

Fabrication of a Single Metal Nanowire Connected with Dissimilar Metal Electrodes and Its Application to Chemical Sensing

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We report a convenient method for the fabrication of a single metal nanowire connected with dissimilar metal electrodes and its application to chemical sensing. The method is based on a combination of atomic force microscopy nanomachining and conventional photolithography. The success of this integrated approach is confirmed by the linear current–voltage behavior of the created nanowires and comparable resistivities with those reported previously. The chemical sensing capability is demonstrated by the selective binding of a self-assembled monolayer onto a single Au nanowire connected with Ti electrodes and the subsequent resistance increase due to increased surface scattering effects after adsorption. It is found that the resistance increases by around 9% after the complete coverage of either octadecanethiol or dodecanethiol molecules onto a 20 nm thick Au nanowire. A theoretical explanation for the relationship between the resistance increase and the alkanethiol concentration is also given.

In recent years, metal nanowires have been the focus of extensive research activities due to their unusual electrical, magnetic, and optical properties and physical applications such as electrical interconnects,^{1,2} optical waveguides,^{3,4} and so forth. Furthermore, they can also be used for highly sensitive detection of gas,^{5–7} chemical,^{8–11} or biological specimen^{12–15} owing to the large surface-to-volume ratio. Fabrication techniques of metal

nanowires are consequently of great interest, and various physical and chemical methods, such as electron-beam lithography,^{2,4,16} chemical reduction,^{3,17} electrochemical deposition,^{5–9} templated electrochemical deposition,^{1,12–14,18,19} electromigration,²⁰ scanning probe nanolithography,^{21–24} etc., have been developed.

In a metal nanowire, the electrical resistivity is much higher than its bulk resistivity due to surface and grain boundary scattering effects of conduction electrons when one dimension of the nanowire is comparable to or smaller than the electron mean free path.^{10,16} When adsorbates are adsorbed onto a metal thin film or nanowire, a resistance increase caused by increased surface scattering due to electronic coupling between adsorbates and conduction electrons can be observed. This phenomenon is well-known in the case of metal thin films both theoretically and experimentally.^{25,26} Persson has formulated a model for calculating the resistivity increase due to adsorption with the equation

$$\Delta\rho = Mn_a/n^2e^2d\tau \quad (1)$$

where $\Delta\rho$ is the resistivity increase, M and n_a are the adsorbate mass and number density, respectively, n is the electron number density in the film, e is the electron charge, d is the film thickness, and τ is the adsorbate vibrational lifetime due to the excitation of electron–phonon pairs.^{25,26} Although there is no explicit formula for the case of metal nanowires to our knowledge, the resistance increase due to adsorbates has already been utilized for chemical sensing.^{8–11}

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For sensing applications based on measuring the resistance change of a single nanowire or multiple nanowires, it is a prerequisite to bridge the nanowire or nanowires between electrodes. Several methods have already been reported including electron beam lithography,^{21,27,28} focused ion beam deposition,^{27,28} the dielectrophoresis process,^{29,30} and so forth. For highly sensitive detection, it is also preferred or necessary that the nanowire(s) and the electrodes are made of different metals or the electrodes are protected, so that the chemical reaction or binding responsible for the resistance change occurs in the nanowire(s) only but not in the electrodes. This criterion is especially important for gas sensing and detection of selective binding of chemical or biological specimen.^{8,9}

Despite the great potential of achieving high sensitivity, reports of sensing applications based on the resistance change of a single metal nanowire are rare in the literature except for the following works. Quantized conductance change of a single Au or Cu atomic wire due to the adsorption of molecules has been observed and studied previously.^{8,9} Gas sensing with a single Pd nanowire⁷ and chemical sensing of the adsorption of a self-assembled monolayer (SAM) on a single Au nanowire have been recently reported.^{10,11} Apparently, there remains much to be explored for this interesting subject.

Recently, we have reported a convenient approach for both fabrication and bridging of a single metal nanowire via a combination of atomic force microscopy (AFM) nanoscratching on a polymer resist, metal coating, and lift-off.²³ The advantages include ease of operation and applicability on insulating substrates. In the present work, a modified approach by integrating AFM nanomachining and standard photolithography is presented. The additional benefits of the approach are much-reduced tip wear and controllability of different nanowire and electrode metals. Furthermore, this integrated approach is potentially valuable for the mass-production of single metal nanowire nanosensors with the employment of parallel tips such as a Millipede chip.³¹

To reveal the application of the fabricated nanowires to chemical sensing, the selective binding of an alkanethiolate SAM to a single Au nanowire connected with Ti electrodes is chosen as a demonstration. The specific binding occurs due to the strong S–Au bonding between the alkanethiols and the Au nanowire and the weak interaction between the molecules and the oxidized Ti electrodes.³² It is found that the resistance increases by around 9% after the complete coverage of either octadecanethiol or dodecanethiol molecules onto a 20 nm thick Au nanowire. The results indicate that the present fabrication approach is a valuable technique for the construction of single metal nanowire gas, chemical, or biological nanosensors.

EXPERIMENTAL SECTION

A schematic diagram of the experimental procedure is shown in Figure 1. A poly(methylmethacrylate) (PMMA) film with a

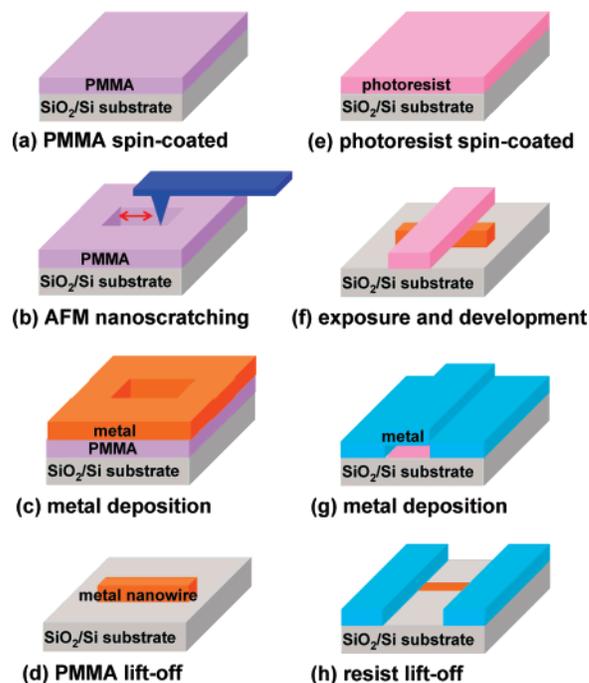


Figure 1. A schematic diagram of the fabrication of a metal nanowire connected with metal electrodes.

thickness of 50 nm was prepared on a thermally oxidized silicon substrate by spin-coating a solution of 1.25 wt % PMMA in chlorobenzene. A commercial AFM (Smena-B, NT-MDT, Russia) and a rectangular silicon probe (NSC15, MikroMasch, Russia) were used to scratch the resist to generate a straight nanogroove. After metal deposition (Au or Ti) by electron-beam evaporation and lift-off in acetone, a metal nanowire was created.²³ (For the Au nanowires, a Ti adhesion layer of around 1 nm was deposited before the deposition of Au.) The substrate was again spin-coated with a layer of photoresist. A mask with a pattern of electrodes was then put on the substrate. The position of the fabricated nanowire was adjusted into the middle of the electrodes under an optical microscope. After a standard photolithography process was performed, the nanowire was connected with a pair of metal electrodes (Au or Ti) that were of the same or a different metal material.

Two different SAMs, namely, octadecanethiol ($\text{CH}_3(\text{CH}_2)_{17}\text{SH}$, ODT) (Tokyo Chemical Industry) and dodecanethiol ($\text{CH}_3(\text{CH}_2)_{11}\text{SH}$, DDT) (Aldrich) were used for chemical sensing. They were prepared in absolute alcohol with concentrations ranging between 0.1 and 50 mM. The procedure for the establishment of chemical binding between the SAMs and an Au nanowire is shown in Figure 2. A 2 μL liquid drop of the SAM solution was deposited onto an Au nanowire that was connected with Ti electrodes. The substrate was then covered for 5 min, carefully washed by absolute alcohol, and dried by nitrogen. The resistances before and after the application of the SAM solution were measured for comparison.

For a precise measurement of the nanowire resistance, the substrate with a nanowire and electrodes was first glued to a printed circuit board that had thick Au contact pads. The electrodes and the Au contact pads were connected with Al wires that were bonded to them by using a wire bonder. Photographs of a resistance measurement unit are shown in Figure 3. The Au contact pads were subsequently connected to a Keithley 2400

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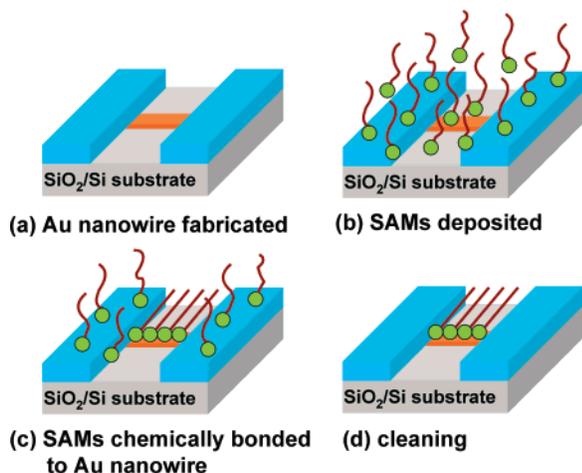


Figure 2. A schematic diagram of the procedure for establishing chemical binding between the SAMs and an Au nanowire.

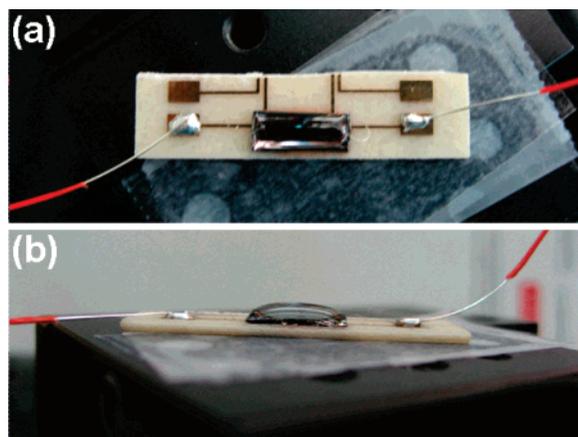


Figure 3. (a) Top-view and (b) side-view photographs of a resistance measurement unit. Note that in part b an excess amount of SAM solution is deposited for visual effect.

source-measure unit in a two-point geometry for current–voltage (I – V) curve measurements. The resistance measurement error was around 0.5%. Additionally, the resistance between an Au electrode and an Au contact pad connected by an Al wire was around 10 Ω . On the other hand, the total resistance for the two paths between Ti electrodes and Au contact pads was around 100 Ω . (It was actually determined by connecting two Al wires on one side of the sensor unit without going through the Au nanowire). This value showed no change after the deposition of the SAM solution and was excluded in the calculation of the resistance increase.

RESULTS AND DISCUSSION

A single metal nanowire connected with metal electrodes of the same material was first fabricated, and the resistance was measured. The SEM images of an Au nanowire and a Ti nanowire bridged between Au electrodes and Ti electrodes, respectively, with a gap of around 7.6 and 7.7 μm are shown in parts a and d of Figure 4, respectively. Both nanowires have a thickness of 20 nm and a length of 16 μm . Zoomed images of the nanowires are shown in parts b and e of Figure 4. The widths of the Au and the Ti nanowires are 52 and 90 nm, respectively. Parts c and f of Figure 4 are the corresponding I – V curves, which exhibit a linear

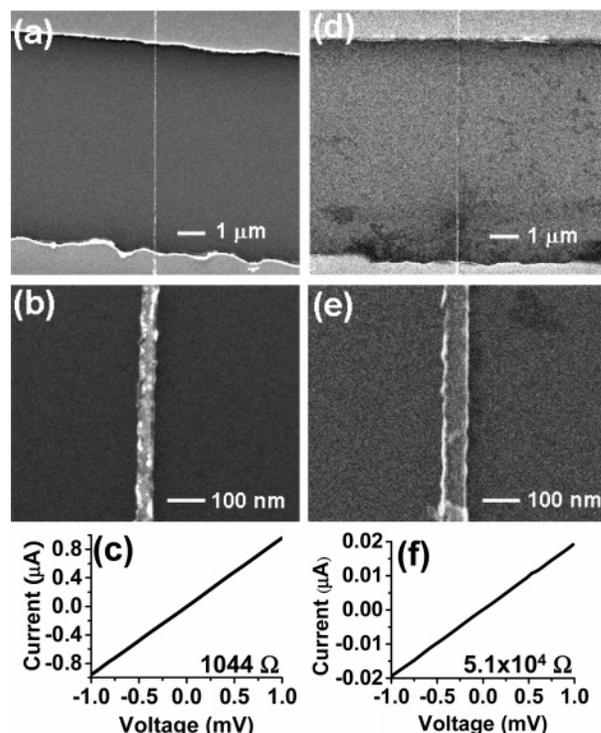


Figure 4. SEM images of (a) Au and (d) Ti nanowires connected with Au and Ti electrodes, respectively. Zoomed images of (b) the Au and (e) the Ti nanowires. (c) and (f) The corresponding I – V curves of the nanowires in parts a and d, respectively.

behavior as expected, and the resistances are 1044 and 5.1×10^4 Ω , respectively. With the formula $\rho = R(A/L)$, where ρ is the resistivity, R is the resistance, A is the cross section area, and L is the length, the resistivities of the Au nanowire and the Ti nanowire are found to be 14.3 and 1192 $\mu\Omega$ cm, respectively. (It should be noted that the length L is taken to be the electrode gap.) The obtained resistivities are comparable to our previous results and those reported in the literature,²³ which indicates that the present integrated approach has no apparent side effects on the electrical properties of the nanowires.

Single metal nanowires connected with dissimilar metal electrodes were also fabricated and characterized. The SEM image of an Au nanowire with a thickness of 20 nm and a length of 16 μm bridged between Ti electrodes with a gap of around 7.9 μm is shown in Figure 5a. A zoomed image of the nanowire is shown in Figure 5b, and the width is 73 nm. Figure 5c shows the linear I – V curve, and the resistance is 1330 Ω . This value is higher than the expected resistance of 774 Ω as determined from the previous resistivity of 14.3 $\mu\Omega$ cm for Au. After the exclusion of the 100 Ω resistance due to the paths between the Ti electrodes and the Au contact pads (see experimental section), the difference reduces to 456 Ω . The difference can be reasonably attributed to the contact resistances between the Au nanowire and the Ti electrodes, which in turn indicates a resistance of around 230 Ω for each contact.

A single Au nanowire bridged between Ti electrodes was then used as a chemical nanosensor. Two types of alkanethiolate SAMs, namely, ODT and DDT, were chosen for demonstration. It is known that strong S–Au bonds form between Au and alkanethiols, whereas Ti is easily oxidized with the result of a sturdy thin oxide layer that prevents bonding and the SAMs can thus be easily

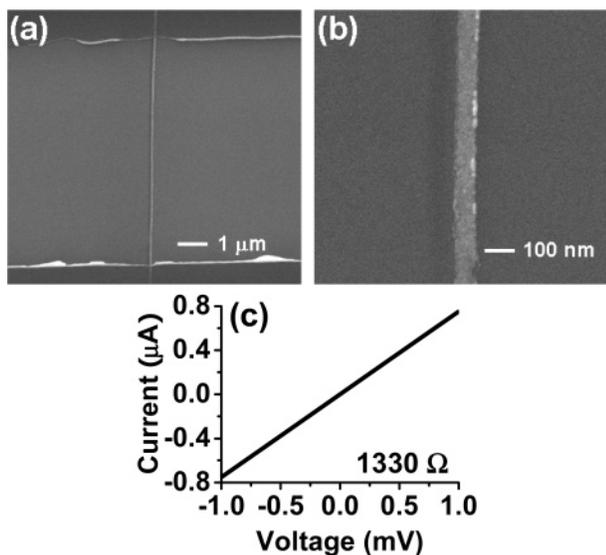


Figure 5. (a) SEM image of an Au nanowire connected with Ti electrodes, (b) a zoomed image of the Au nanowire, and (c) the corresponding I - V curve.

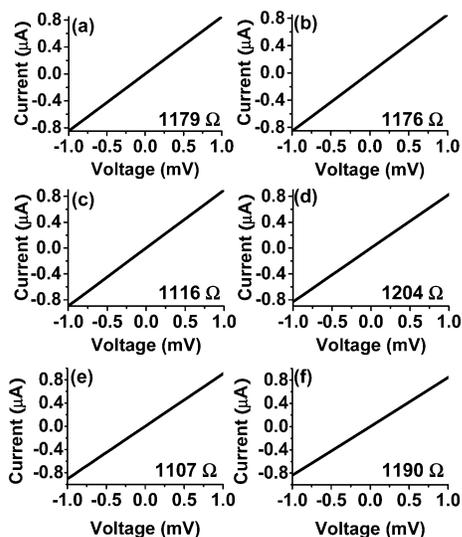


Figure 6. The I - V curves of Au nanowires (a) before and (b) after the deposition of absolute alcohol, (c) before and (d) after the deposition of a 10 mM ODT solution, and (e) before and (f) after the deposition of a 10 mM DDT solution.

washed away.³² An appreciable change in the nanowire resistance is consequently indicative of the selective chemical binding. Because alcohol was used as the solvent for ODT, the resistance change due to solvent was first tested. The I - V curves of an Au nanowire before and after being immersed in alcohol for 5 min are shown in parts a and b of Figure 6, and the resistances are 1179 and 1176 Ω , respectively. The variation is within experimental error and confirms little influence of the solvent on the resistance.

The I - V curves of an Au nanowire before and after being immersed in a 10 mM ODT solution for 5 min are shown in parts c and d of Figure 6, and the resistances are 1116 and 1204 Ω , respectively. After subtracting the 100 Ω resistance for the two paths between the Ti electrodes and the Au contact pads (see experimental section) from both values, the increase is 8.7%. In the calculation, the exclusion of the 100 Ω resistance is justifiable

due to the large size of the Al connection wires. On the other hand, the total contact resistance between the Au nanowire and the Ti electrodes is not excluded due to the small size of the contacts. The I - V curves of an Au nanowire before and after being immersed in a 10 mM DDT solution for 5 min are shown in parts e and f of Figure 6, and the resistances are 1107 and 1190 Ω , respectively. An increase of 8.2% is obtained after the subtraction of the 100 Ω resistance. The two resistance increases are within small difference and represent the effect of nearly full coverage of the molecules onto a nanowire (see below).

As mentioned previously, the resistance increase in an Au nanowire after the chemical binding of the SAM molecules originates from increased surface scattering. Such influence has already been observed on ultrathin Au films²⁶ and recently on single Au nanowires.^{10,11} Furthermore, the similar resistance increases for both ODT and DDT molecules reveal that the surface scattering is only influenced by the S-Au bond but not the chain length, which is in agreement with previous observation on ultrathin Au films.²⁶ Additionally, the present increase of around 9% is much larger than the result of around 3% from nanoporous Au nanowires with a diameter of 360 nm¹⁰ and the result of around 2% from Au films²⁶ at full coverage. As can be seen from eq 1, the larger increase can be reasonably attributed to the thinner thickness of the employed nanowires that results in stronger surface scattering.^{16,33} Another interesting observation is that the resistance increase after the deposition of the as purchased DDT solution (98 wt %) is only 2%. The smaller increase is presumably due to the agglomeration of the molecules on the nanowire surface with a result of smaller packing density. At suitable concentrations, the molecules have an ordered arrangement on the nanowire with a result of higher packing density and a higher resistance increase.

To further explore the effect of concentration on the resistance increase, the relationship between the increase and the ODT concentration for an immersion time of 5 min has been obtained and plotted in Figure 7a. It can be seen that the increase saturates at concentrations of 10 and 50 mM, and the saturation value is around 8.7%. This value signifies the resistance increase due to the full coverage of ODTs on an Au nanowire. At the lower side, the increase is around 0.5%, which is the noise level of present measurements. In Figure 7b, the relationship in the range 1–10 mM is replotted in linear scale. A few tests for DDT molecules at various concentrations were also conducted, and the results are simultaneously shown in Figure 7b. The excellent agreement of the resistance increases for the two different alkanethiols again exemplifies the independence of the increase on the chain length.

For a quantitative description of the results, it can be assumed that the resistance increase of an Au nanowire is linearly proportional to the adsorbate number density, or the coverage density, based on eq 1. To correlate the coverage density and the concentration, the adsorption kinetics has to be considered. Because an Au nanowire has an extremely small surface area of around 1 μm^2 and thus an adsorbed amount of around 10^{-17} mol of molecules even at a full coverage density of 4.6×10^{14} molecules cm^{-2} ,³⁴ the solution concentration can be considered uniform

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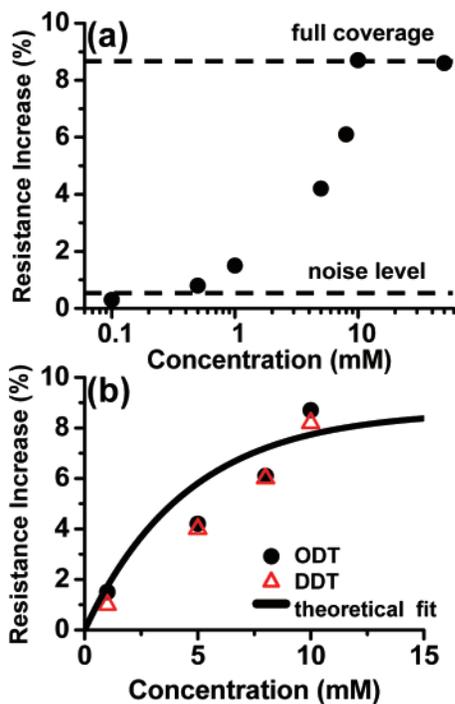


Figure 7. (a) The relationship between the resistance increase and the ODT concentration for an immersion time of 5 min. (b) The relationships between the resistance increase and the concentration in the range between 1 and 10 mM for ODTs and DDTs and a theoretical fit based on eq 4.

during the adsorption process. On the basis of the theoretical formulation in ref 35, the following equations can be established

$$\frac{d\theta}{dt} = S_0 \left(1 - \frac{\theta}{\theta_{\max}}\right) J = S_0 C \nu \left(1 - \frac{\theta}{\theta_{\max}}\right) \quad (2)$$

$$\theta = \theta_{\max} \left[1 - \exp\left(-\frac{S_0 C \nu t}{\theta_{\max}}\right)\right] \quad (3)$$

where θ is the number of adsorbed molecules per unit area (the coverage density), t the time, S_0 the probability that a molecule will adsorb upon its collision (sticking probability), θ_{\max} the maximum number of molecules per unit area (the full coverage density), J the molecule flux density, C the concentration, ν the molecular velocity. On the basis of eqs 1 and 3, the resistance increase has an identical time and concentration dependence as that in eq 3 and can be expressed as

$$\frac{\Delta R}{R} = \left(\frac{\Delta R}{R}\right)_{\max} \left[1 - \exp\left(-\frac{S_0 C \nu t}{\theta_{\max}}\right)\right] \quad (4)$$

Although there are not enough data points, a rough theoretical fit can still be obtained. Taking a maximum resistance increase

of 8.7%, a theoretical fit based on eq 4 is also plotted in Figure 7b. The fit gives a value of 0.22 mM^{-1} for the product of the parameters in front of the concentration C in the exponential function. Taking a t of 300 s and a θ_{\max} of 4.6×10^{14} molecules cm^{-2} , the product of S_0 and ν is equal to $5.6 \times 10^{-7} \text{ cm s}^{-1}$. The value of S_0 is around 10^{-6} and consequently ν is around 0.56 cm s^{-1} .³⁵ Although the determination of these two parameters is beyond the scope of the present work, it seems promising that the nanowire nanosensor can be an alternative technique for the exploration of adsorption kinetics.

Despite an ultimate detection sensitivity of around 10^{-17} mol for a single Au nanowire, the detectable concentration range is only between 1 and 10 mM in the present work and not much different from that obtained by using an ultrathin Au film.²⁶ This situation can be improved by using a low-noise resistance measurement technique, a longer immersion time, or adding a fluidic circulation device, such as a flow cell or a microfluidic channel, into the nanowire nanosensor. Such investigations are currently underway.

CONCLUSION

To summarize, a single metal nanowire connected with similar or dissimilar metal electrodes has been successfully fabricated by a combination of atomic force microscopy nanomachining and conventional photolithography. The advantages include ease of operation, applicability on insulating substrates, much-reduced tip wear, controllability of different nanowire and electrode metals, and potential for mass production. Single Au and Ti nanowires with widths ranging between 50 and 90 nm connected with electrodes have been created, and linear I - V relationships with reasonable resistivities have been observed, indicating the success of the present approach. For chemical sensing, it is found that the resistance increases by around 9% for either ODT or DDT molecules at full coverage after the molecules are selectively bound onto a single Au nanowire connected with Ti electrodes. The consequence implies that the resistance increase is due to the S-Au bonding and not influenced by the chain length. A theoretical explanation for the adsorption kinetics is also provided. The present work exemplifies the potential of this integrated fabrication approach for the construction of single metal nanowire nanosensors.

ACKNOWLEDGMENT

The authors acknowledge Yi-Jen Wu for technical assistance. Financial support from the National Science Council under Grant No. 96-2120-M-002-017 (National Nanoscience and Nanotechnology Program) and Grant No. 96-2221-E-007-100 are gratefully acknowledged.

Received for review September 12, 2007. Accepted January 14, 2008.

AC701911J

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