1/*f* noise in gold nanoparticle chemosensors

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We present a systematic study of low-frequency noise in Au nanoparticle chemosensors. All the sensors we have studied exhibit $1/f$-type noise at low frequencies. The magnitude of the $1/f$ noise was smaller in devices with a larger device area, indicating that the $1/f$ noise is caused by intrinsic processes. The noise amplitude was found to be strongly temperature dependent between 40–300 K, with a local peak at around 100 K, and weakly dependent below 40 K. The noise data could not be fit by a single activated process indicating that multiple noise processes must be present in our sensors. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1865324]

There has been increasing interest in thiolate-coated Au nanoparticles as they are shown to self-assemble in periodic structures.[1,2] The possibility of tuning their properties makes them promising candidates for a range of electrical and optical applications. Recently, these materials have also been used for gas/vapor sensors.[3–6] In such an application, the Au nanoparticle film is deposited on an insulating substrate and the electrical resistance of the film is monitored in the presence of chemical species. The dominant electrical transport mechanism in films lacking ionic contaminants is via tunneling of electrons between neighboring nanoparticles.[7] The reversible partitioning of the chemical species affects the tunnel coupling, and thus the resistance of the Au nanoparticle film typically changes in the presence of chemical species. Because the tunnel coupling is exponentially dependent on the properties of the medium in between the nanoparticles, they are highly sensitive sensors. Even a small amount of swelling associated with the absorption of chemical species into the thiolate coating can lead to a significant increase in film resistance. Such sensors are currently being developed as the detector elements of a microfabricated gas chromatography system which can analyze complex mixtures of gases for a wide range of applications, including monitoring of industrial emissions, detection of explosives, and medical diagnostics.[8,9]

The detection limit of a sensor is given by the ratio of the sensitivity to the background noise. The sensitivities of a wide range Au nanoparticle sensors have been reported for different vapors. Despite their significance, the background noise of such sensors has not been studied systematically and the fundamental limits for detection are not known. In this work, we have studied the low-frequency noise of a large number of Au nanoparticle chemosensors. At low frequencies, the sensors exhibit $1/f$-type noise. In principle, any intrinsic or extrinsic processes that can change the resistance of the film can be responsible for the $1/f$ noise. Our temperature dependent noise measurements indicate that there are multiple intrinsic processes that contribute to the background noise of these sensors. Understanding and, if possible, eliminating some of these noise processes will help us to improve the performance of such sensors.

The Au nanoparticles used in this work are synthesized by using a process similar to the Brust method.[10] The modified synthesis, described in detail elsewhere, avoids the use of a phase transfer catalyst leading to nanoparticles that are free of ionic contaminants and this is a critical requirement for measuring tunneling behavior.[7] Au nanoparticles with various coatings and different core sizes are synthesized using this technique. We performed noise measurements on two kinds of Au nanoparticle films where the nanoparticles were capped by either 1-octanethiolate (C8) or by 1-dodecanethiolate (C12). The average core diameter of the C8- and C12-coated nanoparticles were determined using transmission electron microscopy measurements to be 4.3 ± 0.9 and 4.2 ± 1.2 nm, respectively.

For electrical characterization of Au nanoparticle films, we fabricated three different sizes of Au interdigitated electrodes on insulating silicon dioxide layers using electron-beam lithography. The active areas of the three types of devices were 90, 910, 3600 μm^2 and the electrode spacings were 0.1, 0.3, and 1 μm, respectively. The nanoparticles dissolved in toluene were deposited on interdigitated electrodes using an airbrush. The average thickness of the films varied greatly. Based on the spraying conditions, we estimate the average thickness of most of the films to be in the 50–500 nm range. All of the films prepared by this technique were found to be highly nonuniform in thickness, with fluctuations comparable to the thickness of the films.

Current-voltage (*I-V*) and noise measurements were performed on 20 devices with different coatings (C8 and C12) and different electrode spacings. At room temperature, the *I-V* characteristics of the devices were nearly linear and the resistance of devices varied from 0.3 to 32 MΩ. Noise measurements are performed using a setup consisting of a battery operated dc power supply, a PAR181 low-noise current sensitive amplifier, and an SR780 spectrum analyzer. The intrinsic noise and frequency response of the amplifier is characterized by measuring the thermal noise of metal film resistors at different temperatures. In all of our measurements, the excess noise of the sensors were much larger than the intrinsic noise of the amplifier. At room temperature, the excess noise of all devices was found to scale quadratically with the bias current, indicating that the excess noise was due to fluctuations in device resistance. A typical normalized noise

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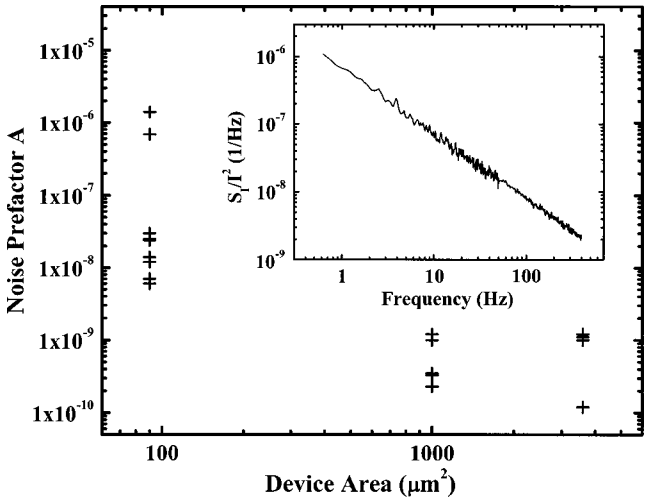

FIG. 1. Noise prefactor A vs device area obtained from 20 different C8- and C12-coated Au nanoparticle sensors at room temperature. The inset shows typical normalized noise spectra S_I/I^2 obtained from a C8-coated Au nanoparticle sensor with an electrode spacing of 100 nm.

spectrum, S_I/I^2, obtained from the C8-coated device is shown in the inset of Fig. 1. All excess noise spectra that we obtained could be fit using a $1/f$-type functional dependence, $S_I/I^2=Af^{\alpha}$, where the noise exponents, α, extracted from such fits were close to 1 (within 20%). However, there was a large scatter in the measured noise prefactor A. In Fig. 1, we plot A versus the device area obtained from different devices at room temperature. Despite the large scatter in data, it is clear that the magnitude of the $1/f$ noise is smaller for large-area devices. If the noise were caused by an extrinsic process, such as temperature fluctuations, the excess noise would not have depended on the area of the device. In other words, the $1/f$ noise observed in our sensors must be caused by many independent events that are occurring throughout the device. In principle, resistance fluctuations can arise from a number of different intrinsic processes, such as absorption and desorption of molecules, motion of nanoparticles or other configurational changes, and changes in offset charges.

From the size of the $1/f$ noise data, we can now get an order of magnitude estimate for the detection limit of a typical Au nanoparticle sensor. Note that the sensitivity does not vary with the area of the device,[11] whereas the background noise is expected to scale inversely with device area. For the better C8-coated Au nanoparticle chemosensors, the normalized resistance noise power spectrum is $S_R/R^2 \approx 10^{-18}/(\text{Area}\cdot f)$. The sensitivities of Au nanoparticle sensors are measured for different analytes. At low concentrations (10–1000 ppm), the relative change in the resistance of the sensor $(\Delta R/R)$ is proportional to the vapor concentration of the analyte C_V. The sensitivity is $s=(\Delta R/R)/C_V$. The vapor concentrations are typically given in units of ppm; however, in this letter, we will use a dimensionless notation where $C_V=10^{-6}$ will correspond to a concentration of 1 ppm. In ideal operation conditions where the temperature fluctuations and amplifier noise is negligible, the detection limit of a nanoparticle sensor for different analytes can be calculated using the concentration power spectrum $S_{C_V} \approx 10^{-18}/(s^2\cdot\text{Area}\cdot f)$. For example, the equation suggests that a Au nanoparticle chemosensor with a device area of 1 cm^2 for typical analytes (i.e., toluene, chlorobenzene, or perchloroethylene)[8] with a sensitivity of $s\approx 10-100$ should have a detection limit close to 1–10 ppb level.

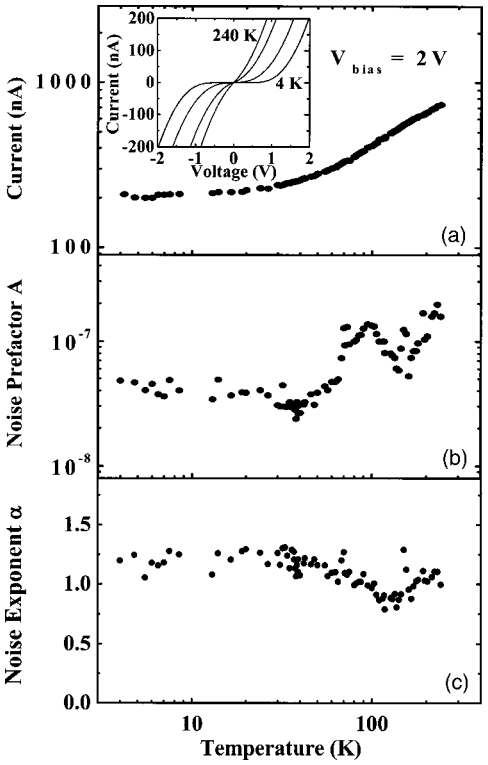

FIG. 2. (a) The device current, (b) the noise prefactor A, and (c) the noise exponent α vs temperature for Sample A at a bias voltage of 2 V. The inset shows the I-V characteristics at different temperatures, 4 K, 80 K, 160 K, and 240 K.

To understand the physical origin of the noise processes responsible for the excess noise, we studied the temperature dependence of noise and the I-V characteristics for some of our sensors using a Janis variable temperature cryostat. To ensure temperature stabilization, we typically waited a few hours in between measurements at different temperatures. Similar to room-temperature measurements, at cryogenic temperatures $1/f$ noise is found to be larger for small area devices. Here, we present results from two small area sensors.

The I-V characteristics of these two devices (Samples A and B) are shown in the insets of Figs. 2 and 3. The nonlinearity of the I-V characteristics at low temperatures arises from the Coulomb blockade behavior; the device current exhibits a threshold behavior and scales as $I\propto(V-V_{\text{th}})^{\zeta}$, where V_{th} is the threshold voltage and ζ is the scaling exponent.[12–14] Near the threshold region, the current is expected to flow nonuniformly in a few energetically favorable channels. For bias voltages smaller than or comparable to V_{th}, the device current is strongly temperature dependent and as we lower the temperature fewer nanoparticles are expected to participate in conduction. This effect must be included in the description of the temperature dependence of $1/f$ noise near the threshold region. If the intrinsic noise processes are not strongly temperature dependent, then the excess $1/f$ noise can increase at low temperatures due to the fact that fewer nanoparticles would participate in the current. Indeed, we have observed that near the threshold region the normalized noise spectra S_1/I^2 were much larger at low temperatures than at room temperature.

To study the intrinsic noise processes in a chemosensor, we must perform noise measurements at high bias voltages

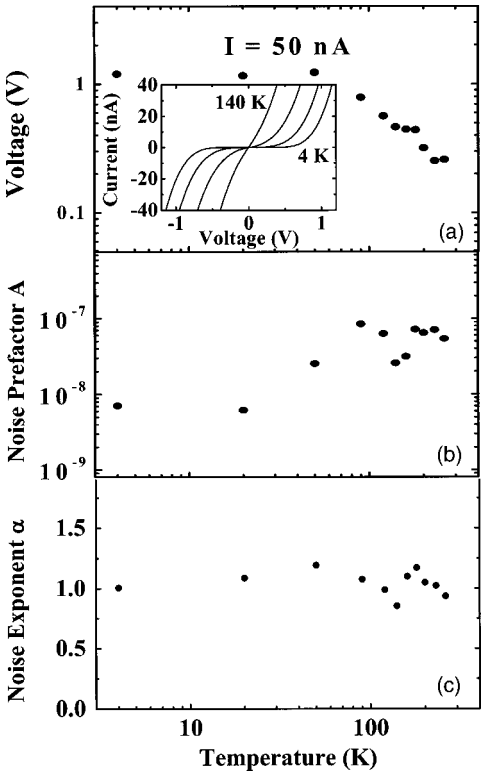

FIG. 3. (a) The device voltage, (b) the noise prefactor A, and (c) the noise exponent α vs temperature for Sample B at a bias current of 50 nA. The inset shows the I-V characteristics at different temperatures, 4 K, 50 K, 90 K, and 150 K.

or high bias currents to avoid complications due to the Coulomb blockade physics. In practice, however, we are constrained as the application of very large bias destroys these small sensors. In Sample A, we performed noise measurements at a bias voltage of 2 V which is about a factor of 10 larger than the measured threshold voltage. The temperature dependence of the device current at such a bias voltage is shown in Fig. 2(a). For contrast, we present data from Sample B at a constant bias current of 50 nA. The temperature dependence of device voltage at this bias current is shown Fig. 3(a). Note that, in comparison to the low bias regime where the device exhibits activated temperature dependence, the temperature dependence is relatively weaker at these bias conditions.

The excess noise measured at different temperatures was fitted to $S_I/I^2=Af^{\alpha}$. The noise prefactor A and the noise exponent α extracted from these fits are shown in Figs. 2(b), 2(c), 3(b), and 3(c). The noise exponent α is weakly temperature dependent and was close to 1. The prefactor A, which is a measure of the magnitude of $1/f$ noise, was strongly temperature dependent between 40–300 K, had a local peak at around 100 K, and was weakly temperature dependent below 40 K. The peak around 100 K was unexpected, since typically $1/f$ noise arises from intrinsic processes that are thermally activated.

Any process that can affect the tunnel coupling between neighboring nanoparticles can lead to $1/f$-type noise. For example, the motion of nanoparticles, conformation changes of the ligand molecules, and the changes in offset charges can all lead to $1/f$ noise. The complex temperature dependence of the magnitude of $1/f$ noise indicates that multiple noise processes must be present in Au nanoparticle films. Quantifying the contribution of individual processes to the $1/f$ noise will be important to the development of higher performance chemosensors.

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