac{I_g}{I_0} = \frac{r_{cg}^2}{r_{c0}^2}, \quad (6)$$

where r_{c0} , I_0 and r_{cg} , I_g are the radius of the conducting region of the nanowire and current in vacuum and with physisorption, respectively. Substituting the solution for r_{c0} from Eq. (5) for the unbiased Schottky contact ($V_g=0$) into Eq. (6) yields a value of r_{cg} for a particular ratio of currents I_g/I_0 . Then, substituting the value of r_{cg} back into Eq. (5) yields the value of the bias V_g induced by the gas molecules on the gold nanoparticles. Experimentally, the current drop through the Au nanoparticle functionalized GaN nanowires ranges from 10% to 50% depending on the species of the gas (Fig. 3).

The calculated radius of the conducting channel r_c as a function of carrier concentration in a 100 nm radius nanowire is plotted in Fig. 5. The range of carrier concentration over which r_c has been plotted $[(1-5) \times 10^{17} \text{ cm}^{-3}]$ is the range for which the carrier concentration of intrinsic GaN (as is used here in the nanowires) has been reported to span.^{22,23} For an ungated nanowire, $V_g=0$ V (in Fig. 5), we find that no conducting channel exists below a critical value, $N_c=1.8 \times 10^{17} \text{ cm}^{-3}$. Below this critical carrier concentration, the nanowire is completely insulating and adsorption of molecules will not change the I - V characteristics. As expected, for higher carrier concentrations, the size of the conducting channel increases. For $N > N_c$, the size of the conducting channel will depend on the potential of the nanoparticles on the surface induced by physisorbed molecules and can be used as a sensor.

In Fig. 5 we have also plotted the calculated change in the conducting channel size as a function of carrier concentration for various relative changes in current ($\Delta I/I_0$) of 10%, 25%, and 50% that correspond to the range of experimentally observed current drops. From these calculations of how the radius of the conducting channel changes for a given relative drop in current, we have computed what extra potential must be applied to the gold layer in order to produce that change in the current. These results are plotted as the solid

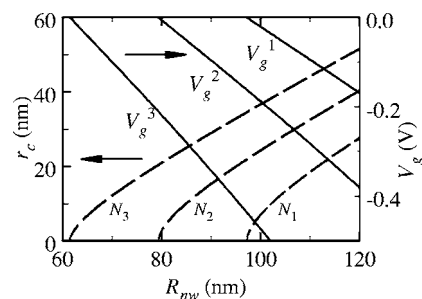


FIG. 6. The radius of the conducting channel of a nanowire r_c and the induced potential V_g as a function of nanowire radius R_{nw} for three carrier concentrations: $N_1=2 \times 10^{17} \text{ cm}^{-3}$, $N_2=3 \times 10^{17} \text{ cm}^{-3}$, and $N_3=5 \times 10^{17} \text{ cm}^{-3}$. All the curves correspond to the case where there is a 50% drop of current through the nanowire due to the induced potential.

lines in Fig. 5. As can be seen from the plots, for larger carrier concentrations, a more negative bias is required to change the current by a given amount. We conclude from this analysis that for a given molecule which would induce a specific potential on the nanoparticle, the amount of depletion, and hence, the relative change in the conducting channel size will be greater for nanowires with smaller carrier concentrations as compared to those with larger carrier concentrations. For instance, for an extra applied potential of -0.2 V, a 25% drop in current will occur for $N \sim 4.8 \times 10^{17} \text{ cm}^{-3}$ and a 50% drop in current will occur for $N \sim 3.0 \times 10^{17} \text{ cm}^{-3}$. If the carrier concentration is too high, the potential needed to induce a significant drop in current will be excessive. However, if the carrier concentration is too low, only an extremely small potential would be required to change the nanowire from conducting to insulating. Thus depending on the carrier concentration, the sensor can measure the amount of adsorbed analyte (i.e., analog, $\Delta I/I_0 < 100\%$), or just the presence of an analyte (i.e., digital, $\Delta I/I_0=100\%$).

The analysis of conducting channel size as a function of carrier concentration suggests that a minimum average nanowire radius is required for a mat of nanowires to be sensitive to molecular physisorption for a given carrier concentration. In order to illustrate this point we consider the dependences of the radius of the conduction channel r_c and gate voltage V_g as a function of nanowire radius R_{nw} for three different carrier concentrations, where the relative current drop ($\Delta I/I_0$) through the nanowire is fixed at 50% (Fig. 6). Examination of Fig. 6 reveals two significant points. The first is that for low carrier concentrations, e.g., $N_1=2 \times 10^{17} \text{ cm}^{-3}$, only nanowires with a radius of 97 nm or greater are responsive to gas adsorption, while for a carrier concentration of $N_3=5 \times 10^{17} \text{ cm}^{-3}$ nanowires with radii as small as 63 nm are responsive. Consequently, doping can be used to control the sensitivity of nanowires of a given radius. Or for a fixed carrier concentration, changing the radius of the nanowires will change the overall sensitivity. The second significant point is the sensitivity of the nanowires to physisorption as a function of carrier concentration. For example, a 90 nm nanowire with a carrier concentration of $N_3=5 \times 10^{17} \text{ cm}^{-3}$ requires a gate voltage of -0.35 V to achieve a 50% drop in the current relative to the ungated current, while a 90 nm nanowire with a smaller carrier concentration of $N_3=3$

$\times 10^{17} \text{ cm}^{-3}$ requires a gate voltage of only -0.10 V to achieve the same relative drop in the current.

Since the gating potential induced by physisorbed gas molecules is limited, changes in nanowire conductivity with physisorption become insignificant for nanowires with larger radii. If we define the minimal acceptable response of a nanowire to physisorption to be when $W_0/R_{\text{nw}} \geq 5\%$, where W_0 is a depletion depth of the unbiased cylindrical Schottky contact (Fig. 4), then nanowires of radii larger than $\sim 1 \mu\text{m}$ will have an insignificant response to physisorption of gases. In order to maximize the sensitivity of this type of sensor, the synthesis of the GaN nanowires must be carried out in such a way that the radii and carrier concentration dependent effects are optimized. The analysis presented here demonstrates that the synthesis of the nanowires only needs to be controlled such that the distribution of the nanowire radii fall within a particular interval, which according to our estimations is between 60 nm and $1 \mu\text{m}$.

Throughout this discussion of the depletion of the carriers within the nanowires, we have assumed a uniform layer of metal on the surface of the nanowire. From our analysis, it can be seen that for carrier concentrations expected for *n*-type, intrinsic GaN, our calculations predict depletion depths (~ 50 to 100 nm) that are much larger than the nanoparticle spacing ($\leq 5 \text{ nm}$). Thus the large ratio calculated for the depletion depth to nanoparticle spacing, in conjunction with the measured *I-V* data, justifies the use of the uniform metallic shell model. However, others have attempted to predict the depletion due to nanoscale metal particles on semiconductor surfaces. Zhdanov²⁴ modeled metal nanoparticle-semiconductor surface contacts using a geometry where the particle is treated as a metallic sphere half immersed in a planar semiconductor surface. A comparison of the cylindrical Schottky contact model and the Zhdanov model with the experimental data reveals that the former gives a more accurate explanation of the observed phenomena. In the Zhdanov²⁴ approximation, the superposition of local depletion regions arising from noninteracting nanoparticles does not produce a sufficiently large depletion region, i.e., a lowering of the radii of the conduction regions of the nanowires. The deficiencies of the Zhdanov model are expected. The small radii of the nanowires and the high density of the nanoparticles on the surfaces of the nanowires, in conjunction with the curvature of the nanowire, produce a collective depletion that is more consistent with the uniform depletion achieved with the cylindrical Schottky contact.

CONCLUSIONS

In conclusion, we have demonstrated that by functionalizing the surface of GaN nanowires with Au nanoparticles a chemical sensor can be constructed that is sensitive to the relatively reactive gas methane and the extremely unreactive gas N_2 . Furthermore we find that a sensor consisting of gold nanoparticle coated GaN nanowires is completely self-refreshing, (i.e., reversible). The sensitivity of the sensor has been modeled in terms of local depletion regions forming beneath the Au nanoparticles within the GaN nanowires. The change in the currents is a consequence of a change in the

depletion layer with the physisorption of gases onto the surface of the Au nanoparticles. The treatment of the metal nanoparticle-semiconducting nanowire interface as a cylindrical Schottky contact was found to give better agreement with the experimental data as opposed to Zhdanov model²⁴ of noninteracting nanoparticles semiembedded in the semiconductor surface. The cylindrical Schottky contact model indicated that metallization of the surface of the GaN nanowires completely depletes nanowires with smaller radii, thereby rendering them insensitive to the physisorption of gases. Furthermore, it was shown that carrier concentration of the semiconductor plays a significant role in determining the sensitivity of the nanowires as a function of their radii. The cylindrical Schottky model indicated that a mat of Au nanoparticle decorated GaN nanowires will be self-regulating in the sense that only those nanowires that have radii that fall within a range of 60 nm to $1 \mu\text{m}$ will be responsive to physisorption of methane. The experimental results and modeling demonstrate that mats of nanowires coated with metal nanoparticles can be used to construct chemical sensors that exhibit equivalent responses to single nanowire devices. The ease of fabrication of these sensors should have important ramifications for the economic viability of integrating nanowire-based chemical sensors into commercial applications.

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