Detection of Heavy Metal Ions Based on Quantum Point Contacts

3 **AUTHORS**, INCLUDING:

Nongjian Tao

Arizona State University

223 PUBLICATIONS **12,785** CITATIONS

Detection of Heavy Metal Ions Based on Quantum Point Contacts

Vasanth Rajagopalan, Salah Boussaad, and Nongjian J. Tao*

Department of Electrical Engineering and Center for Solid State Electronics Research, Arizona State University, Tempe, Arizona 85287

ABSTRACT

We report on a method to detect trace amounts of metal ions using electrodes separated by atomic scale gaps. By sweeping the electrode potentials cathodically, we deposit metal ions into the gap and form a point contact between the two electrodes, which triggers a quantum jump in the conductance. The deposition time required to form the point contact increases as the ion concentration decreases. We can also dissolve the point contact by sweeping the potentials anodically, which causes a sharp decrease in the conductance. The potentials at which a point contact is formed and dissolved provides the identity of the ions.

Introduction. As materials and devices shrink in size, interesting quantum phenomena begin to emerge, which offer not only exciting opportunities to study fundamental chemistry and physics but also lead to new applications. An important example is the electron tunneling between two electrodes separated by a small gap, which is the basis of the scanning tunneling microscope (STM),[1] tunnel diodes,[2,3] and field-emission flat panel display. A more recent example is single electron charging phenomenon in quantum dot systems, which has led to single electron transistors,[4] molecular switches,[5] and chemical sensors[6] and has provided important new insights into basic electron-transfer chemistry.[7,8] Using two quantum phenomena, conductance quantization and electron tunneling, we have recently developed an electrochemical technique to fabricate electrodes separated by molecular-scale gaps.[9–11] In the present work, we demonstrate a method to detect trace amounts of metal ions using such electrodes.

The ability to detect trace amounts of metal ions is important because of the toxicity of heavy metal ions on many living organisms and the consequence of heavy metal ions not being biodegradable. To date, heavy metal ions in the environment are usually measured by spectroscopic techniques, which require samples to be collected and transported to the laboratory for analysis. In situ measurements are highly desirable because they provide an early detection of trace metal contaminants while minimizing errors, labor, and cost associated with collection, transport, and storage of samples. One of the promising in situ sensors is based on anodic stripping voltammetry.[12–16] To achieve a detection below the ppb level, a preconcentration technique is normally required, in which metal ions are electrochemi-cally deposited onto a Hg electrode. Following the preconcentration, the electrode potential is scanned to a more positive value to oxidize and strip the deposited metals from the electrode. The oxidation current reaches a peak at a potential characteristic of the metal, which provides the identity of the metal. Other methods include fluorescence detection,[17–23] porphyrin derivatives as complexing agents,[18] array-based sensors,[24,25] magnetic effects,[26] ion-sensitive field effect transistors,[27] and microfabricated cantilevers.[28,29] While each method has its own advantages and disadvantages, development of a reliable and sensitive sensor requires further efforts.

Our method starts with electrodes separated by a narrow gap (Figure 1). When the electrodes are exposed to a solution containing heavy metal ions, the ions can be deposited into the gap by controlling the electrode potentials. Once the deposited metal bridges the gap, a point contact is formed between the electrodes and the conductance jumps by many orders of magnitude, which can be easily detected. Since the gap can be made as narrow as the size of a single atom, deposition of even a few ions into the gap is enough to trigger a large change in the conductance, thus providing a sensitive detection of metal ions. Our previous experiments[9,10] have shown that the conductance of such a small contact is quantized and given by NG_0, where N is an integer and G_0 is the conductance quantum ($G_0 = 2e^2/h$, e is the electron charge and h is the Planck constant). For this reason, the contact is often called a quantum point contact.[30–32] The point contact can also be stripped off (or dissolved) by sweeping the potential anodically. The potentials at which deposition and dissolution take place provide the identity of the metal ions, a principle similar to that of the anodic stripping analysis.
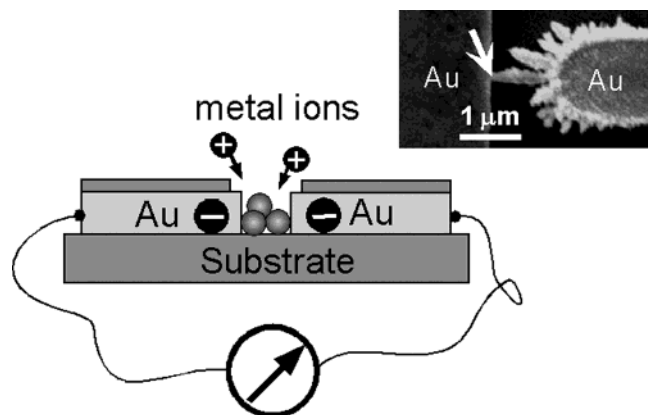
Figure 1. Pair of electrodes separated by an atomic-scale gap on a silicon chip exposed to a solution containing metal ions. If holding the electrodes below the electrodeposition potential of the metal ions, electrodeposition of a single or a few metal ions into the gap can form a point contact between the two electrodes and result in a quantum jump in the conductance. Inset: scanning electron Micrograph of a pair of Au electrodes, where the arrow points to the atomic-scale gap (not resolved).

Experimental Section. A key task of our experiment is to fabricate electrodes separated by an atomic scale gap, which was accomplished using an electrochemical method described previously.[11] Briefly, we started with a pair of Au electrodes separated by a μm-scale gap on a Si or glass substrate in 0.1 M HCl. We then applied a bias voltage ($\sim$1.2 V) across the gap and an external resistor ($R_{ext} = 1$ MΩ) connected in series to form a voltage divider circuit. Initially, the gap resistance was very large ($\gg R_{ext}$) so the entire bias fell across the gap and Au atoms were etched away from the anode and deposited on the cathode. Because the deposition was a diffusion limited process, the cathode grew directionally towards the anode and the gap decreased consequently. When the gap decreased below $\sim$1 nm, tunneling current began to flow across the gap and the gap resistance dropped sharply. As a result, the voltage across the gap also dropped sharply, which terminated the etching and deposition processes with the pair of electrodes separated by a gap of 0.4$-$0.6 nm as estimated from the tunneling current (see inset of Figure 1). The success rate of forming such a gap was about 50%, and the rest ended up with a point contact between the two electrodes. The contact could be broken by flowing a large current through it based on the electromigration effect,[33] which allows us to restart the etching and deposition procedure described above.

We prepared the starting Au electrodes by two methods. The first one simply used a parallel array of 25 μm diameter Au wires glued manually on a glass slide. The wires were coated with a uniform layer of epoxy to reduce the current leakage. By cutting the wires with a razor blade, we formed an array of electrode pairs, in which the electrodes in each pair were separated by a gap of a few μm. The second method used conventional optical lithography to fabricate an array of Au electrode pairs on an oxidized Si wafer. To minimize possible damage to the anode due to etching, we used an anode that was much bigger than the cathode (Figure

1, inset). The initial separation between the cathode and the anode in each pair was 1 μm.

For heavy metal ion detection, we controlled the potentials of the two electrodes in each pair independently using a bipotentiostat (Pine Instruments, model AFRDE 5) with a Pt wire as the counter electrode and a Ag wire as quasi-reference electrode. The potentials were calibrated against the commonly used Ag/AgCl (in 3 M KCl). We tested two metal ions, Pb^{2+} and Cu^{2+}, by dissolving $Pb(NO_3)_2$ and $CuSO_4$ in 50 mM HNO_3 and H_2SO_4 (Alfa Aesar) supporting electrolytes (prepared using Nanopure water from a Biore-search Grade purification system). The metal ions were deposited into or stripped out of the gap by controlling the electrode potentials. During the electrodeposition and stripping processes, we monitored the conductance between the electrodes continuously by maintaining a small bias voltage (50 mV) between the electrodes.

Results and Discussions. We performed experiments using two approaches. In the first approach, we held the electrodes at various potentials. When the potentials were above the electrodeposition potential, no conductance change was observed because no metal ion deposition took place. However, when the potentials were decreased below the electrodeposition potential, conductance jumped above 1 G_0, the conductance of roughly a single atom contact between the two electrodes, after a certain period. Figure 2a shows an example of the experiment of 1 mM Cu^{2+}. The conductance is not measurable initially, but it jumps to $\sim$25 G_0 several seconds after holding the potentials at -0.3 V. The conductance continues to increase as the contact size increases by further electrodeposition. The contact size can be determined from the measured conductance (G) using equation[34]

$$G = G_0\left(\frac{\pi^2 D^2}{4\lambda_F^2} - \frac{\pi D}{2\lambda_F}\right) \qquad (1)$$

where D is the diameter of the contact and λ_F is the Fermi wavelength of the electrons in the metal. The later is about 0.1$-$0.2 nm for a typical metal at room temperature. For a conductance of 25 G_0 found in Figure 2a, the corresponding diameter of the contact is only a few atoms across according to eq 1.

The deposition time required to form the contact depends on the concentration of the metal ions. We have determined the deposition time as a function of concentration and plotted the results in Figure 2b. As we might expect, the time increases as the concentration decreases, but it is almost proportional to the logarithmic of the ion concentration. Another unexpected observation is the relatively slow deposition time for an atomic-scale contact, which is probably due to the slow diffusion process of the metal ions in the small gaps. A quantitative understanding of the diffusion process requires further study. Nonetheless, the observed simple dependence of the deposition time on the concentration provides us with a method to estimate the metal ion concentration. This measurement also shows that we can detect a concentration of 10 nM Cu^{2+} ($\sim$0.6 ppb), which is
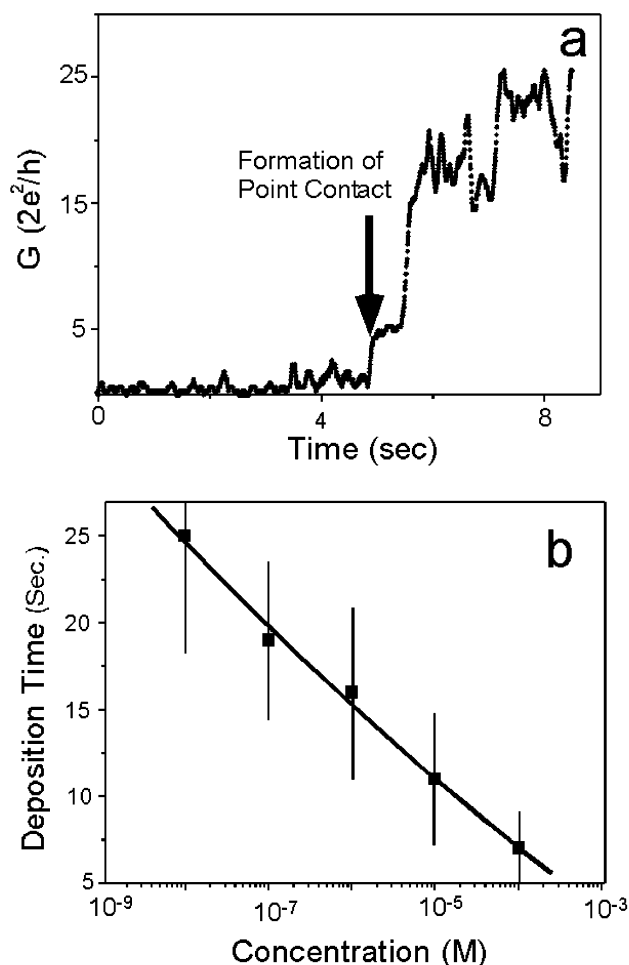
Figure 2. (a) Conductance of a pair of Au electrodes in 10^{-4} M Cu^{2+} solution as a function of time. The electrodes were held near -0.25 V with a bias of 50 mV applied between the two Au electrodes. The sudden jump in the conductance (marked by an arrow) corresponds to the formation of a Cu point contact between the Au electrodes. (b) Deposition time required to form a Cu point contact vs Cu^{2+} concentration, where the solid line is a guide to the eye.

Figure 3. (a) Deposition time required to form a Pb point contact between two Au electrodes vs Pb^{2+} concentration. (b) Dissolution time of Pb point contacts vs the conductance of the contact. The diameters of the contacts estimated from the conductance using eq 1 are indicated also in the figure. The solid lines are used as a guide to the eye.

several orders of magnitude lower than the EPA limit. Lower concentration is achievable, but the run-to-run variation in the deposition time is larger.

We performed similar experiments for Pb^{2+} ions, whose electrodeposition potential is lower than Cu^{2+}. The dependence of the deposition time as a function of Pb^{2+} concentration is plotted in Figure 3a. It shows that 0.1 nM Pb^{2+} can be detected within a few tens of seconds. The concentration limit is also 3 orders of magnitude below the current EPA limit. We determined the time required to strip off (dissolve) the point contact by raising the electrode potentials (Figure 3b) and found that the stripping time increased with the conductance of the electrodeposited point contact. This is understandable because the contact size increases with the conductance, as described by eq 1. To illustrate this point, we have marked the contact diameter extracted from eq 1 ($\lambda_F = 0.15$ nm) in Figure 3b.

The experiments described above were performed by holding the electrode potentials at fixed values. We have also formed and dissolved the metal point contacts by
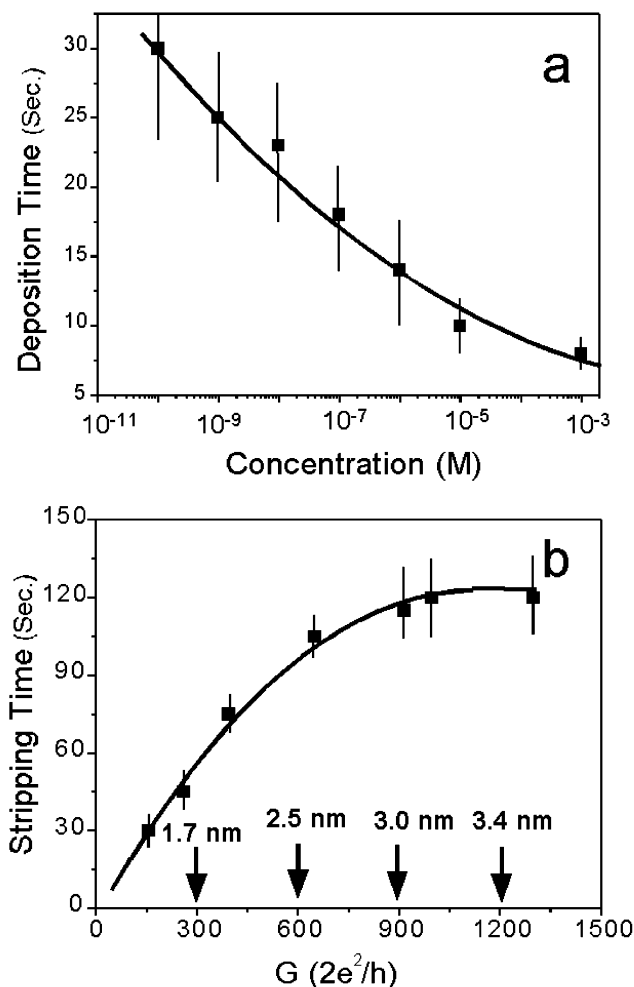
sweeping the electrode potentials over a certain range at a constant rate. Figure 4a shows an example of a pair of Au electrodes in the presence of Cu^{2+}. The potential was swept from $+0.35$ V to -0.65 V at a rate of 5 mV/sec. During the sweeping process, we monitored the conductance continuously. Initially, the conductance between the two electrodes was negligible. When the potential was swept to approximately -0.25 V, the conductance jumped to ~ 50 G_0 as the deposited Cu formed a point contact between the two electrodes. Further sweeping the potential from -0.25 to -0.65 V, the conductance increased to ~ 80 G_0 as more Cu was deposited to the point contact. When the potential was swept in the anodic direction to ~ 0.15 V, the conductance dropped to zero abruptly, due to the dissolution of the Cu point contact.

We have performed the potential sweeping measurements for Pb^{2+} ions in a similar way. Because Pb^{2+} ions have different electrodeposition and dissolution potentials, we swept the potential back and forth between 0.3 V and -0.9 V. A typical potential cycle is plotted in Figure 4b. It shows a sharp jump in the conductance from zero to ~ 20 G_0 when
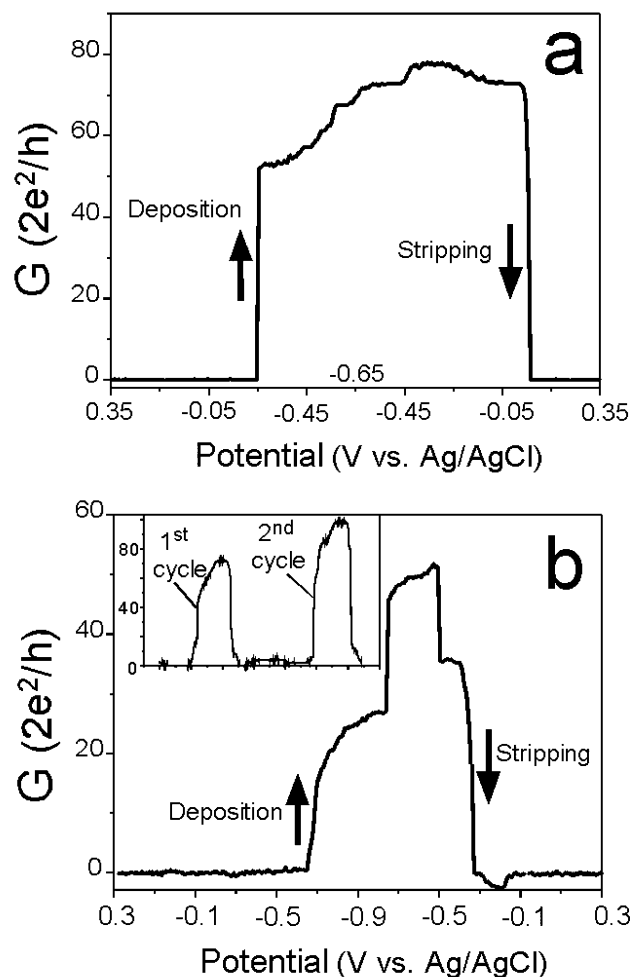
Figure 4. (a) Conductance of a pair of Au electrodes in 10^{-4} M Cu^{2+} solution as the potential was swept between 0.35 and -0.65 V at a sweep rate of 5 mV/sec. The sudden increase and decrease in the conductance correspond to the formation and dissolution of a Cu point contact (marked by two vertical arrows). (b) Conductance of a pair of Au electrodes in 10^{-4} M Pb^{2+} solution as the potential was swept between 0.3 and -0.9 V at a sweep rate of 5 mV/sec. The inset shows that while the potentials at which a point contact forms or dissolves are rather reproducible, the conductance of the contact varies from cycle to cycle.

the potential was swept from 0.3 to approximately -0.65 V, corresponding to the formation of a Pb point contact between the Au electrodes. The conductance increased further to $\sim$50 G_0 when the potential was swept from -0.65 to -0.9 V, due to the increase in the contact size. When the potential was swept in the anodic direction to approximately -0.35 V, the conductance dropped to zero again, corresponding to the dissolution of the Pb point contact. By cycling the electrode potentials, we can often repeatedly form and strip off the point contact (inset of Figure 4b), which shows that the Au electrodes can be repeatedly used for metal ion detection. In general, the conductance of the electro-deposited point contact tends to vary from run to run (inset of Figure 4b), but the potentials at which individual point contacts are formed or dissolved are rather reproducible. Table 1 lists the deposition and stripping potentials for both Cu^{2+} and Pb^{2+} (averaged over 10 experiments). It shows that

Table 1. Electrode Potentials at which Cu and Pb Contacts Form and Dissolve between Two Au Electrodes[a]

copper		lead	
avg deposition potential	avg stripping potential	avg deposition potential	avg stripping potential
-0.25 ± 0.05 V	0.10 ± 0.02 V	-0.6 ± 0.05 V	-0.35 ± 0.03 V

[a] The results are averaged over 10 pair of electrodes and the errors are the maximum run-to-run deviations.

the variation in the stripping potentials is smaller than that in the deposition potentials, indicating that the point contact dissolves at a more well-defined potential than it forms.

In summary, we have demonstrated a simple method to detect trace amount of metal ions ($\sim$10 ppt) using a pair of electrodes separated by an atomic-scale gap. By controlling the electrode potentials, metal ions can be deposited into the gap to form a point contact between the electrodes, which can be sensitively detected as a quantum jump in the conductance. The deposition time required to form a point contact increases as the ion concentration decreases. We have also shown that the deposition and stripping potentials at which a point contact forms and dissolves are different for different metal ions, which can be used to identify the ions. The basic principle of our approach resembles the anodic stripping voltammetry, but it measures the conductance of a point contact rather than electrochemical current. Because conductance change due to even a single atom contact is large (7.7 μA for a bias of 100 mV) and easily measurable, our approach offers great potential for a highly sensitive and miniaturized device. We are aware that the present experiment can be regarded only as a proof-of-concept experiment. For practical applications, a number of issues (also exist in many other sensors) must be addressed, including possible interference of different species in water and regeneration of the electrodes. In addition, the deposition and stripping processes in the atomic-scale gaps requires further study and the sensitivity and the response time need to be optimized, which will be carried out in the future.

References

(1) Binnig, G.; Rohrer, H.; Gerber, C.; Weibel, E. *Phys. Rev. Lett.* **1982**, *49*, 57−61.
(2) Esaki, L. *Phys. Rev.* **1958**, *109*, 603.
(3) Davis, R. H.; Hosack, H. H. *J. Appl. Phys* **1963**, *34*, 864.
(4) Likharev, K. K. *Sci. Am.* **1992**, *266*, 80−85.
(5) Gittins, D. I.; Bethell, D.; Schiffrin, D. J.; Nichols, R. J. *Nature* **2000**, *408*, 67−69.
(6) Brousseau, L. C., III; Zhao, Q.; Shultz, D. A.; Feldheim, D. L. *J. Am. Chem. Soc.* **1998**, *120*, 7645.
(7) Fan, F.-R. F.; Bard, A. J. *Science* **1997**, *277*, 1791−1793.
(8) Chen, S. W.; Ingram, R. S.; Hostetler, M. J.; Pietron, J. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Alvarez, M. M.; Whetten, R. L. *Science* **1998**, *280*, 2098−2101.
(9) Li, C. Z.; Tao, N. J. *Appl. Phys. Lett.* **1998**, *72*, 894−897.
(10) Li, C. Z.; Bogozi, A.; Huang, W.; Tao, N. J. *Nanotechnology* **1999**, *10*, 221−223.

(11) Boussaad, S.; Tao, N. J. *Appl. Phys. Lett.* **2002**, *80*, 2398−2400.

(12) Wang, J. *Stripping Analysis: Principles, Instrumentation and Applications*; VCH Publishers: Deer Field Beach, FL, 1985.

(13) Zhou, F. M.; Aronson, J. T.; Ruegnitz, M. W. *Anal. Chem.* **1997**, *69*, 728−733.

(14) Lai, R.; Huang, E. L.; Zhou, F. M.; Wipf, D. O. *Electroanalysis* **1998**, *10*, 926−930.

(15) Herdan, J.; Feeney, R.; Kounaves, S. P.; Flannery, A. F.; Storment, C. W.; Kovacs, G. T. A.; Darling, R. B. *Environ. Sci. Technol.* **1998**, *32*, 131−136.

(16) Feeney, R.; Kounaves, S. P. *Anal. Chem.* **2000**, *72*, 2222−2228.

(17) Segura-Carretero, A.; Costa-Fernandez, J. M.; Pereiro, R.; Sanz-Medel, A. *Talanta* **1999**, *49*, 907−913.

(18) Delmarre, D.; Meallet, R.; Bied-Charreton, C.; Pansu, R. B. *J. Photochem. Photobiol., A* **1999**, *124*, 23−28.

(19) Kuswandi, B.; Narayanaswamy, R. *Anal. Lett.* **1999**, *32*, 649−664.

(20) Fabbrizzi, L.; Licchelli, M.; Parodi, L.; Poggi, A.; Taglietti, A. *Eur. J. Inorg. Chem.* **1999**, 35−39.

(21) Malcik, N.; Caglar, P. *Sens. Actuators, B* **1997**, *39*, 386−389.

(22) DeSantis, G.; Fabbrizzi, L.; Licchelli, M.; Mangano, C.; Sacchi, D.; Sardone, N. *Inorg. Chim. Acta* **1997**, *257*, 69−76.

(23) Czolk, R.; Reichert, J.; Ache, H. J. *Sens. Actuators, B* **1992**, *7*, 540−543.

(24) Prestel, H.; Gahr, A.; Niessner, R. *Fresenius J. Anal. Chem.* **2000**, *368*, 182−191.

(25) Kim, J.; Wu, X. Q.; Herman, M. R.; Dordick, J. S. *Anal. Chim. Acta* **1998**, *370*, 251−258.

(26) Petrov, N. K.; Kuhnle, W.; Fiebig, T.; Staerk, H. *J. Phys. Chem. A* **1997**, *101*, 7043−7046.

(27) Ben Ali, M.; Kalfat, R.; Sfihi, H.; Chovelon, J. M.; Ben Ouada, H.; Jaffrezic-Renault, N. *Sens. Actuators, B* **2000**, *62*, 233−237.

(28) Ji, H. F.; Finot, E.; Dabestani, R.; Thundat, T.; Brown, G. M.; Britt, P. F. *Chem. Commun.* **2000**, *6*, 457−458.

(29) Ji, H. F.; Thundat, T.; Dabestani, R.; Brown, G. M.; Britt, P. F.; Bonnesen, P. V. *Anal. Chem.* **2001**, *73*, 1572−1576.

(30) Krans, J. M.; Ruitenbeek, J. M. v.; Fisun, V. V.; Yanson, I. K.; Jongh, L. J. d. *Nature* **1995**, *375*, 767−769.

(31) Landman, U.; Luedtke, W. D.; Salisbury, B. E.; Whetten, R. L. *Phys. Rev. Lett.* **1996**, *77*, 1362−1365.

(32) Pascual, J. I.; Mendez, J.; Gomez-Herrero, J.; Baro, A. M.; Garcia, N.; Binh, V. T. *Phys. Rev. Lett.* **1993**, *71*, 1852−1855.

(33) Park, H.; Lim, A. K. L.; Alivisatos, A. P.; Park, J.; McEuen, P. L. *Appl. Phys. Lett.* **1999**, *75*, 301−303.

(34) Torres, J. A.; Pascual, J. I.; Saenz, J. J. *Phys. Rev. B* **1994**, *49*, 16581.