A Chemically-Responsive Nanojunction within a Silver Nanowire

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ABSTRACT: The formation of a nanometer-scale chemically responsive junction (CRJ) within a silver nanowire is described. A silver nanowire was first prepared on glass using the lithographically patterned nanowire electrodeposition method. A 1−5 nm gap was formed in this wire by electromigration. Finally, this gap was reconnected by applying a voltage ramp to the nanowire resulting in the formation of a resistive, ohmic CRJ. Exposure of this CRJ-containing nanowire to ammonia (NH3) induced a rapid (<30 s) and reversible resistance change that was as large as ΔR/R0 = (+)138% in 7% NH3 and observable down to 500 ppm NH3. Exposure to water vapor produced a weaker resistance increase of ΔR/R0,H2O = (+)10−15% (for 2.3% water) while nitrogen dioxide (NO2) exposure induced a stronger concentration-normalized resistance decrease of ΔR/R0,NO2 = (−)10−15% (for 500 ppm NO2). The proposed mechanism of the resistance response for a CRJ, supported by temperature-dependent measurements of the conductivity for CRJs and density functional theory calculations, is that semiconducting p-type Ag2O is formed within the CRJ and the binding of molecules to this Ag2O modulates its electrical resistance.

KEYWORDS: Sensor, ammonia, nitrogen dioxide, electrodeposition, oxide, electromigration

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Nanowire field effect transistors have dominated work in the area of nanowire-based sensing since their discovery by Lieber et al. in 2001.1 These devices, which are based upon semiconducting nanowires composed of In2O3,2 Si,1,3 or single walled carbon nanotubes (SWNTs),4,5 operate based upon the same charge-gating principle exploited by ion-selective field-effect transistors (ISFETs) first described by Bergveld in 1970.6,7 Metal oxide nanowires, especially those of SnO2,8−10 have also been successfully implemented as gas sensors but charge gating in these materials can involve reactions of analyte molecules with reactive surface oxygen species.11,12 Metal nanowires cannot detect molecules by a charge gating mechanism because of their high carrier concentrations. However two other mechanisms for the detection of molecules have been demonstrated at metal nanowires. The first involves the inelastic surface scattering of electrons at wire surfaces, a process first described for ultrathin metal films by Fuchs in 1938.13 The adsorption of molecules on the metal surface increases the cross-section for inelastic scattering and, provided the film or nanowire has dimensions that approach the mean free path for electrons (e.g., ∼40 nm for gold14), this results in an increased electrical resistance for the film or nanowire. The magnitude of this effect is relatively small for metal films with ΔR/R0 < 5%,15,16 but Bohn et al. observed ΔR/R0 up to 10% for the adsorption of n-alkane thiols on gold nanowires.17−19 N.J. Tao et al.20−23 have reported a second mechanism that operates at metal nanowires with widths of 1 nm and below. Such nanowires show a conductivity that is quantized in units of 2e2/h. Exposure to adsorbates, including mercaptopropionic acid, 2,2′-bipyridine, and dopamine induces a transition to a lower conductivity state, corresponding to an increased resistance of up to 100%, for these junctions.22

In 2005, we discovered that the resistance of electrodeposited, polycrystalline silver nanowire arrays could increase dramatically, with ΔR/R0 up to 1000%, upon exposure to NH3 vapor.24,25 By interrogating these nanowires during NH3 exposure using a conductive atomic force microscope tip, we discovered that the increased resistance induced by NH3 exposure was concentrated at short, submicrometer sections of these nanowires, not uniformly distributed along the length of the nanowire.25 On the basis of this and other data,24,25 we hypothesized that at these “chemically responsive junctions” consisted of semiconducting Ag2O layers that were embedded at grain boundaries present in the silver nanowire.24,25

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Consistent with this proposed mechanism, we found that solid Ag$_2$O nanowires also exhibited a response to NH$_3$ that was indistinguishable to that seen at silver nanowires.$^{26}$ The formation of chemically responsive junction (CRJ) in our silver nanowire experiments, however, was uncontrolled with formation of chemically responsive junction (CRJ) in our exposure to NH$_3$. In this paper, we document the stepwise shown schematically in Figure 1, is reversibly modulated by electrical response with a resistance in the M range that, as $R_0$; (2) the increase of $E_{app}$ by 0.2 V whenever the resistance change ratio ($R/R_0$) exceeds a predefined threshold (typically +1.5%). After this occurs, steps (2) and (3) are repeated until the program terminates when the formation of a nanogap is signaled by the measurement of $R > 10$ k$\Omega$ at $\sim$1300 s in Figure 2c). The decrease in $E_{app}$ at step (3) generates the sawtooth pattern seen in both the applied voltage (Figure 2c, red trace) and resistance (blue trace) measured during this process.30 Once the nanogap is formed, $R > 100$ M$\Omega$ and the nanowire does not respond to NH$_3$. To reconnect the nanogap and form a CRJ, a voltage ramp is again applied to the nanowire (Figure 2d). In this case, $E_{app}$ is increased from 0 V at 50 mV/s while the tunneling current is monitored.

![Figure 1. Schematic depiction of the formation of a CRJ within a silver nanowire. Starting with a silver nanowire (top), a nanogap is formed by feedback-controlled electromigration (middle). Neither the as-fabricated silver nanowire, nor the electromigrated nanowire, show a significant change in resistance upon exposure to pulses of NH$_3$. But when the nanogap is reconnected by the application of a voltage ramp (bottom), the resulting nanowire shows a rapid, reversible increase in its electrical resistance upon exposure to NH$_3$ as well as other molecules.](image1)

![Figure 2. Formation of a CRJ. (a) Photograph of a 1 in $\times$ 2 in microscope glass slide with three sets of four-point probes used to electrically characterize the nanowire and to form the CRJ. (b) SEM showing four gold electrodes separated by 10 $\mu$m, and a silver nanowire spanning these four electrodes. (c) A nanogap is first formed within the silver nanowire using feedback-controlled electromigration, as previously described. Here, the nanowire resistance and the applied potential ($E_{app}$) are plotted as a function of time during the electromigration process. This nanogap is 1−5 nm in width. (d) Reconnection of the nanogap is accomplished by applying a linear voltage ramp. Shown here is a typical current versus voltage plot of the reconnection process. (Inset) Fowler-Nordheim plot of the reconnection process. (e) 1−V curves of the as-fabricated, electromigrated, and reconnected nanowire. (Inset) Same data with rescaled current axis showing ohmic response of a CRJ. (f) High-magnification SEM image of a CRJ within a reconnected nanowire.](image2)
An increase in the current above baseline is seen at a threshold voltage, $V_{th} = 2.25$ V (Figure 2d), corresponding to a change in the slope of the Fowler–Nordheim (F-N) plot of $\ln(I/V^2)$ versus $1/V$ (Figure 2d, inset). This deviation from an ideal linear slope in F-N plot is explained by a transition from thermionic to field emission as $E_{app}$ increases. The voltage bias was removed when the measured current exceeds 1 $\mu$A, at a final applied voltage ($V_f$) of 3.05 V in Figure 2d, signaling the reconnection is complete. A comparison of the current versus voltage curves obtained after each of the first three steps of this process (Figure 2e) shows the high electrical conductivity of the as-fabricated silver nanowire ($R = 241$ $\Omega$, green trace), the disconnected nanowire after electromigration ($R > 1$ G$\Omega$, Figure 2e, inset: blue trace) and the intermediate resistance of the CRJ after reconnection ($R = 5.5$ M$\Omega$, red trace). A typical CRJ structure produced by this three-step procedure is seen in the high-magnification scanning electron micrograph (SEM) image of Figure 2f.

The formation of a CRJ can be monitored using atomic force microscopy (Figure 3). An 8 $\mu$m length of an as-fabricated Ag nanowire is seen in the atomic force microscopy (AFM) image of Figure 3a, together with two defects, one at the top and a second near the middle of the imaged region of the nanowire. After electromigration, the same section of nanowire was imaged again and the nanogap can be observed (Figure 3b). At higher magnification (Figure 3c), this nanogap has a minimum width of $\sim 5$ nm and a 4–5 nm island can be seen within the gap itself. After reconnection and formation of the CRJ, the nanogap closes and subtle changes in the morphology of the adjacent silver grains can be observed (Figure 3d). Our success rate for preparing CRJ that respond reversibly to ammonia is approximately 20%.

The resistance response of the silver nanowire to NH$_3$ is dramatically altered by the formation of a CRJ. An as-fabricated silver nanowire shows a slow decrease in its resistance ($\Delta R / R_0 \approx -1.3\%$) during exposures to pulses of NH$_3$ in N$_2$ ranging in concentration from 200 ppm to 7% (Figure 4a). The total change in $R$ is virtually constant across this range of NH$_3$ concentrations, that spans a factor of 350. Ammonia is known from UHV studies to adsorb molecularly, without decomposition, on silver surfaces, to form hydrogen-bonded multilayers, and to desorb over a broad temperature range from 145 to 210 K. The observed reversibility of the resistance change seen in Figure 4a, then, is presumably caused by the spontaneous desorption of NH$_3$ from the nanowire surfaces at $\sim 300$ K, and is consistent with the known behavior of NH$_3$ on silver surfaces in vacuum. After the formation of a CRJ, the baseline resistance of the nanowire, $R_0$, is elevated by a factor of 17 500 and exposure to NH$_3$ causes an abrupt increase in $R$ with $\Delta R / R_0$ ranging from 1 to 2% at 200 ppm to 138% at 7% (Figure 4b). A similar resistance response is observed for exposures of the CRJ to methyl amine (CH$_3$NH$_2$) and dimethyl amine ((CH$_3$)$_2$NH) (Supporting Information, Figure S1). When plotted as $\Delta R / R_0$ (Figure 4c), the decreased resistance of an as-fabricated silver nanowire upon exposure to 2, 5, and 7% NH$_3$ is imperceptible as compared to the increased resistance of a CRJ. At all of the NH$_3$ concentrations, the $R$ versus time transient has a peaked shape with $R$ first increasing in 20–30 s to a maximum $R$ value and then decaying during the NH$_3$ exposure. Similar behavior has been observed in prior work involving the detection of NH$_3$ at tungsten oxide nanowire mats and vertical arrays of silicon nanowires, but the origin of this effect is not yet understood. When NH$_3$ is turned off, a rapid decrease of $R$ in $\sim 30$ s is followed by a slow exponential decay with a time constant of 200–800 s (Figure 4d).
Thus, $R$ response of a CRJ to NH$_3$ is a factor of 3 more rapid than recovery of the $R$ to the baseline value in the absence of NH$_3$ (Figure 4e). A calibration plot for $\Delta R/R_0$ versus [NH$_3$] (Figure 4d) shows downward curvature that is consistent with the progressive occupation of NH$_3$ binding sites on the CRJ with increasing NH$_3$ concentration.

Finally, we find that the sensitivity of the CRJ to NH$_3$ and the resistance of this structure in the absence of NH$_3$ (i.e., $R_0$) are correlated. In Figure 4f, we plot the $\Delta R/R_0$ measured for exposures to 7 and 0.7% NH$_3$ versus $R_0$ for seventeen different CRJ devices. For most of these devices, between 1 and 5 data points were obtained as $R_0$ shifted over time. Despite the considerable scatter, a clear correlation between $R_0$ and $\Delta R/R_0$ in ammonia is seen in these data. This trend reproduces the behavior seen for silver nanowire arrays in our earlier study.$^{25}$

In summary, the influence of a CRJ on NH$_3$ detection by a silver nanowire is (1) to invert the direction of the $R$ change, (2) to increase by a factor of $>100$ the magnitude of this $R$ change, and (3) to dramatically accelerate the time rate of change of $R$ at the onset of NH$_3$ exposure.

What is a CRJ and how does it function? In an attempt to probe the nanometer-scale structure of CRJs we have examined these structures using transmission electron microscopy (Supporting Information, Figure S2) but it has been impossible to resolve compounds other than silver within them. The electronic properties of a CRJ, however, clearly diverge from those of the "parent" silver nanowire. We measured the temperature-dependent resistance for a silver nanowire across the temperature range from 200 to 300 K (Figure 5a) and then fabricated a CRJ and repeated this measurement (Figure 5b). Current versus voltage curves are ohmic for both types of samples, but the metallic temperature dependence of the silver nanowire (Figure 5c) is replaced by a thermally activated conduction in the CRJ (Figure 5d). Specifically, for the silver nanowire, $R$ is directly proportional to the temperature $T$:

$$ R = R_0\left(1 + \alpha - \frac{T}{T_0}\right) $$

where $R_0$ and $T_0$ are the reference resistance and temperature, respectively, and $\alpha$ is the temperature coefficient of resistivity. For this nanowire, $\alpha = 1.96 \times 10^{-3}$ K$^{-1}$, which is somewhat smaller than the bulk value, $3.74 \times 10^{-3}$ K$^{-1}$. Qualitatively, this difference is expected based upon the greater prevalence in the nanowire of temperature-independent scattering mechanisms including surface and grain boundary scattering.$^{36}$ On the
other hand, the thermally activated behavior of the CRJ suggests that a semiconducting barrier to conduction now exists and its \( R \) versus \( T \) behavior is well described by an equation of the Arrhenius form

\[
R = R_0 \exp \left( \frac{E_a}{kT} \right)
\]

(2)

where \( E_a \) is the activation energy and \( k \) is Boltzmann’s constant. An Arrhenius plot of these data is linear (Figure 5d, inset) and yields \( E_a = 57.6 \text{ meV} \). The observation of thermally activated transport through a CRJ suggests that conduction through this structure is controlled by a semiconducting domain and considering that CRJs are produced in air, a chemically reasonable candidate for the composition of this domain is Ag\(_{x}O\). While precise measurements of the bandgap for nonstoichiometric Ag\(_{x}O\) are not available, Ag\(_{x}O\) is a semiconductor with a direct gap estimated at 1.3 eV\(^{37} \) while AgO has an indirect gap of 1.2 eV\(^{38} \). Are the majority carriers within this Ag\(_{x}O\) electrons or holes? We answered this question by directly measuring the Seebeck coefficient, \( S \), of Ag\(_{x}O\) film was generated by oxidation of silver metal, simulating the formation of a CRJ within a silver nanowire in air (Supporting Information, Figure S3).\(^{39,40} \)

Briefly, a 100 \( \mu \text{m} \) wide Ag\(_{x}O\) was formed by electrooxidation of an evaporated silver film located in a microfabricated chip which enabled the imposition of a temperature gradient, \( \Delta T \), along the nanowire while the Seebeck voltage, \( V_S \), was simultaneously measured (Supporting Information, Figure S4).\(^{39,40} \) The value of \( S \) is then given by\(^{41} \)

\[
S = \frac{-V_S}{\Delta T} = \frac{-\left( V_{\text{hot}} - V_{\text{cold}} \right)}{T_{\text{hot}} - T_{\text{cold}}}
\]

(3)

\( S \) values ranging from \(+13 \) to \(+25 \) \( \mu \text{V/K} \) were obtained over this temperature range (Supporting Information, Figure S4) indicating that holes are the majority carriers.

We used density functional theory (DFT) to test the hypothesis that a CRJ consists of an Ag\(_{x}O\) “gate”. First, we studied the alternative possibility that the CRJ consists of an ultrathin Ag atomic chain or quantum point contact. On the basis of our DFT calculations of simulated all metal nanostructures, even a monatomic Ag chain is metallic (Figure S5 and Supporting Information). CRJs also fail to exhibit other attributes of sub-1 nm nanowires, such as quantized conductance.\(^{20–23} \) Next, we constructed a nanoscopic Ag\(_{x}O\) conduit. We presumed a diameter of \( \sim 1 \) nm for this structure, and we calculated a series of compositions, with \( x = 1.23, 1.37, 1.55, 1.78, \) and \( 2.0 \), using the ab initio molecular dynamics method. From the quadratic fitting for the formation energy versus \( x \) as in Supporting Information Figure S6, the equilibrium composition for this ultrathin Ag\(_{x}O\) wire is \( x = 1.56 \). This value should approach 2 when the diameter increases gradually. We chose the Ag\(_{1.78}O\) nanowire as the prototype to investigate effects of NH\(_3\) adsorption on wires that are likely to be in the \( 1.0–2.0 \) nm range (Figure 6a,b).

We found that NH\(_3\) molecules bind more strongly to Ag sites within this structure, forming strong Ag–N bonds and weaker O–H bonds, with binding energies ranging from 0.5 to 1.3 eV on different Ag sites (Table 1). The large adsorption energies (>0.1 eV) may account for the fast response and slow recovery of the resistance change observed. To study how the NH\(_3\) adsorption electronically affects the transport property of the Ag\(_{1.78}O\) nanowire, we choose one configuration with four NH\(_3\) molecules on the Ag\(_{1.78}O\) nanowire and give the charge transfer plot in Figure 6c. Interestingly, all four NH\(_3\) molecules donate electron charges to the Ag\(_{1.78}O\) bridge. \(^{6} \)Sensitivity in units of %\(^{-1}\) was calculated for each gas as the relative resistance change normalized by the concentration of the gas exposure: \( \Delta R/R_0/\text{[gas]%} \). Error bars represent \( \pm \sigma \) for multiple gas exposures. Configuration A refers to the bonding of NO\(_2\) through the nitrogen to silver atoms in the Ag\(_{x}O\) bridge; configuration B refers to bonding through both oxygens to two silver atoms in the Ag\(_{x}O\) bridge.

![Figure 6. DFT model of a CRJ consisting of a Ag\(_{x}O\) conduit. (a,b) Ag\(_{x}O\) conduit shown in side view (a) and axial view (b). Cyan and red spheres represent Ag and O atoms, respectively. (c–e) Axial views of the same bridge shown in (a,b) with chemisorbed NH\(_3\), H\(_2\)O (d), and NO\(_2\) (e). Yellow and dark blue isosurfaces map charge differences \( \Delta \rho = \rho(\text{bridge + molecules}) - \rho(\text{bridge}) \) with a cutoff of 0.02 e/Å\(^3\). Yellow volumes denote charge depletion whereas dark blue volumes show charge accumulation. Numerical labels indicate the net charge state of each adsorbed molecule.](image-url)
stronger the binding. Therefore, charge transfer actually plays two roles: binding and sensing.

To further validate this mechanism, we also investigated the effects on CRJ of two other analyte molecules: H₂O vapor and NO₂ gas both experimentally (Figure 7) and by DFT analysis of the Agₓ₁.₇₈O nanowire (Figure 6d,e). Experimentally we find that H₂O induces an increase in R, but the sensitivity of a CRJ to water is just 20% as high as for NH₃ (Figure 7, red trace) while NO₂ induces a decrease in R with a sensitivity approximately an order of magnitude higher than seen for NH₃ (Figure 7, blue trace). In the context of the DFT calculations, we find that H₂O molecules form Ag–O bonds and that they also donate electrons to the Agₓ₁.₇₈O nanowire (Figure 6d, Table 1). One may predict that H₂O vapor causes a positive ΔR, just as observed experimentally (Figure 7). For NO₂ molecules, two different bonding configurations must be distinguished: (A) the N atom binds with Ag (Supporting Information, Figure S7), or (B) two O atoms bind with two Ag atoms (Figure 6e). The average binding energy of configuration A (∼1.0 eV) is only slightly smaller than that of configuration B (∼1.1–1.3 eV). In both cases, NO₂ molecules take electron charges from the Agₓ₁.₇₈O nanowire (Figure 6e). The charge of configuration B is larger than that of configuration A, also in accordance with their binding energies (Table 1). Using the mechanism proposed above, the adsorption of NO₂ molecules should result in opposite resistance change in contrast to the case of NH₃ adsorption. Furthermore, the magnitude of charge transfer of NO₂ is higher than that of NH₃, so the nanowire should be more sensitive to NO₂ than to NH₃, just as seen in the experimental observations of Figure 7. On the basis of this analysis, we believe that the underlying physics or chemistry of the gas-induced resistance change through Ag nanowires is the charge transfer between adsorbates and Ag,O at the CRJ region.

In summary, we have described a three step process for transforming a chemically unresponsive silver nanowire into a chemical sensor. More precisely, our process embeds a chemically responsive nanometer-scale junction within this silver nanowire. This three step process involves (1) nanowire growth, (2) nanogap formation by electromigration, and (3) reconnection of the nanogap and formation of the CRJ. The resistance of the CRJ responds rapidly and reversibly to the presence of amines, water vapor, and NO₂. A comparison of our experimental data with DFT calculations leads to the hypothesis that the CRJ consists of a p-type Ag,O bridge approximately 1–2 nm in size, which is undetected in our TEM images of these structures. Further work will be required to optimize the sensitivity of the CRJ, to extend the limit-of-detection, and to enhance the selectivity of these structures for the detection of particular molecules. The CRJ represents a new enabling concept that should lead to the development of highly miniaturized sensors and sensor arrays based upon this new modality.

■ ASSOCIATED CONTENT

3 Supporting Information
Experimental procedures and materials required for the formation of nanojunctions and for the incorporation of these nanostructures into working sensors is provided as well as additional characterization data in the form of comparisons of the response of nanojunctions for three analyte molecules, transmission electron micrographs of nanojunctions, measurements of the thermopower for electrodeposited silver oxide films, and details relating to the DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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