

The Characterization of Silicon-Based Molecular Devices

N. Gergel-Hackett*, C.A. Hacker*, L.J. Richter[†], O.A. Kirillov*, C.A. Richter*

**Semiconductor Electronics Division, [†]Surface and Microanalysis Science Division, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD, 20899*

Abstract. In order to realize molecular electronic (ME) technology, an intermediate integration with more traditional silicon-based technologies will likely be required. However, there has been little effort to develop the metrology needed to enable the fabrication and characterization of CMOS-compatible ME devices. In this work, we used two different characterization techniques to evaluate the potential of molecular electronic device materials with increased CMOS-compatibility. The first technique was the electrical characterization of a simple prototypical molecular electronic device structure fabricated on a silicon substrate with a (111) crystalline orientation. To compare these electrical results with the structure of the molecular monolayers (which is critical to confirm that the molecules are playing a role in charge transport), a novel backside incident FTIR technique (the second technique) was used to spectroscopically characterize the molecular monolayers under a full top-metallization. The combination of these two characterization techniques showed that silver top contacts, unlike gold top contacts, do not penetrate and displace the molecular monolayer. We then fabricated and electrically characterized a prototypical molecular electronic device structure using the silicon orientation that is traditionally used for CMOS devices (Si (100)). Assembly on Si (100) can enable integrated ME-CMOS structures that allow on-chip characterization of molecular devices and is a major step on the route to hybrid molecular-CMOS circuitry.

Keywords: molecular electronics, self-assembled monolayer, hybrid silicon/molecular devices

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INTRODUCTION

The field of molecular electronics is based on the potential of organic molecules with functional electrical properties to be used in place of traditional semiconducting devices.¹⁻³ Yet, one of the leading materials used in the fabrication of molecule-based devices, gold,⁴⁻¹⁰ is CMOS incompatible due to its propensity to form energy traps in silicon. Additionally, there is evidence that many of the materials used in molecular electronic devices chemically react with and/or migrate through the molecular monolayer, resulting in electrical device behavior that is dominated by artifacts, rather than the electrical behavior of the organic molecules.¹¹⁻¹³ Thus, it is imperative that methodologies are established to not only determine the electrical characteristics of integratable silicon-based devices, but to test that the device and substrate materials do not chemically react or migrate and disrupt the integrity of the molecular monolayer.

This work describes two techniques that were used to evaluate the potential of two different top contact materials (silver and gold) for use in silicon-based molecular electronic devices. The first technique

consisted of the fabrication and characterization of a silicon-based molecular electronic device structure (Figure 1). Then, in order to ensure that the mobility and/or reactivity of the top contact did not disrupt the molecular (octadecanol) monolayer during or after metallization, we performed a novel backside FTIR technique.¹⁴ This technique allowed for more in-depth understanding of the electrical characterization of the molecular devices. We then fabricated and electrically characterized Si (100) molecular electronic device structures.

The electrical and backside FTIR characterization techniques showed Ag to be a superior top contact material to Au and Si (100) to be a viable alternative molecular device material to Si (111). Because (100) is the Si orientation used for traditional CMOS devices, establishing its use in molecular electronic devices increases the potential for realizing a ME/CMOS hybrid circuit.

DEVICE FABRICATION AND ELECTRICAL CHARACTERISTICS

In order to evaluate different device top contact materials and bottom substrate crystalline orientations, we first fabricated a prototypical, planar, silicon-based, molecular electronic device structure (Figure 1). The substrates for the devices were 760 mm n-type silicon (111) wafers (0.001-0.1 ohm-cm resistivity). After cleaning the substrates with an RCA clean, we thermally grew 200 nm thick silicon dioxide films. Next, micron-sized square wells (with widths of 150 μm , 100 μm , 50 μm , 20 μm , 10 μm , 5 μm , and 2 μm) were patterned using standard photolithography techniques and etched using a 6:1 buffered oxide etch. The wafers were again cleaned, and a 10 nm thick sacrificial oxide was thermally grown. The wafers were then diced into pieces that were approximately 1.5 cm by 1.5 cm, and the sacrificial oxide was removed by dipping the samples into a 2 % hydrofluoric acid (HF) 98 % DI water solution (by volume), rinsed with DI water, and dried with streaming nitrogen. The samples were then immediately placed in a previously cleaned reaction vessel inside a nitrogen-atmosphere glove box with low water and oxygen levels (< 10 ppm).

Octadecanol monolayers were assembled in the oxide-defined wells following a procedure previously published.¹⁵ Briefly, the Si samples were immersed in a CH_2Cl_2 solution containing $\sim 10\text{mM}$ of octadecanol and were illuminated for 2 h on each side using a 6 watt UV lamp (254 nm) with an estimated intensity of $\sim 1.5 \text{ mW}/\text{cm}^2$ at the sample. After illumination, the samples were rinsed with CH_2Cl_2 .

After the monolayer assembly, the samples were double wrapped in air-tight containers and transported to the thermal evaporator for the top metallization. Immediately prior to the evaporation the control samples, which consisted of wells etched in the silicon dioxide without a molecular monolayer, had their native oxide removed using an HF/DI water solution (as described above) and were loaded into the evaporator.

The desired top metal (either silver or gold) was evaporated through a shadow mask with a 150 μm diameter circular opening at a chamber base pressure of less than $6.5 \times 10^{-4} \text{ Pa}$ ($5 \times 10^{-6} \text{ Torr}$). The evaporation rate was approximately 0.02 nm/sec for the first 10 nm and was gradually increased to approximately 0.5 nm/sec until the metal was approximately 150 nm thick. At this point the devices were removed and electrically characterized. The final molecular device structure is shown in Figure 1.

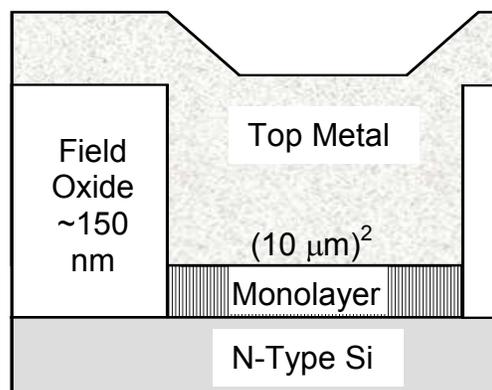


Figure 1. The molecular electronic device structure.

This prototypical molecular electronic device structure has increased CMOS integration potential due to its planar design and silicon substrate. Yet, in order to investigate improving this potential further, we fabricated and electrically characterized devices with different top contact materials. Electrical characterization was accomplished by probing the top evaporated metal contact and a backside wafer contact.

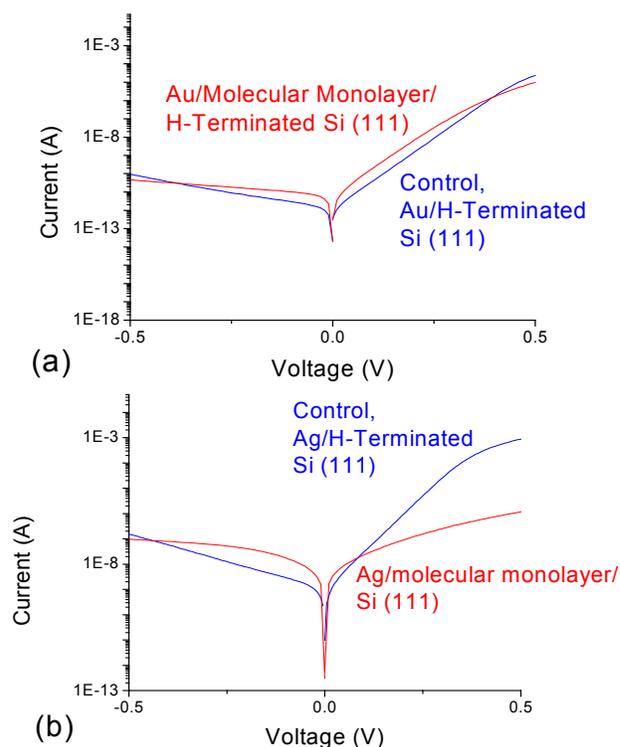


FIGURE 2. Representative electrical results for an octadecanol monolayer assembled on highly doped Si (111) in a 10 μm molecular device structure using a gold top contact (a), a silver top contact (b).

The electrical results from the molecular electronic device structures fabricated on Si (111) with gold top contacts (Figure 2(a)) and silver top contacts (Figure 2 (b)) are shown. Figure 2 (a) shows that when the top contact is gold, the material that is most widely used for molecular assembly and characterization, there is only a marginal difference between the I-V curve from the molecular device and that of the non-molecular control device. This may suggest that the electrical conduction of the gold-contacted molecular device is dominated by the current through the Schottky barrier formed by the top metal penetrating through the monolayer and contacting the bottom silicon.

The electrical results from the molecular electronic device structure capped with silver are distinctly different than the control. In fact, the current from the molecular device is actually higher at low biases than that from the control device. By modeling this junction at low bias as a Schottky barrier with the monolayer shifting the silicon surface dipole and associated silicon surface potential barrier, this increase in current is as would be expected for the octadecanols on n-type moderately doped silicon.^{16,17} At higher biases, the monolayer may act as a simple tunneling barrier, lowering the overall current.

These electrical characteristics show that, although gold may be a widely-used top contact material for molecule-based devices, the devices fabricated with gold show less of a molecular influence. Yet, when silver is used, which also happens to be a more CMOS-compatible material than gold, the electrical behavior is dependent on the presence of a molecular monolayer. These results suggest that silver is a superior contact material to gold.

BACKSIDE FTIR MEASUREMENTS

Although the electrical characterization of the molecular electronic device structures provided a valuable comparison between the structures with different top contact materials, a novel backside FTIR spectroscopy technique was used to provide additional insight into the physical differences between the molecular device structures that resulted in such characteristics. This technique is described in greater detail elsewhere¹⁴, but basically consists of using p-polarized backside reflection absorption infrared spectroscopy (pb-RAIRS) to characterize octadecanol monolayers assembled on an IR transparent substrate (such as silicon) capped with a metal layer (see Figure 3 (a)). We used this technique to evaluate whether or not the top metal used in our prototypical molecular device structures reacted with the monolayer or the bottom silicon and/or displaced the monolayer. For this characterization, we assembled the molecular

monolayers on pieces of Si (111) (2 Ohm-cm to 15 Ohm-cm resistivity), capped them with silver or gold, and performed the backside spectroscopy (pb-RAIRS).

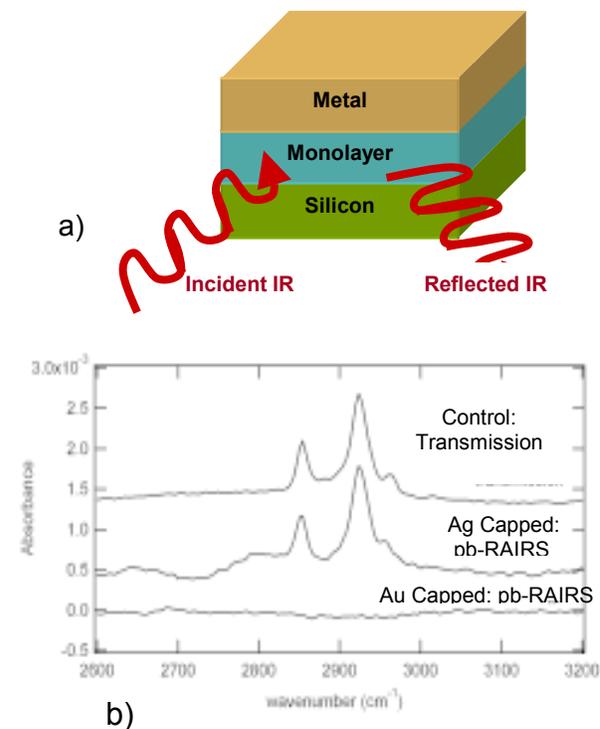


FIGURE 3. a) Backside FTIR technique (pb-RAIRS), b) transmission spectroscopy of a monolayer with no metallization, pb-RAIRS of a monolayer capped with silver, and pb-RAIRS of a monolayer capped with gold.

Shown in Figure 3 (b) are the IR spectra of the initial monolayers (recorded in transmission) and the monolayers after metal deposition (recorded via pb-RAIRS). The dominant features in this spectral range arise from CH stretching vibrations. The intensity can be related to density, while the specific frequencies provide insight into local chain conformation. The initial monolayer is representative of a dense, moderately well ordered film.¹⁴ Following the deposition of Au, all monolayer features were absent, indicating that the molecules are no longer at the interface. The monolayer features persist following the deposition of Ag, indicating that Ag is significantly less perturbative of the film. These results support the electrical characterization and provide further evidence of the advantages of silver over gold as a top contact material.

THE FABRICATION OF MOLECULAR ELECTRONIC DEVICE STRUCTURES WITH INCREASED CMOS-COMPATIBILITY

Although most of the research of monolayer assembly on silicon to-date has been performed on Si (111),^{15,18-21} because Si (100) is more widely used in the CMOS industry, we also fabricated and characterized molecular device structures using this Si orientation (Figure 4). Molecular device structure fabrication was performed as previously described, but on Si (100) wafers (<0.001 Ohm-cm resistivity). Prior to fabrication, we first established that molecular monolayers assembled on Si (100) are comparable in quality to monolayers assembled on Si (111).²² Because the use of silver as a top contact for the Si (111) devices resulted in a more distinct difference between the electrical characteristics of the molecular and control device structures (see Figure 2), we used silver as the top contact for the Si (100) device structures.

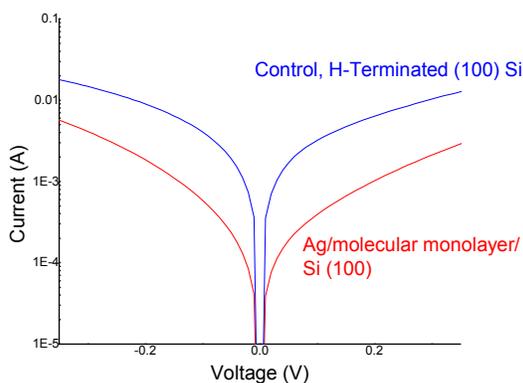


Figure 4. Representative electrical results for an octadecanol monolayer assembled on degeneratively doped Si (100) in a 5 um molecular device structure.

Figure 4 shows a distinct difference in the electrical characteristics of the molecular and non-molecular device. However, rather than showing a higher current at low biases as seen in Figure 2 (b), the molecular devices showed lower current than the controls at all biases tested. This discrepancy may be explained by the use of degeneratively doped silicon rather than the highly doped silicon that was used for the Si (111) devices; the monolayer on the degeneratively doped silicon may simply act as a tunnel barrier at all biases. The use of degeneratively doped silicon also resulted in more symmetric I-V curves and higher current magnitudes for both the control and

molecular devices. Work is currently being performed to establish the specific relationship between substrate doping, molecular monolayer dipoles, and electrical characteristics. Overall, the electrical characterization showed that Si (100) is a comparable device material to Si (111).

CONCLUSIONS

This work has demonstrated how two different techniques, electrical characterization of a prototypical molecular electronic device structure and backside FTIR, were used to evaluate the possibility of molecular electronic device fabrication using more CMOS-compatible materials. The characterization techniques found silver to be a far superior top contact, due to gold's propensity to displace the monolayer and dominate in electrical transport. This work also showed that the use of Si (100), in place of the more widely explored Si (111), is a viable possibility for increasing the potential for molecular electronic devices to be integrated with traditional CMOS technology.

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