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Metrology for Molecular Electronics[†]

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Abstract

We discuss some of the complex issues associated with the metrology of molecular electronic devices and describe an electrical characterization method to assess molecular crossbar devices. Experimental data is shown for an eicosanoic acid crossbar device that exhibits controllable switching hysteresis. This two-state system is due to the presence of molecules in the sample, but it is unlikely that it is due to an intrinsic property of the eicosanoic acid. A mechanism associated with the molecule/electrode interface is the most likely cause of this hysteresis. These data exemplify the need for improved control and understanding of the detailed chemistry of molecule/electrode interfaces and illustrate that the properties of molecular electronic devices are determined by the entire device structure consisting of the molecules and the electrodes.

1. INTRODUCTION

Scaling the size of the component devices in integrated circuits has been the driving force behind computer performance increases for over 30 years. The silicon-based CMOS FET (complimentary metal oxide semiconductor field effect transistor) which is the current basis of ULSI (Ultra Large-Scale Integration) circuits, has been scaled so serverely that it is beginning to encounter fundamental limits associated with the laws of quantum mechanics and the limitations of fabrication techniques. In order for computer performance to continue to increase, entirely new nanoelectronic device structures and computational paradigms may be required to augment and/or replace the standard planar CMOS devices. Molecular electronics is one technology being aggressively pursued by DARPA [1] and others that may enable a future generation of much smaller, more densely integrated devices which will ultimately be more powerful, more sophisticated, and more portable.

Recently, impressive laboratory demonstrations of molecular electronic structures have been widely reported in both scientific journals and the popular press. [2-9] However, the results reported for these exciting new devices are difficult to independently reproduce, and many scientific researchers are only concerned with initial, proof of concept demonstrations. In order for these new types of devices to successfully and rapidly develop into a viable technology, reliable and reproducible measurement and analysis methods are required. In other words, molecular electronic metrology is needed.

A fundamental understanding of charge transport through molecules and molecular ensembles will greatly aid the development of molecular electronics technology. However, determining the correspondence between synthesized molecular properties and subsequent device behavior remains difficult,

largely because electrode-molecule interfaces are often poorly defined. To develop the needed understanding, a reliable electronic method to measure molecular monolayers and small numbers of molecules is needed. Molecular measurements have been reported from a variety of molecular electronic test structures (METS) such as nanopores [3,6], break junctions [7, 8], crossbars [2,4], and crossed wires [9]. To date, crossbar devices consisting of a molecular monolayer and a tunneling barrier sandwiched between crossed metal lines have been one of the most successful METS. Also, a crossbar-based architecture is the dominant scheme being explored for molecular electronics applications. [10]

We report here the results of electrical measurements of alumina (AlO_x) tunnel-junction based eicosanoic acid crossbar devices. These devices exhibit a switching hysteretic behavior that is due to the presence of molecules in the sample, but it is unlikely that the hysteresis is due to an intrinsic property of the eicosanoic acid. The switching arises from the interaction of the molecules with the electrodes. This example illustrates that the properties of molecular electronic devices are often determined not by the molecule alone, but by the entire device consisting of both the molecules and the attachment electrodes.

2. EXPERIMENTAL RESULTS

It is critical that METS are well characterized to ensure that electrical results can be attributed to the molecules and not an artifact of the test structure itself. A methodology to characterize tunnel junction based crossbar METS [2,4,10] (one example is shown schematically in the Figure 1a insert) is as follows: (1) crossbars free of molecules are measured to determine the maximum conductivity through the tunnel barrier; (2) two lines that do not cross are measured to determine the leakage paths through the substrate, etc.; and (3) crossbars containing a monolayer of molecules that are expected to be insulators (for example, long chain alkanes such as eicosanoic acid (Figure 1a insert)) are electrically measured. This set of measurements should determine the electrical characteristics of the crossbar METS and allow the properties of candidate molecular electronic molecules to be decoupled from the METS.

The crossbar devices used in this study are fabricated by defining Al lines (nominally 5 μm, 10 μm, and 20 μm wide) on an oxidized Si-substrate. A molecular monolayer of eicosanoic acid (CH₃(CH₂)₁₈CO₂H, a.k.a. arachidic acid) -- a ≈2.5 nm long "molecular insulator" with a large band gap (≈8 eV) -- was deposited onto the wafer as a Langmuir-Blodgett (LB) film. A second set of lines (5 nm Ti/100 nm Al) was deposited (via a shadow-mask) on the molecular monolayer, perpendicular to the original lines to form devices (schematically shown in the insert to

Figure 1a). The quality of the LB films allows relatively large area

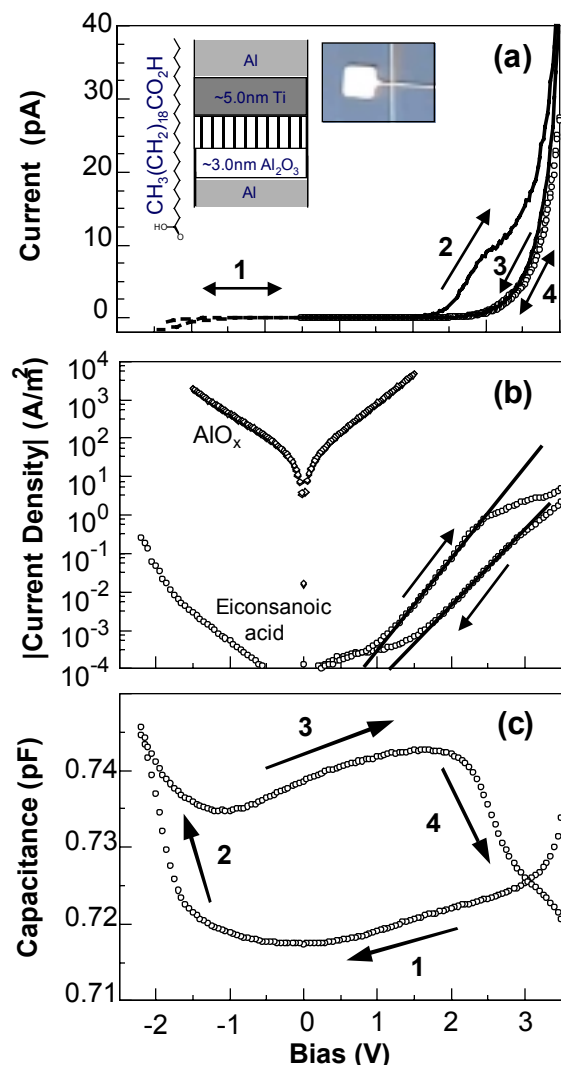


Figure 1. (a) Typical current-voltage (IV) curves for an eicosanoic acid crossbar device. [1] (dashed line) By sweeping to negative bias and back, the device is set to the high-current state. [2] (solid line) The device is in the high-current state as it is swept forward to positive bias where the device switches to the low-current state. [3] (solid line) The device is in the low-current state as it is swept down to 0 V bias. [4] (open circles) the device stays in the low-current state until it is set high again by the application of a large negative bias. (a) INSERTS: Schematic of the chemical structure of eicosanoic acid. A schematic cross-section and a top-view photograph of an eicosanoic acid crossbar device. (b) Typical IV curves for an AlO_x tunnel junction (no-molecule control) device (open diamonds) and for an eicosanoic acid device (open circles). Tunnel theory fits are shown for the eicosanoic acid device. (c) Capacitance-voltage (CV) curves (1 MHz) for an eicosanoic acid crossbar device. [1] The device is swept down from high bias in its low-capacitance state. [2] At “large” negative bias (≈ 2 V), the device switches to the high-capacitance state. [3] The device remains in the high-capacitance state as it is swept forward. [4] The device

devices to be formed by this process. Devices were

simultaneously fabricated with and without molecular monolayers on the same wafer in order to have optimal no-molecule control devices.

Ambient environment, room-temperature dc current-voltage (IV) and ac capacitance-voltage (CV) measurements were used to electrically characterize these device structures. The total direct current through these moderately large area devices is substantially larger than in devices with nanoscale areas. The larger current improves experimental signal to noise in our IV measurements. The large device areas lead to experimentally measurable capacitance values, allowing us to take what we believe are the first CV curves of molecular-monolayer-based devices.

Figure 1b shows IV curves for crossbars with and without molecules. The control devices without molecules shows typical tunneling IV curves for an AlO_x barrier. The molecules have a dramatic effect on the IV measurements, lowering the current at a given voltage by about five orders of magnitude and giving rise to a hysteresis in the positive direction. The total leakage current and instrumentation noise for these devices is <10 fA, as determined from measurements of two disconnected lines. These IV data are direct evidence that the molecules affect the device current; the IV measurements are not arising from artifacts of the METS.

Capacitance voltage curves were also measured for eicosanoic acid devices (Figure 1c) and no-molecule controls (not shown). From the capacitance ($C = \epsilon_0 \kappa A/d$; where ϵ_0 is the permittivity of free space, κ is the dielectric constant, A is the area, and d is the thickness) of the no-molecule control devices, it can be found that the thickness of the AlO_x tunnel barrier is ≈ 3 nm. The capacitance of the eicosanoic monolayer can be inferred from the total molecular device capacitance and the capacitance of the no-molecule control devices. By using a dielectric constant typical of this category of molecules ($\kappa \approx 2.4$), it is determined that the effective thickness of the LB film is 1.1 nm. While the film is thinner than expected, it is in agreement with the values obtained by “Simmons” analysis [12] of the dc tunneling current.

The strong hysteresis in the dc IV curves indicates that these molecular tunnel junction devices exhibit bi-stable properties. These states can be set by applied voltage, as illustrated by the data in Figure 1a (described more fully in the figure caption). A negative bias (slightly larger in magnitude than -2 V) sets the device to the “high” current state. When the voltage is swept forward, the device stays in this high current state until reaching moderate positive voltages at which time it drifts to the low current state. The device will stay in the low current state as shown in figure 1a until it is reset to the “high” current state at negative bias. It should be noted that IV measurements of these programmable two-state molecular devices were independently obtained in two laboratories (HPRC, Palo Alto, CA, and NIST, Gaithersburg, MD) illustrating the robust nature of these devices and giving strong evidence that the observed hysteresis is intrinsic to the device structures and not a measurement artifact.

A two-state capacitance loop is also measured (Figure 1c) in the eicosanoic acid devices corresponding to the two states observed in the IV data. Once set to the low capacitance state at positive biases, the device stays in this state until reaching negative

voltages slightly lower in magnitude than -2 V. The capacitance rapidly increases (with further decreasing bias) to a high capacitance state. This increase in the capacitance corresponds to setting the high dc current state. The capacitance remains in this high-capacitance state until it reaches positive biases slightly larger than $+2$ V, where the capacitance abruptly drops with increasing bias corresponding to setting the low-current state.

A remnant capacitance measurement, similar to the dc remnant molecular signature described in [4], was used to confirm this small capacitance hysteresis and ensure that it is a feature of the device, and not arising from time-dependent drift or other instrumental errors. To obtain a remnant capacitance curve, the bias is switched between a “setting” voltage (which is stepped) and a “monitor” voltage (in this case 2 V), as illustrated in the inset to Figure 2. The measured capacitance at the monitoring voltage is then plotted as a function of the “setting” bias. Figure 2 shows a typical remnant capacitance curve for these eicosanoic acid devices. The observed hysteresis is similar to that measured by the CV hysteresis measurement. Because the hysteresis is recorded at a single voltage in this case, it is perhaps the most reliable method for probing the switching. The same two-state capacitance observed in the CV hysteresis loop is observed by this remnant capacitance technique.

3. DISCUSSION

Because eicosanoic acid is a long chain alkane, it is expected to form good insulating layers; therefore, it is highly improbable that the two-state system giving rise to the observed IV and CV hysteresis is an intrinsic property of this molecule. Similar switching hysteresis has also been observed for other molecules (chlorophyll B and fast-blue, an azo-dye) in this AlO_x tunnel junction type of crossbar [13], indicating that the mechanism underlying the hysteresis is associated with the combination of the molecules with the Al/AlO_x and Ti/Al electrodes. (It should be noted that no hysteresis is observed for the no-molecule control samples in either the IV or CV curves.) While a detailed mechanism that describes this two state system cannot be determined, a charge-transfer model does account for the observed electrical data. In this charge-transfer model, at negative biases sufficient to set the “high” state, charge is trapped in the molecular region. This trapped charge lowers the tunneling barrier leading to the higher current state. When the device is under positive bias, the charge leaks out (or is neutralized), returning the device to its original low current state (i.e., a larger tunneling barrier). It is most likely this change in charge occurs at the carboxylate/alumina interface, and not in the bulk of the molecule or at the Ti/alkane interface. (Although it could be argued that it occurs near this $\text{Ti}/\text{molecule}$ interface.) These data highlight the need for improved characterization and control of the interfaces between molecules and electrodes.

Technologically, these devices can be viewed as reconfigurable switches, the switch being closed when the “high” current state is set at negative bias while the switch is opened at positive bias when the device is set to the low-current state. Such switches are highly sought after to form circuitry such as dense molecular memories. However, there are transient effects in these devices that appear to limit their technological value. First, the amplitude of the high current state decreases with subsequent sweeps. Further, the hysteresis is largest in the range of $+2.5$ V to $+3$ V.

These positive biases are large enough that the device is being

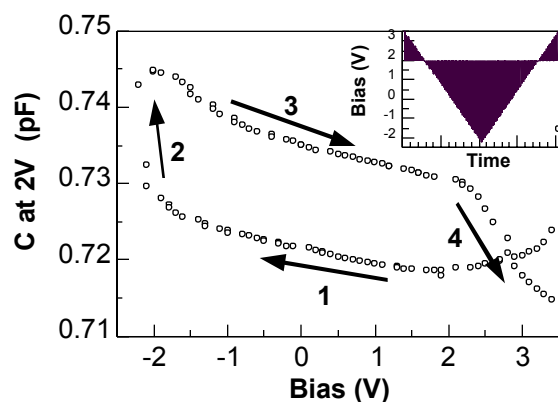


Figure 2. Remnant capacitance-voltage curve (1 MHz) for an eicosanoic acid crossbar device. INSERT: The voltage bias sequence for this remnant CV curve. It should be noted that this is a more reliable method for observing the device cycle (1-4) described in Figure 1c.

driven towards the low current state.

4. CONCLUSIONS

In conclusion, we have shown measurements of molecular electronic devices that exhibit controllable, hysteretic electrical properties. In addition to dc IV curves, ac CV measurements were used to characterize these devices in an attempt to better understand the underlying physical mechanisms. Because eicosanoic acid is a long-chain alkane with a carboxylate head group, it is expected to be an insulating film in electrical devices. The measurements shown here, in which an exciting two-state conducting system is obtained from devices containing a “control” molecular monolayer, illustrate that the final electrical properties of molecular devices are determined by the combination of the molecular film and the attachment electrodes. This seems to indicate that these alumina tunnel junction based devices are not ideal test structures for determining the intrinsic electrical properties of the molecules themselves. Better control and understanding of the molecule/electrode interfaces is needed in order to observe the intrinsic conduction properties of candidate molecular electronic molecules. While this need is illustrated here for tunnel junction based molecular devices, improved control of contacts is also needed for other types of molecular devices such as those based upon nanopores [3,6 14]. In order to achieve this improved control, the complex chemistry of the molecular/electrode interfaces must be thoroughly characterized, as done, for example, by Fisher et al. for the $\text{Al}/\text{carboxylate}$ system. [11] This two-state behavior was independently measured in two separate laboratories, indicating that the effect is not a measurement artifact and illustrating that these devices are robust enough to ship via conventional methods and remain active.

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6. References

- † Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.
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