Hirakawa Lab
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Fabrication of Molecular Probes Using Safe, Simple Electroplating Technique

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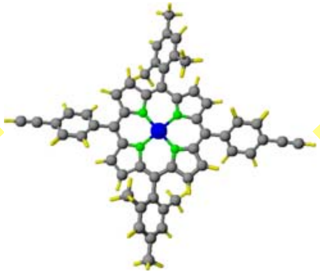
Iodine tincture was used as an electrolyte during the electroplating of gold on to the surface of two probes, creating a nanogap with spacing in the range of single molecules. The electrolyte preparation involved a commercially available dilute iodine tincture. A thin sheet of high purity gold was dissolved in the iodine solution until the solution became saturated, and an appropriate amount of vitamin C was added to turn the brown solution in to a transparent solution so that the electroplating process could be monitored by optical microscope. Gold sub-micron gaps were patterned on to semi-insulating GaAs by photo and e-beam lithography followed by gold evaporation and lift-off. Experiments were performed in which gold was plated using a DC counter electrode while the conductance between the probes was monitored with a low amplitude AC signal. As the gold was deposited on to the probes, the conductance was monitored, and plateaus were observed at various integer multiples of conductance quantum. Previously, the full role of vitamin C in the deposition process was unknown. Recent experiments involving the use of the iodine electrolyte without the addition of vitamin C resulted in the formation of a dense forest of crystalline structures on the surface of the probes. The formation of crystals was observed when both a negative and positive counter electrode bias was applied. Depending on the applied bias, two types of crystals were grown with different morphologies. It is now conclusively known that vitamin C plays an important role in gold deposition during the electroplating process. These results will be important for optimization of the electroplating conditions and will contribute to a better understanding of the mechanism by which gold is electroplated using the iodine tincture method. The long-term applications of a well-understood electroplating process could involve the fabrication of gold nanogaps capable of probing single molecules.

Towards Single-Molecule Probing

USING GOLD ELECTROPLATING TO CLOSE THE GAP ON THE MYSTERY OF MOLECULES



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Why Probe Molecules?

Chemistry has traditionally been a bulk science. What will happen when you dissolve a few grams of some powdered solid in with a few liters of some liquid? The predictable outcomes are based on stoichiometric proportions and statistics involving many millions of molecules.

As the design of new technologies shrinks to the nano-scale, the bulk chemistry of millions of molecules must scale down to a chemistry of single molecules. This new precision in design should not just take place in laboratories using expensive equipment and dangerous chemicals, but should be done using simple and safe procedures which can be readily used by many types of laboratories on any budget.

The benefits of simple single-molecule probing could be seen in all fields converging on the nano-scale. New areas of study could include:

- Molecular scale circuitry and molecular computing
- Photovoltaic properties of organic molecules for advanced solar energy devices
- Chemical sensing for harmful biological agents

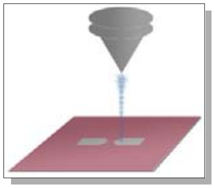
If a cheap and safe method for molecular probing is found, new avenues for "homebrew" nanotechnology could open up, bringing high-tech development to the casual garage-based technologist or hobbyist.

Gold Electroplating Could Lead The Way

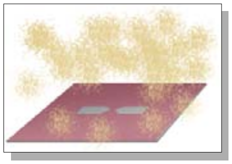
Research being done at the University of Tokyo shows promising development towards molecular probing using a simple electroplating process. Electroplating has typically been done using strong acids and other dangerous chemicals such as certain organometallics. It has been shown that successful electroplating can be performed using **iodine tincture**, a safe and commercially available medical fluid normally used as a disinfectant. By slowly electroplating gold on to closely spaced probes, the spacing between the probes approaches distances on the scale of single molecules.

Approaching the Nanoscale

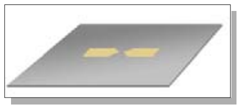
A layer of resist is applied to a wafer of Gallium Arsenide. Using **photolithography** and **electron beam lithography**, two small electrodes are patterned on to the surface.



Electrons are accelerated in to a crucible containing a **gold** ingot in a process known as **electron beam evaporation**. The gold is deposited over the surface of the wafer.



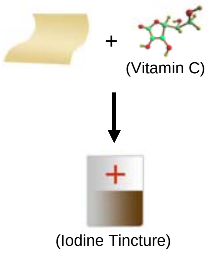
The layer of resist is dissolved in acetone, leaving only two small gold electrodes with spacing near **100nm**. This is small, but is still a few orders of magnitude larger than small single molecules.



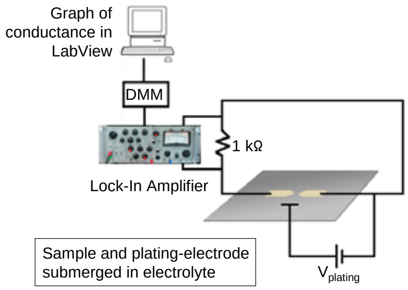
Closing the Gap on Molecules

An electrolyte is prepared by dissolving a thin sheet of pure gold in to a dilute iodine tincture (ethanol, water, KI, I_2).

Pure ascorbic acid (vitamin C) is added to the solution, turning it from a deep brown to transparent.



Earlier, it was thought that the Vitamin C was only useful for the clarification of the electrolyte for visualization purposes. Further studies have shown that, without vitamin C, electrically-stimulated crystal growth occurs on the surface of the electrodes. The mechanism of the vitamin C reaction is not known at this time, nor is the composition of the crystals.



By setting $V_{plating}$ to a **DC positive voltage**, electroplating of gold begins. The lock-in amplifier sends a **low amplitude, 13 Hz AC signal** through the gold electrodes.

During the plating process, the 13 Hz AC signal is monitored by the lock-in amplifier. The output from the amplifier is a DC signal whose magnitude corresponds to the original low amplitude 13 Hz signal. A DMM unit sends the magnitude information to a custom designed LabView application. In LabView, a live graph displays the **conductance** between the gold electrodes.

What does Conductance Tell Us?

As gold is deposited on to the electrodes, the gap size slowly decreases. As the gap decreases, the chance of an electron jumping from one electrode to the other increases. Eventually, the two electrodes come within a single gold atom of one-another, corresponding to a rapid increase in conductance (fig. 1).

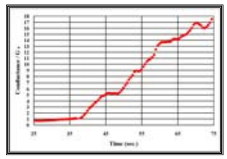


Fig. 1

By studying the behavior of the conductance curves, more is learned about the nature of the electrode contacts when the spacing distance approaches a single gold atom. It is hypothesized that the plateaus seen in Fig. 1 correspond to the transport of single electrons through quantum-point contacts. This effect is known as **quantum conductance**.

Future works include the optimization of the electrolyte solution and better designs for the gold electrodes. The goal is to develop a consistent process by which the electroplating of gold on to the electrodes is stopped at the moment gap size is on a molecular scale. Specially prepared molecules can then be introduced, allowing for the probing of molecular behavior during the transfer of single electrons.

This poster prepared by Ryan VanGundy, a North Carolina State University undergraduate in the Chemical Engineering department. Research performed during the Rice University NanoJapan program at Tokyo University during Summer 2006. The NanoJapan program is sponsored by a grant from the National Science Foundation.