

Complex Nanostructures of Dissimilar Elements

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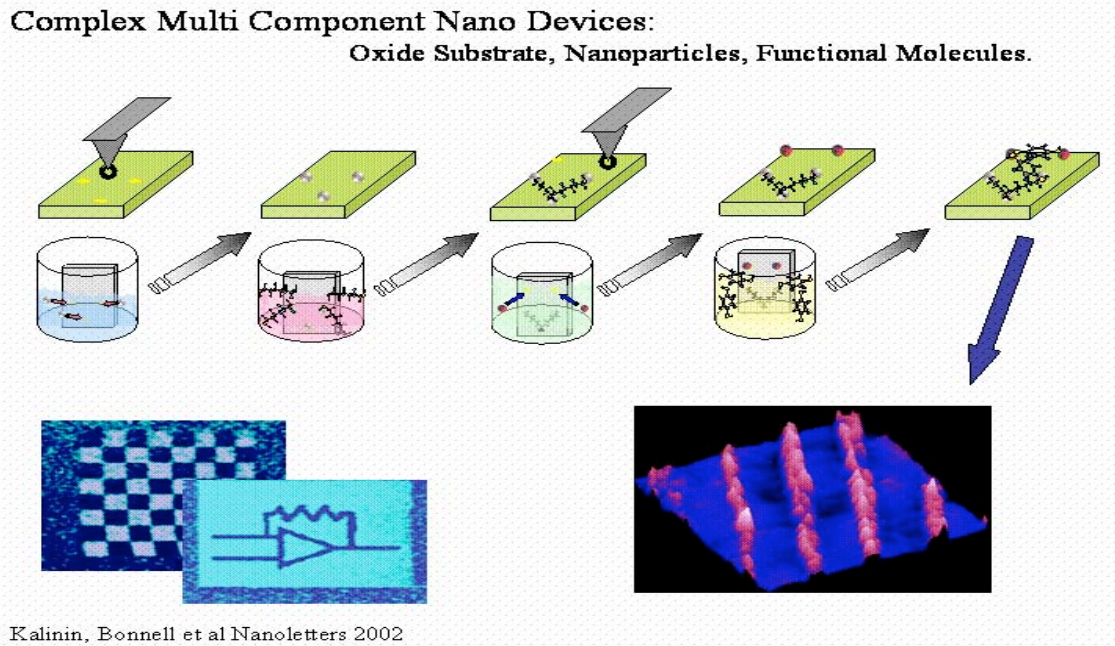
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It is now possible to make molecular and nano elements with a variety of electrical, optical and chemical properties. Semi conducting and metallic nanowires, organic molecules, carbon nanotubes and biological molecules exhibit properties that might be combined to produce complex functionality. The challenge remains to assemble multiple elements with differing properties in predefined arrangements in order to achieve complex functionality. Self assembly is effective at producing 2D and 3D periodic structures of similar elements, but it is generally acknowledged that some form of directed process will be necessary to produce complex structures.

We present a new approach to fabricating multi component nanoscale structures that combines many advantages of self assembly with the ability *to selectively position dissimilar nanoscale elements*. The approach exploits coupling to atomic polarization of ferroelectric domains and the specificity of nucleotide interactions. Engineered nanostructural elements are designed to be incorporated into complex configurations; optically active porphyrin based compounds, designed polypeptides, and particles. Several approaches are being used to determine the properties of individual nanostructure elements and proximity effects in electrical and optical behavior of multi component structures

Ferroelectric Nanolithography exploits the fact that electron exchange reactions are domain specific. Domains terminating at a surface result in a local surface charge that alters the electronic structure. In the context of a band model description, valence and conduction bands are bent up at negative domains and down at positive domains. Electrons can leave the surface at a

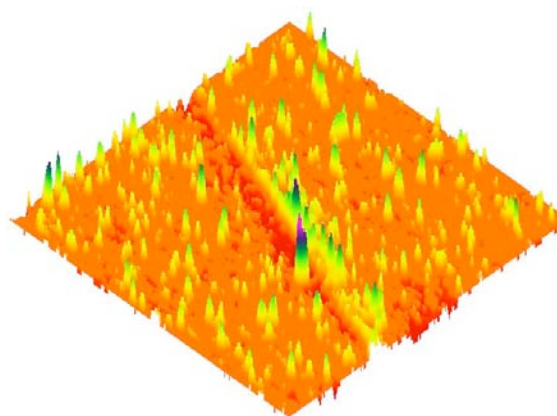
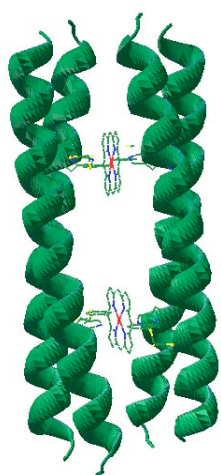
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positive domain and participate in a reduction reaction. Oxidation can occur at a negative domain. In the case of photo reduction of metal, the reaction product is 3nm-30nm diameter

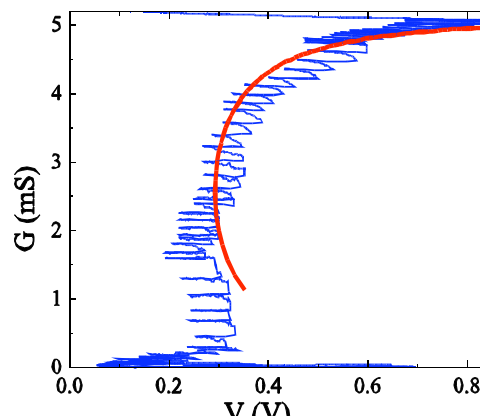
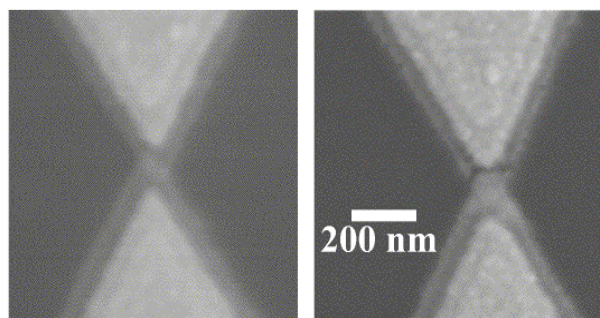
particles selectively on positive domains. This is followed by specific reactions to the nanoparticle or by patterning again and performing another electron exchange reaction, as illustrated above. We have demonstrated this process for 8 reactions, including transition metal reduction and oxidation

Functional polypeptides are designed in a multi step process. Statistical mechanics models are used to predict the backbone sequence that will locate a functional cofactor on the peptide (complementary work by Saven). Optically active non biological cofactors are synthesized in the group of Therien. The DeGrado group synthesizes the functional peptide with the goal of producing molecules sufficiently long to act as molecular electronic components. The peptides are made with thiolated end groups to facilitate attachment to patterned nanoparticles.



A model of the synthetic peptide with Fe based cofactors. When attached to atomically flat Au surfaces the peptides give the dimensions expected for vertically attached molecules in STM topographic images acquired in air.

One of bottle necks in molecular electronics characterization is the ability to make robust, routine measurements of properties of individual molecules. We are taking several approaches to this, including the development of new multiple modulation scanning probe techniques. A recent result involves making controlled nm gap electrodes in an automated, reproducible manner in ambient conditions. We have designed a sensitive conductance feedback process with which electro migration can be controlled. The gap evolution at early stages shows good agreement with a heating model (in red) and verifies our understanding of the process. The gap later crosses over to a quantum regime with integer multiples of the quantum of conductance ($G_0=2e^2/h$). The gap is formed after passing below G_0 .



SEM images (left) of a nano gap electrode produced by controlled electro migration. The gap is not visible at this resolution. The conductance is used to monitor the process as the voltage is ramped.

Summary

This project combines a new paradigm of assembly, Ferroelectric Nanolithography, with innovative design of functional biological molecules and new probes of single molecule properties to develop complex multi component nanostructures.

References

- [1] For further information about this project link to nanotech.upenn.edu or email Bonnell@lrsn.upenn.edu
- [2] Sergei Kalinin, D. Bonnell, T. Alvarez, X. Lei, Z. Hu, J.Ferris, Q Zhang, S. Dunn, Atomic Polarization, Charge Compensation and Local Reactivity on Ferroelectric Surfaces: a new route toward complex nanostructures, *Nano Letters* **2** (2002) 589
- [3] S.V. Kalinin, D.A. Bonnell, T. Alvarez, X. Lei, Z. Hu, R. Shao, and J.H. Ferris, Ferroelectric Lithography of Multi Component Nanostructures *Adv. Mat Adv. Mat* **16** (2004) 795-99
- [4] Role Of Single Defects In Electronic Transport Through Carbon Nanotube Field-Effect Transistors
M. Freitag, S. Kalinin, D. Bonnell, A. T. Johnson *Phys Rev Letters* **89** (2002) 216801