

Chemical Approaches to the Improved Performance of Nanoelectronic Devices

Noel N. Chang

Final Seminar

May 6, 2014

Rapid advances in lithographic methods have enabled miniaturization of silicon-based information storage and processing at a steady rate for the past fifty years.¹ As feature size approaches the atomic limit, however, further improvements are beginning to be limited by the fundamental physical constraints of the materials.² To overcome these challenges and continue the technological advances embodied in Moore's law, it is vital to investigate alternative materials and fabrication methods.

Molecule-based systems in particular have the potential to extend Moore's law by utilizing the intrinsic characteristics of single molecules rather than the cooperative properties of bulk materials. Molecular bistability, the phenomenon in which molecules possess two commutable states, could provide a basis for replacing transistor-based memory storage components by encoding 0's and 1's in individual molecules.³ Many bistable mechanisms have been investigated; however, a main challenge to overcome is the persistence of the written states. Often, the readout process injects sufficiently high energy to scramble the molecular state. To prevent this, we propose a bistable molecular device in which the writing and readout processes employ independent mechanisms using different probing methods.

The proposed system utilizes redox-triggered spin reorganization in a transition metal complex as the bistable parameter. Using the proper metal-ligand pairing, a one electron redox process can lead to a change from a low-spin to a high-spin state, and cause a significant change in the magnetic and electronic properties (Figure 1a). The writing process can be achieved electrochemically by STM, whereas the readout process can be achieved magnetically by scanning magnetic microscopy.

Substituted cobalt(II/III) tris(pyrazolylborate) species, CoTp_2 , were selected as the synthetic target (Figure 1b). These species exhibit the desired electronic configurations, are chemically and thermally robust, and can be functionalized at boron to provide surface attachment capabilities.

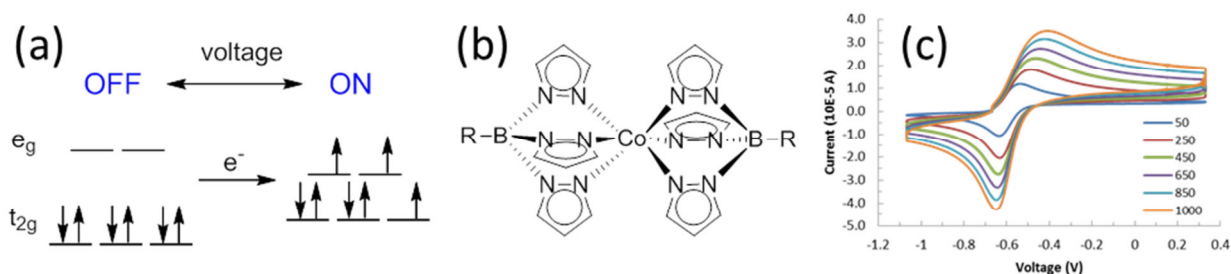


Figure 1. (a) Proposed bistable system utilizing spin-reorganization. (b) Synthetic target based on the electron configuration requirements. (c) Scan rate dependence of redox processes.

Several functionalized species of stoichiometry $\text{Co}[(\text{pz})_3\text{BC}_6\text{H}_4\text{R}]_2$ where $\text{R} = \text{Br}, \text{CO}_2\text{H}, \text{CH}_2\text{OH},$ thiazolidine, and $\text{CH}_2\text{NH}(\text{CH}_2)_2\text{SH}$ were synthesized. Chemical and electrochemical characterizations were performed in both bulk and thin film forms. The cyclic voltammograms of

the CoTp_2 complexes are scan rate-dependent due to the kinetic barrier associated with the spin reorganization upon oxidation (Figure 1c).⁴ Monolayer depositions of thioazolidine and thiol-substituted species were conducted in two ways. Gold substrates were either immersed in the precursor solutions, or exposed to precursor vapor in a vacuum chamber. The resulting samples showed features by in both STM and AFM due to surface-bound CoTp_2 species (Figure 2).

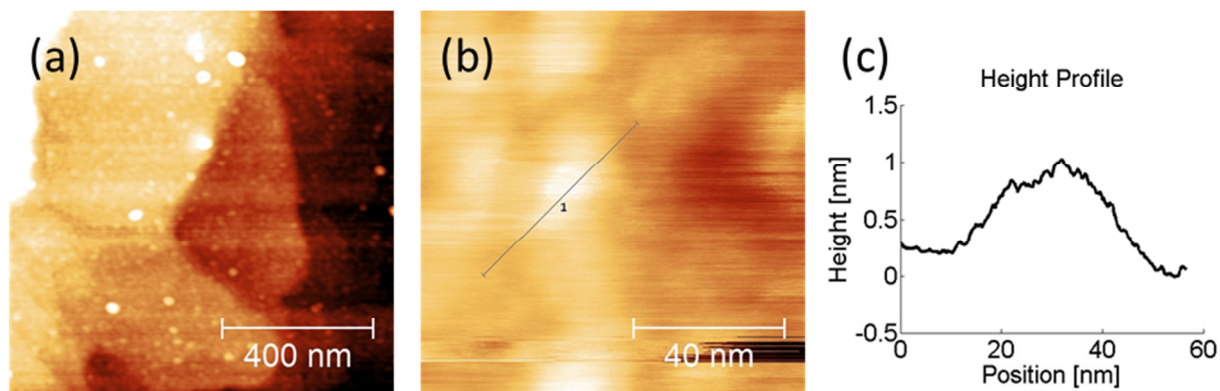


Figure 2. (a-b) Ambient AFM images of a gold substrate treated with a toluene solution of thiazolidine substituted CoTp_2 . (c) Height profile along line indicated in figure (b). Features of similar dimension were observed throughout the substrate.

Carbon-based nanomaterials, such as carbon nanotubes (CNTs) and graphene, are increasingly being examined for applications in nanoelectronics. CNT networks and polycrystalline graphene can be made in large quantities, but the electrical properties of these materials suffer from resistive defect sites—intertube junctions in CNT networks and grain boundaries in polycrystalline graphene.⁵ We aim to develop a chemical treatment that could remedy these deficiencies.

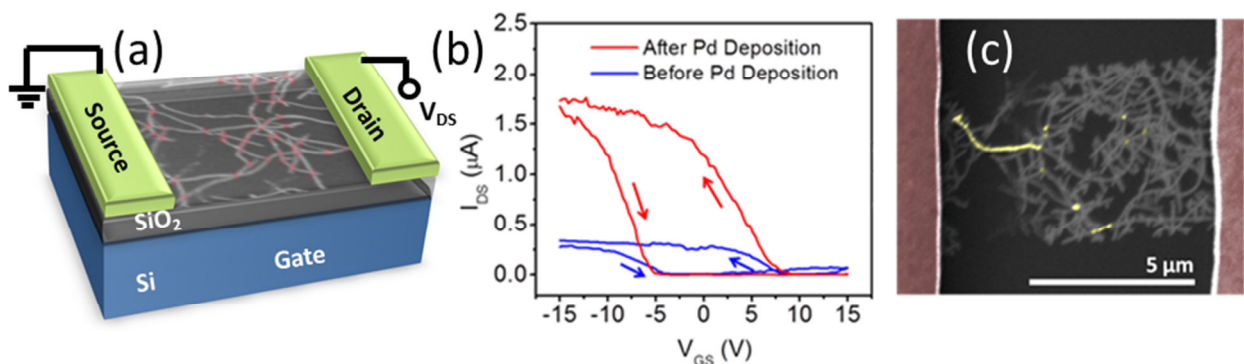


Figure 3. (a) Proposed nanosoldering reaction scheme. (b) Typical electrical characterization before and after treatment. (c) SEM image of a CNT network device after treatment with HfB_2 .

In a process we named “nanosoldering,” a conductive material is deposited at the resistive junctions by operating the device in an atmosphere of a chemical precursor (Figure 3a).⁶ The

resistive heating that occurs at “bad” junctions induces a thermal CVD process. The conductive material that is deposited at these junctions improves the overlap between the two nanotubes and decreases the junction resistance. Two precursors were utilized for this method: CpPd(allyl) to deposit Pd(0) and Hf(BH₄)₄ to deposit HfB₂. In the SEM images post treatment, deposition can be observed on intertube junctions as well as along the length of some tubes (Figure 3c). The latter can be eliminated by selecting the appropriate experimental conditions. For treatment with the Pd precursor, the I_{ON}/I_{OFF} ratio improved by a factor of 6 on average (Figure 3b). On the other hand, no improvement was observed for samples treated with the HfB₂ precursor; this is due to the large mismatch in workfunctions between the individual CNTs and deposited HfB₂, which creates a Schottky barrier. On the other hand, the workfunction of Pd is better matched with that of CNTs.

A solution process was developed to improve the scalability of the nanosoldering process by eliminating the necessity of using a vacuum system and highly volatile chemical precursors. To do so, the chemical precursor was introduced by spincoating onto the solid substrate. The nanosoldering process was conducted in a commercially available probe station either in air or under vacuum, after which the excess material and byproduct were removed by a solvent rinse. Using this method, we showed a comparable degree of device performance improvement using a nonvolatile Pd precursor, Pd₂(dba)₃. We also obtained improved device performance with a new carbon-based precursor, 1,3,5-tris(2-bromophenyl)benzene. Finally, preliminary experiments were conducted on graphene devices, which showed that nanosoldering occurred along the grain boundary without significant device degradation, and suggesting that the nanosoldering process is compatible with graphene devices.

References

1. Moore, G. E. Cramming More Components Onto Integrated Circuits. *Proc. IEEE* **1998**, *86*, 82-85.
2. Tour, J. M. Molecular Electronics. Synthesis and Testing of Components. *Acc. Chem. Res.* **2000**, *33*, 791-804.
3. Minkin, V. I. Bistable organic, organometallic, and coordination compounds for molecular electronics and spintronics. *Russ Chem Bull* **2008**, *57*, 687-717.
4. De Alwis, D. C. L.; Schultz, F. A. Metal–Bis[poly(pyrazolyl)borate] Complexes. Electrochemical, Magnetic, and Spectroscopic Properties and Coupled Electron-Transfer and Spin-Exchange Reactions. *Inorg. Chem.* **2003**, *42*, 3616-3622.
5. Zhong, H.; Lukes, J. R. Interfacial thermal resistance between carbon nanotubes: Molecular dynamics simulations and analytical thermal modeling. *Phys. Rev. B* **2006**, *74*, 125403.
6. Do, J.-W.; Estrada, D.; Xie, X.; Chang, N. N.; Mallek, J.; Girolami, G. S.; Rogers, J. A.; Pop, E.; Lyding, J. W. Nanosoldering Carbon Nanotube Junctions by Local Chemical Vapor Deposition for Improved Device Performance. *Nano Lett.* **2013**, *13*, 5844-5850.