Copper Phthalocyanine (CuPcb) is studied here for use in tunneling diodes. A stable monolayer can be made, whose molecular orientation can be determined using Atomic Force Microscopy (AFM) using information about the molecule. It has a diameter of 1.5 nm and a width of 0.6 nm. The eight organic strands attached in the para position are perpendicular to the ring. This causes the molecule to stand normal to a substrate. A monolayer will, therefore, be 1.5 nm high, and will allow the tunneling of electrical current beginning at a given voltage. We have looked at the best films, meaning those that were the most complete in
coverage and the most uniform in height, to determine the most advantageous conditions for making these films. We have begun work within the molecular electronic application.

Langmuir-Blodgett Sample Surface Pressure = 20 mN/m, Dipping Speed = 5mm/min
Spin Doped Sample Spun for 30 Seconds

The benefit of the Langmuir-Blodgett (LB) technique for film deposition is the ordered nature of the films. Spin doped samples, made by placing a drop of 0.0001 M CuPcb onto mica and spinning for 30 or 60 seconds, had little coverage and no long-range order. LB monolayers contain islands of ordered molecules. The LB method also provides parameters which may be varied in order to develop the best conditions for consistently good films. We have studied the effects of the surface pressure of the water subphase, the deposition speed of the substrate, and the number of compression and relaxation cycles. All samples were made at room temperature without adjusting the pH as CuPcb is not pH sensitive.

All Samples: Dipping Speed = 20 mm/min, 1.5 Compression Cycles
Surface Pressure = 30 mN/m

Surface Pressure = 25mN/m
Surface Pressure = 20 mN/m, Sample Height 1.5nm

Surface Pressure = 15 nmN/m, Sample Height = 1.2-1.4nm
Dipping Speed = 10mm/min
Sample Height = 1.5nm
Dipping Speed = 20mm/min
Sample Height = 1.5nm
Dipping Speed = 30mm/min
Sample Height = 0.5-0.7nm
Isothermal plots of the surface area versus area/molecule as a function of compression and relaxation of the LB film show that the films are stable up to two complete cycles. Beyond that it seems that the layer begins to tear, and the order becomes less complete. For our samples we use the pattern of compression, relaxation, compression before the deposition of the substrate.

Surface Pressure = 20mN/m, Dipping Speed = 20mm/min, Sample Height = 1.451nm
The films which consistently gave good results were done using a surface pressure of 20 mN/m. At lower pressures, order is not complete; leaving larger gaps in the film. At higher pressures, the islands become smaller, and ridges begin to form at the edges. The best dipping speed was 20 mm/min. Using lower speeds caused large water droplets to remain on the substrate, and higher speeds prevented the film from transferring thoroughly from the subphase; the sample height of these films was only 0.5-0.7 nm, which matches the width of the molecule. This indicates that the molecule is lying almost flat on the substrate. Isotherms showed that the films were stable up to two compression cycles, but that beyond that, the layer begins to tear and does not give good coverage. Section analyses indicate that the depth of the monolayers was roughly 1.5 nm, matching the diameter of the molecule. This shows that the CuPcb molecules are packed normal to the substrate.

The next step for this line of research is to study the application of CuPcb as an electronic material in metal-insulator-metal, M-I-M, devices. Such devices are useful in molecular electronics because of their capacity to behave like switches. Electron tunneling from one metal to another through an insulating barrier begins at a specific voltage. Therefore, upon application of a given level of bias, current is able to flow through the device.

The benefits of using Langmuir-Blodgett films of a molecule within a diode is inherent in the method of preparation and the structural orientation characteristics of the molecules in the film. Fabrication of a LB film requires no vacuum
and may be done at room temperature, and the number of layers the film is easily controlled. Multi ordered layers may be applied with ease, and molecules can be stacked in a variety of different ways. Working with several different molecules is simple using the LB technique because different vapor pressures is not a concern in open air. The CuPcb molecules themselves provide flexibility in application. They are sturdy and withstand high temperatures without melting.

We will begin now to study the electronic properties of a LB monolayer of CuPcb in the tunnel diodes by applying voltages and observing current flow.
The Tunnel Diodes were made as follows:

Glass Slides (76mm x 25 mm x 1mm) were cleaned. They were placed in a solution of 20 parts HNO$_3$, 5 parts deionized water, 2 parts H$_2$O$_2$, which was boiled mildly for one hour. Slides were washed in deionized water, then stored in deionized water until use.

A slide was then placed in a vacuum system (pressure < 6 x $10^{-7}$ Torr). A film 100 nm thick of Al was deposited from W wire. 90 mTorr of Oxygen gas was admitted. A plasma was created using a 400-V ac discharge. This was done 3 times for a total period of 15 minutes. The slide was then removed from the vacuum system and placed over a tray of deionized water for a period of 1-2 hours to form a thick
oxide layer. This is necessary for withstanding several volts of bias.

Then an LB monolayer of CuPcb was deposited on the slide using a surface pressure of 20 mN/m and a dipping speed of 20 mm/min. The film had undergone 1.5 cycles of compression and relaxation before deposition.

The slide was then returned to vacuum and 100-150 nm of Pb was deposited from an Mo boat.

Metals used had a purity greater than 99%. The CuPcb purchased was not further purified before use.

References:


