AVS 2016; Thin Film Division

TF13 Self-assembled Monolayers, Polymer Brushes and Organic Multi-layers [2700 character limit; current count: 2697 (with spaces)]

Integration of Redox-Active Diruthenium-based Molecular Layer onto Electrodes for Memory Device Applications

S. Pookpanratana,<sup>1</sup> H. Zhu,<sup>1,2</sup> J. W. F. Robertson,<sup>1</sup> S. N. Natoli,<sup>3</sup> E. G. Bittle,<sup>1</sup> C.A. Richter,<sup>1</sup> T. Ren,<sup>3</sup> Q. Li,<sup>2</sup> and C. A. Hacker<sup>1</sup>

<sup>1</sup> Engineering Physics Division, National Institute of Standards and Technology

<sup>2</sup> Department of Electrical and Computer Engineering, George Mason University

<sup>3</sup> Department of Chemistry, Purdue University

Attaching and integrating electrochemically-active molecules to a variety of different surfaces is of importance for applications in catalysis, memory devices, and molecular electronics. With the increasing demand for personal electronics, growth in Flash-based memory has increased dramatically. However, the dimensional scaling of memory components faces many critical material limitations. A critical component to the memory device is the floating gate or charge trapping layer. To scale the charge trapping layer to nanometer dimensions, one approach is to use a discrete charge storage layer that is based on organic molecules.<sup>1,2,3</sup> Reduction-oxidation (redox) active organic molecules hold potential for memory devices due to their nanoscale dimensions, potential for high charge density, and synthetic flexibility that could be tailor-made for specific electronic functionality.

Here, we investigated the potential of diruthenium-bearing organometallic molecules as the charge trapping layer for memory devices. Diruthenium-bearing organometallic molecules display multiple redox states,<sup>4</sup> which makes them ideal to incorporate within non-volatile memory devices. Monolayer assembly is performed in a stepwise fashion by first forming azide-terminated monolayer on SiO<sub>2</sub> by using azidoundecyl trimethoxysilane followed by a Cu-catalyzed azide-alkyne cycloaddition click reaction to attach diruthenium (Ru<sub>2</sub>) compounds (note: SiO<sub>2</sub> serves as the tunneling layer).<sup>5</sup> Infrared spectroscopy and X-ray photoelectron spectroscopy confirmed the Ru<sub>2</sub> attachment. Ultraviolet photoelectron spectroscopy identified the occupied electronic levels of the hybrid organic-inorganic surfaces before and after click reaction. Voltammetric measurements on Ru<sub>2</sub>-terminated SiO<sub>2</sub>/Si and Au electrodes confirm that the Ru<sub>2</sub> is still electrochemically-active with accessible electronic states integrated on both surfaces.

To complete the memory capacitor device, an Al<sub>2</sub>O<sub>3</sub> layer (serving as a charge blocking layer) was deposited by atomic layer deposition over the molecular layer followed by a metal Pd gate. The impact of different Ru<sub>2</sub> compounds on the electronic structure and electrochemical properties of the electrodes and properties of the memory devices will be compared. Our results will provide future design considerations and limitations for molecular-integrated memory devices.

- 1. T. Shaw et al., IEEE T. Electron. Dev. 58 (3), 826-834 (2011).
- 2. D. Beckmeier and H. Baumgärtner, J. Appl. Phys. 113 (4), 044520 (2013).
- 3. H. Zhu, et al., Appl. Phys. Lett. **103** (5), (2013).

- 4. W.-Z. Chen and T. Ren, Inorg. Chem. **45** (20), 8156-8164 (2006).
- 5. S. Pookpanratana, et al., Langmuir **30** (34), 10280-10289 (2014).