Atomistic Nature of Transient and Steady-State Responses

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We find experimentally that a system comprised of nanosized features no longer shows fixed steady characteristics as in solid-state devices, and instead, because of the chemistry of the nanostructure, the thermal motion of the atoms, and the external fields, the nanosized system shows intermittent behavior, that is, transient behavior. This transient response for nanosized systems might misguide conclusions regarding observed negative differential resistance (NDR) which is due to the collective nuclei rearrangements to more stable conformations under the presence of an applied field yielding, in many cases, resonances between conformations that can sustain during the steady-state period. This NDR yields peculiar behavior that needs to be considered to design molecular and nanoelectronic devices. In addition, the commonly sharp contrast between transient and steady responses blurs at the nanoscale. In nanosize systems, the time constants or transient response times depend on the velocity of the rearrangements of the atoms in the system or molecule.

1. Introduction

The study of nanomaterials requires the interaction of theoretical and experimental methods. It is very important that experiments be performed in concert with a theoretical analysis. A major goal in the field is to perform proof-of-concept experiments that will allow us to develop nanosized structured devices for high-performance computing. A specific feature of materials for molecular and nanoelectronics that we need to know is how they respond to external electrical stimulus so we can take advantage of these characteristics to design systems able to perform required functions or to implement new ones. Our objective in the present work is to analyze the response of nanosized gold clusters to electrical signals and to explain such a response using available theoretical tools.

For many physical systems or devices, there is a transient state between two steady ones. The nature of transient and steady responses is determined by the individual characteristics of the system or device. What is most interesting is that most realistic systems have uniquely determined responses by the same parameters, implying that both static and transient responses have a strong dependence on each other. Systems with these characteristics constitute the topic of several if not all of the present engineering.

For example, the transient response is well-known for electrical and chemical systems, shown in Figure 1, with the difference being that they correspond to very different time scales. For the electrical resistor-inductor-capacitor (RLC) circuit, the rising and falling of the voltage is determined by the movement and rearrangement of electrons in the RLC circuit, thus, time scales associated are usually from fractions of seconds to fractions of nanoseconds; however, the chemical plant has a transient behavior depending on the movement and arrangement of big, macroscopic masses involving large portions of fluids and large machines with transient times from minutes to several hours.

Despite this interesting analogy between chemical and electrical systems of totally different sizes, there is a sharp difference between them. In microelectronic systems, we can observe the robustness of the nuclei compared to the pass of

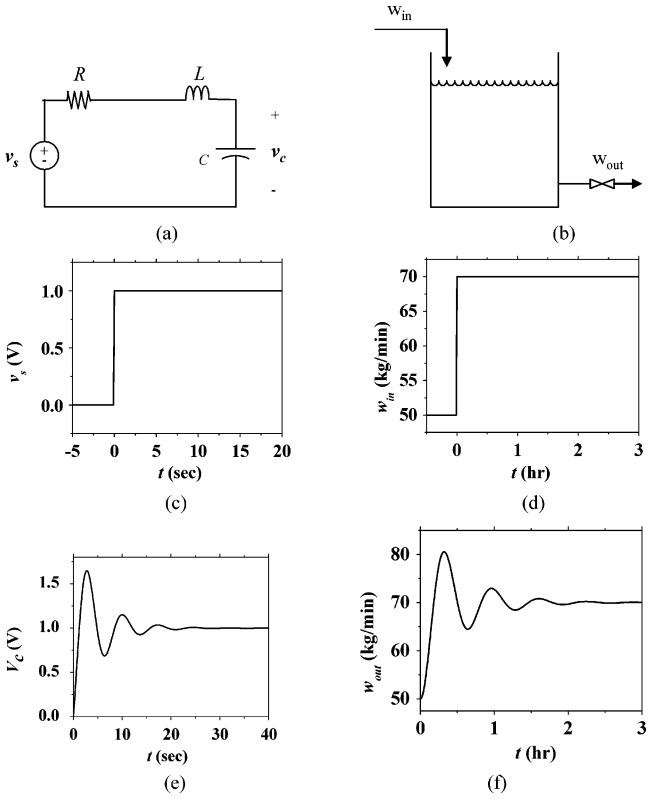

Figure 1. (a) RLC circuit with $R = 10\ \Omega$, $L = 10$ H, and $C = 100$ mF. (b) A chemical liquid storage system that exhibits an underdamped second-order flow-rate response with liquid volume $V = 100$ m^3, liquid density $\rho = 30$ kg/m^3, original input and output mass flow rate $w_{ino} = w_{outo} = 50$ kg/min, damping coefficient $\zeta = 0.2$, and time constant $\tau = V\rho/w_{ino} = 1$ h. (c) At $t = 0$, the voltage source, v_s, in the RLC is switched on and applies a voltage of 1 V. (d) At $t = 0$, the input flow rate changes from 50 m^3/min to 70 m^3/min. (e) The voltage across the capacitor C is $v_c(t) = e^{-Rt/2L}[-\cos(\sqrt{4LC-(RC)^2} \times t/2LC) + RC/\sqrt{4LC-(RC)^2} \times \sin(\sqrt{4LC-(RC)^2} \times t/2LC)]$. (f) The output flow rate after $t = 0$ is $w_{out}(t) = w_{ino} + (w_{out}' - w_{outo}) \times \{1 - e^{-\zeta t/\tau} \times [\cos(\sqrt{1-\zeta^2} \times t/\tau) + \zeta/\sqrt{1-\zeta^2} \times \sin(\sqrt{1-\zeta^2} \times t/\tau)]\}$, where w_{out}' is the output at a steady state, which is 70 kg/min in this case.

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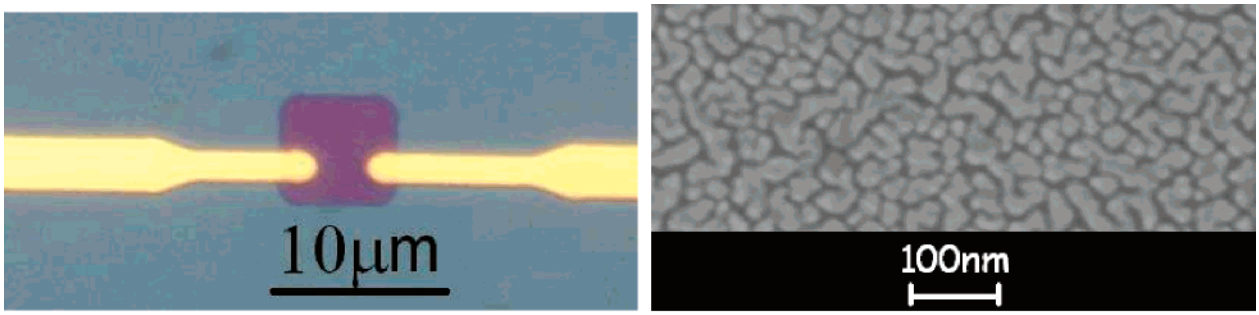

Figure 2. (a) Optical microscope image of the structure tested in this research work. The two yellow leads are made of palladium and titanium. The purple square between the leads is discontinuous gold film. (b) SEM image of the discontinuous gold film. The irregular gray patterns are gold islands with darker color gaps in between. The distance between the gold islands is ~5 nm.

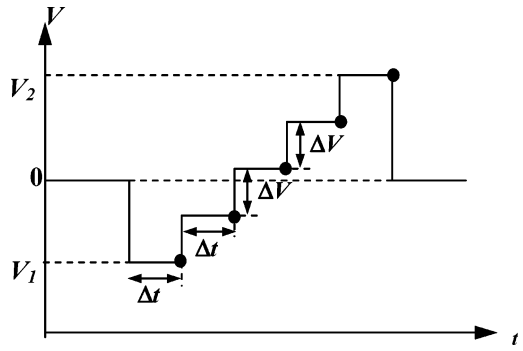

Figure 3. Applied voltage for the transient current−voltage measurements: a staircase voltage sweep starts at V_1; the first measurement takes place after a time delay Δt at constant voltage V_1. After the first measurement, the voltage is increased to $V_1 + \Delta V$, and the measurement takes place after Δt. This process continues until the last measurement is finished, and then the applied voltage goes back to zero.

electrons. For instance, a typical current of 10^{-4} A in an n-channel silicon-based metal oxide semiconductor field effect transistor with channel length, $L = 1$ μm, width, $W = 10$ μm, and depth, $d = 100$ nm, represents a total of 6.25×10^5 electrons flowing through the channel in one nanosecond, corresponding to the typical frequency (~GHz) of today's microelectronic devices. The density of silicon is 7×10^{10} atoms per μm^3;[1] therefore, in such a volume holding the little transistor, one single electron in average causes only a small perturbation to 10^5 atoms. As a result, the nuclei in a crystal are not strongly affected by the dynamics of the electrons. Chemically speaking, when the nuclei are kept together by equally strong chemical bonds in the three dimensions, the strong differences between transient and steady responses are well-established. This also gives rise to specific and sharply defined transient and steady responses. On the other hand, the situation is different at macroscopic levels, for instance, in a chemical plant. Because the mass of the fluids in the chemical plant is in the same order of magnitude as the mass of the materials making the plant, the fluid is not a small perturbation to the plant materials. Actually because the nature of the flows, they may cause much more fluctuations in plants than the electrons do in microsized semiconductors. This also explains why chemical plants require more maintenance.

Then the question of what happens to a nanoscopic system arises. As the electronic device scales down to an extent that the number of transferred electrons through the junction and the number of atoms associated to the junction become comparable, a similar problem encountered in a chemical plant is faced by electrical engineers: the plant components should be robust enough to hold the fluids; similarly, the nanoscopic electrical system should be robust to hold the fluid of information carried by electrons. Moreover, in electronics, the amount of information that can be processed per unit of matter has grown exponentially; however, in classical engineering, the amount of material that can be processed by a plant has undergone only a linear growth. Thus the exponential growth of the former strongly affects the electronic devices at nanodimensions.

As a result, as devices and systems approach the nanoscale driven by the present trends in nanotechnology,[2] the strong relationship and sharp separation between transient and steady responses are broken and blurred as the passing electron−transistor nuclei interactions become major contributions. Thus, from a system point of view, transient times in nanosystems are longer and may differ from those in similar microelectronic systems.

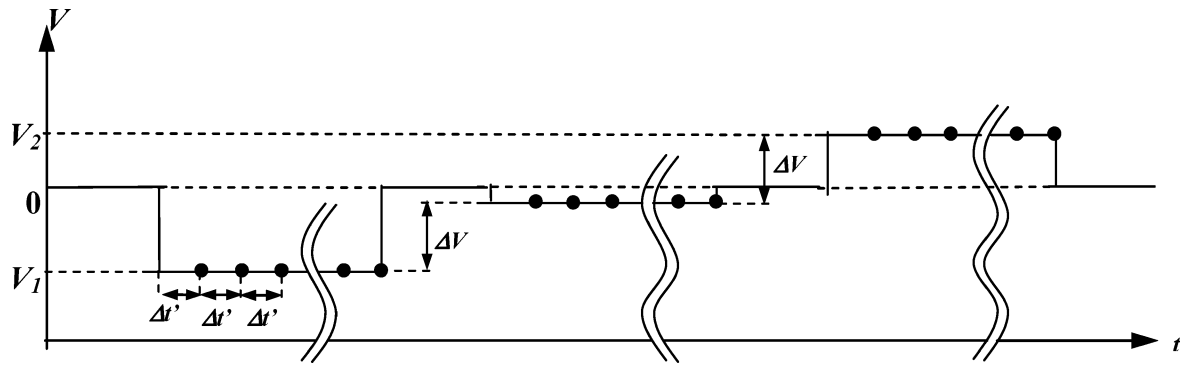

Figure 4. For the static current−voltage measurements, the applied voltage sweeps from V_1 and is held constant at V_1. Current is measured at every $\Delta t'$. When the system enters into a steady state, that is, the current oscillates in a predictable manner, the measurement is stopped manually, the applied voltage is set to zero, and the next step follows.

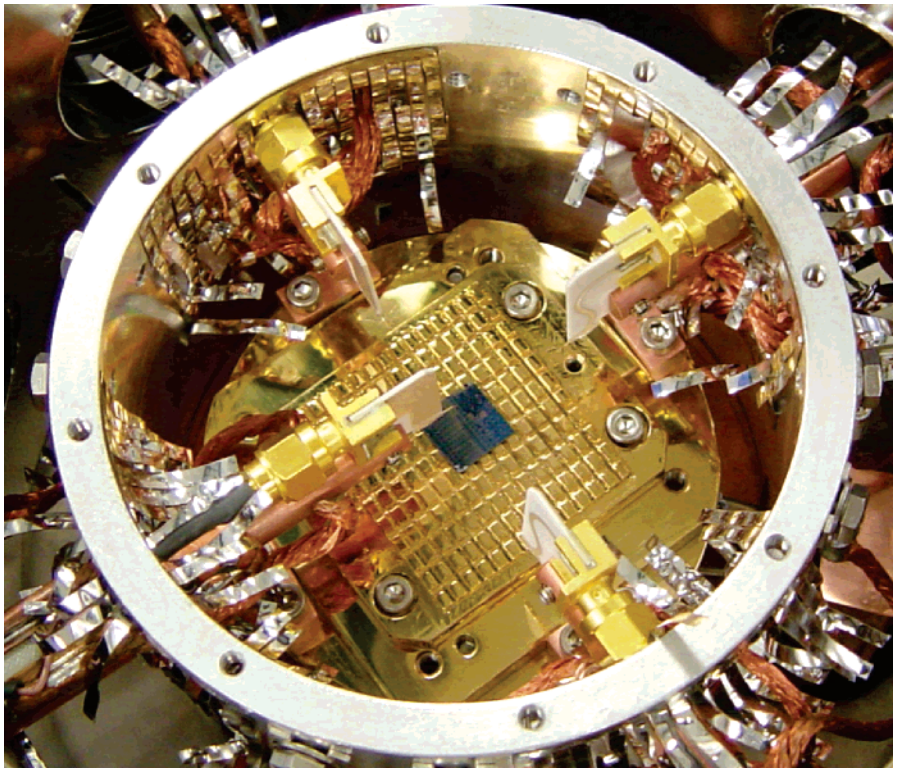

Figure 5. Probe station (Lakeshore cryogenic) used to measure the nanocell device. The probe station provides a high-vacuum environment ($\sim 10^{-7}$ Torr) to eliminate any free particles in the neighborhood of the sample.

2. Procedure and Methods

To test the above assumptions, we have performed several electrical experiments of nanosized metallic structures. The structure we test is a piece of discontinuous gold film deposited on a silicon dioxide substrate, as shown in Figure 2. A scanning electron microscope (SEM) image shows that the gap between the gold islands is around 5 nm. There are two probe tips made of palladium and titanium at each side of the film to allow the application of electric fields. The separation between tips is 3 μm.

The transient current−voltage measurement is performed with a built-in function of a HP4145A semiconductor parameter analyzer.[3] As shown in Figure 3, the applied voltage is swept following a staircase according to the input parameters: start voltage, V_1, stop voltage, V_2, voltage step, ΔV, delay time, Δt. The current is measured at the end of each voltage step.

For the static current−voltage measurements, we combine the time-domain measurement function of the HP4145A and our custom-designed Labview control program.[4] As shown in Figure 4, in the time-domain measurement, a fixed voltage is applied while the current is measured in every $\Delta t'$. Once the current is considered stable or steady, the voltage goes down to zero, and then the next voltage is applied.

Because we are testing a system involving nanoscale features, any free particles in the ambient environment might interfere with the normal operation of the system. To avoid this environmental influence, the sample is placed inside a high vacuum (about 10^{-7} Torr) chamber (Figure 5) during the measurement.

3. Results and Discussions

Before the static voltage sweep is applied, we performed a transient current voltage measurement. The voltage sweeps from 0 to 5 V with a step size of 0.05 V. Figure 6 shows a transient current voltage characteristic obtained from the device constructed by discontinuous gold film. The delay time for the measurements is set to 0.1 s (Figure 3). In the low-voltage region, the current voltage curve is slightly smoother than the high-voltage region.

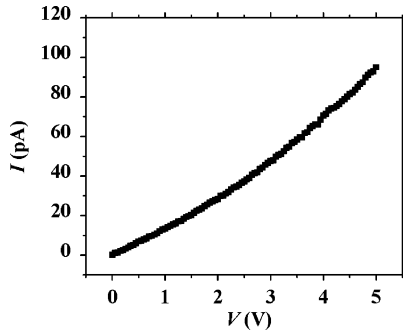

Figure 6. Transient current−voltage characteristic of a discontinuous gold film device.

The static voltage sweeps from 0 to 5 V with a step size of 0.1 V. The current is recorded every 10 s. Figure 7a−c shows the measured current versus time in three different voltage steps: 0.1, 2.4, and 5.0 V. It is clear from the plot that, for a fixed voltage, the current oscillates around a relatively stable value. This current oscillation is the "transient" behavior of the device, as compared to macroscopic electrical devices, for example, a normal resistor, which yields a fixed current when a fixed voltage is applied. The discontinuous gold film is a two-dimensional array of gold clusters with nanosized separations. Because there is no other substance inside the system, the conduction of current is strongly affected by the movement of gold atoms. As the voltage is applied, the gold atoms diffuse by electron migration and form quantum nanosized filaments[5−7] (which are different in nature to the widely studied classical microfilaments). As the current flows through the nanofilaments,

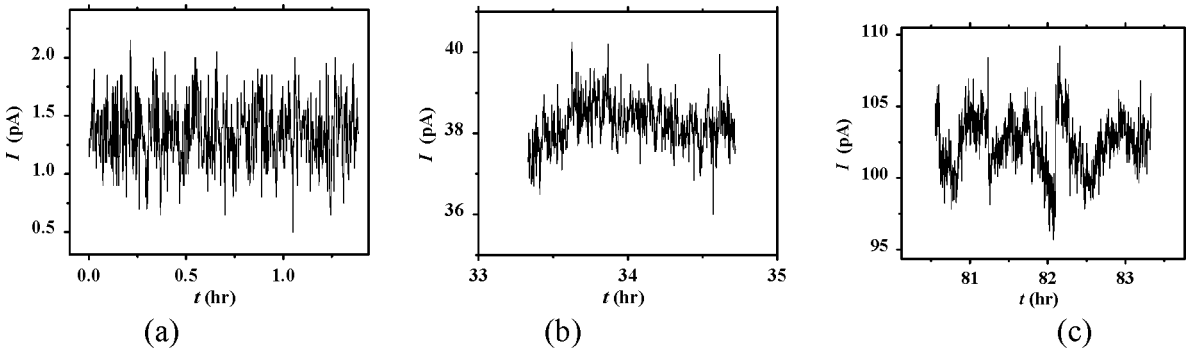

Figure 7. (a) Current vs time plot when the applied voltage $V = 0.1$ V; (b) current vs time plot when $V = 2.4$ V; (c) current vs time plot when $V = 5.0$ V.

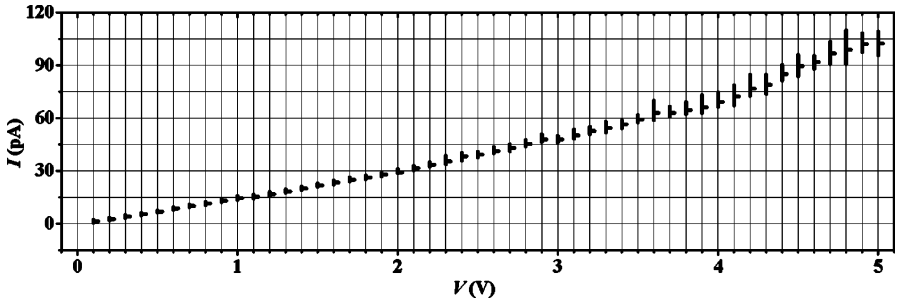

Figure 8. High and low values for the measured current in each voltage step. These values are connected by a vertical line with a tick mark displaying the mean value.

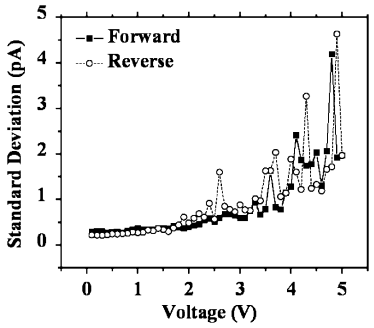

Figure 9. Standard deviation of the current flowing through the nanocell at each applied voltage.

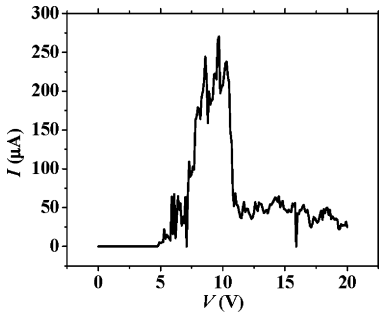

Figure 10. Typical NDR characteristics of a discontinuous gold film.

the local temperature inside the filaments also increases, which results in the breaking of the nanofilaments. As a result, the current increases by the forming of nanofilaments and decreases by the breaking of nanofilaments, forming a variety of nanocluster structures.

Figure 8 displays the high and low values of the measured current connected by a vertical line with a tick mark displaying the mean value. We find that the higher the applied voltage, the more the current oscillates. This feature is also clearly shown by observing the standard deviation of the current versus the voltage plot shown in Figure 9. Because the local temperature increases with the applied voltage and the self-diffusion coefficient of the gold clusters increases accordingly,[6] the gold atoms vibrate more vigorously. This explains the strong oscillation of currents at high voltages.

In addition, the level of uncertainty of the current also increases as the voltage increases. For instance, when the applied voltage is 4.8 V, the current ranges from 80 pA to 100 pA. At the next step, that is, $V = 4.9$ V, the current ranges from 97 pA to 108 pA. This uncertainty has a strong impact on the transient current−voltage measurements, yielding results in the choppy region of the current−voltage curve in the high voltage area, as shown in Figure 6. On the other hand, the current uncertainty also washes out or creates artificial negative differential resistance (NDR) characteristics, as shown in Figure 10. If during a measurement the current is 100 and 98 pA at 4.8 and 4.9 V, respectively, a negative differential resistance behavior is observed. However, if the current is 95 pA at 4.8 V and 100 pA at 4.9 V, then the NDR is not observed. In fact, NDR has been reported in several experimental papers[6,8−12] where maybe "nonstatic" current−voltage measurements were performed. A large amount of work on single molecules has been reported indicating switching and NDR; it would be convenient to reanalyze those results to find out whether they are really electrical in nature as it takes place in standard microelectronics or they are due to nuclear effects, as the experiments reported in this work.

In addition, it takes a longer amount of time for the device to reach a steady state at higher voltage. As seen from Figure 7a, when the applied voltage is 0.1 V, the system immediately enters into a quasi-static stage, that is, although the current oscillates, the mean value of the current remains almost constant. However, at higher voltage, $V = 5.0$ V in Figure 7c, for instance, the current oscillates for more than 4 h and still does not reach a static or quasi-static state.

4. Conclusions

We reveal new insights intrinsic to the nature of nanosized systems under the effect of electric fields. As the dimensions of today's electronic devices scale down to the nanolevel, the relative amount of electrons flowing through devices increases tremendously. This triggers displacements and oscillations of atoms, yielding large time constants or long-lasting transient behavior. The design of nanodevices needs to consider this transient behavior and to utilize these inherent characteristics for some specific functions such as those related to memory, logic, and amplification.

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