

Electrochemical Self-Assembly of Copper/Cuprous Oxide Layered Nanostructures

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As the dimensions of conventional electronic devices such as field-effect transistors continue to shrink, quantum mechanical tunneling begins to affect their performance. If these devices can be designed to be based on tunneling, however, they can be made to be both small and fast, because tunneling is not limited by carrier mobilities in the semiconductor. An example of a device based on quantum-mechanical tunneling is the tunnel diode.^{1–4} Tunnel diodes are presently made of group III–V semiconductors such as GaAs/GaAlAs, which are deposited as layered structures using high-vacuum techniques such as molecular beam epitaxy. Here we show that layered nanostructures of copper (Cu) and cuprous oxide (Cu₂O) can be electrochemically self-assembled in a beaker at room temperature. Electrical transport parallel with the layers shows percolation behavior, with the resistivity varying by over 10 orders of magnitude for a series of films of different copper contents. Transport perpendicular to the layers exhibits negative differential resistance, suggestive of resonant tunneling through the nanometer-scale Cu₂O layers.

We previously showed that nanocomposites of copper and cuprous oxide could be electrodeposited from aqueous solution and that the optical absorption edge blue-shifted due to quantum confinement of carriers in the nanometer-scale cuprous oxide.⁵ Cuprous oxide is a relatively non toxic p-type semiconductor with a band gap of 2.1 eV.⁶ It is also a textbook example of an excitonic solid.⁷ Unbound excitons in Cu₂O have a binding energy of 150 meV and a radius of 0.7 nm.⁸ There is evidence from other laboratories that Bose–Einstein condensation of excitons can occur in Cu₂O at relatively high temperatures.^{9–11} Snoke has suggested that it may be possible to transmit light through a nanometer-scale aperture of cuprous oxide without diffraction losses.¹¹

Interest in the semiconducting properties of Cu₂O began as early as 1926, when Grondahl produced the Cu/Cu₂O rectifier.¹² Since the resistivities of Cu₂O and Cu are 3×10^6 and 1.7×10^{-6} Ω -cm,⁶ respectively, layered nanostructures of Cu₂O and Cu should have highly anisotropic electrical properties. We are

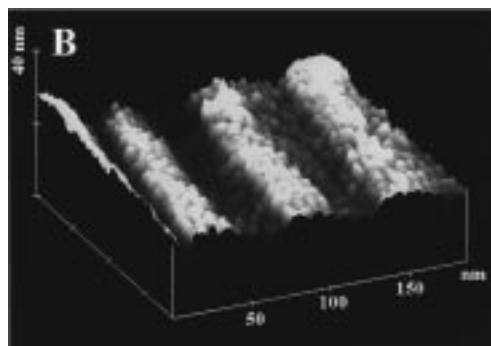
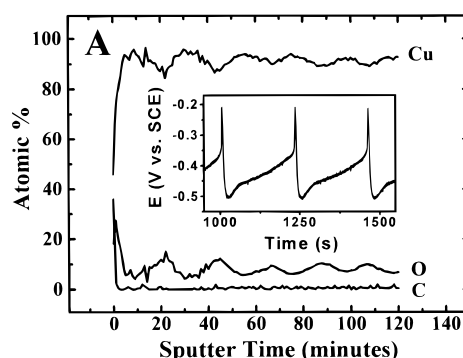


Figure 1. Evidence for layering in a Cu/Cu₂O film that was electrodeposited from a solution of 0.6 M CuSO₄ and 3.0 M lactate ion at a pH of 8.5 and an applied current density of 0.25 mA/cm². (A) Auger depth profile of composition in growth direction showing modulation of the Cu and O contents. Inset shows potential oscillations observed during the deposition of the film. (B) Cross-sectional STM image of film after etching with dilute nitric acid.

particularly interested in the electrical properties of structures in which thin layers of cuprous oxide of tunneling dimensions are sandwiched between layers of copper metal.

Layered nanostructures such as superlattices and multilayers can be electrodeposited by pulsing the applied potential or current during growth.^{13–17} In the present work, the electrode potential spontaneously oscillates when a fixed current density is applied. The films are deposited at 30 °C in a stirred solution of 0.6 M CuSO₄ and 3.0 M lactate ion. Oscillations are observed if the pH is in the 8.5–10 range. In a stirred solution, the oscillations can persist for several days. We have observed oscillations on copper, stainless steel, platinum, gold, and indium–tin oxide electrodes with areas of several square centimeters. The oscillation period, layer thicknesses, and phase composition are a strong function of pH. At an applied current density of 0.25 mA/cm², the oscillation period is 230 s at pH 8.5, but decreases to 31 s at pH 9.0. At pH 9.0, the oscillation period remains in the 25–31 s range even though the current density is varied from 0.25 to 1.5 mA/cm².

Direct evidence for layering is shown in Figure 1 for a large modulation wavelength film grown at a current density of 0.25 mA/cm² at pH 8.5. The modulation wavelength for this film was estimated from the potential oscillations and the electrochemical

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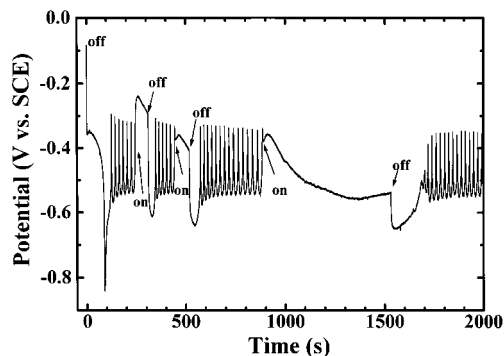


Figure 2. The effect of light on the potential oscillations for a film deposited at pH 9.0 and a current density of 0.2 mA/cm².

quartz crystal microbalance (EQCM)¹⁸ to be 55 nm. The EQCM showed that Cu₂O was deposited during the positive-going spikes in potential, while a composite of Cu and Cu₂O was deposited during the more negative swings in potential. The Auger depth profile using argon ion sputtering in Figure 1a shows modulation of composition in the growth direction. The film was also examined by cross-sectional scanning electron microscopy (SEM) and scanning tunneling microscopy (STM). The modulation wavelength measured using backscattered electrons in the SEM was 58 nm. An STM cross-section of a film that was cleaved and then etched in dilute nitric acid is shown in Figure 1b. The modulation wavelength measured by STM is ca. 62 nm.

Potential and current oscillations are quite common in electrochemistry.^{19,20} The oscillations are often caused by the adsorption and dissolution of a passivating layer. Since Cu₂O is a p-type semiconductor, it should produce a rectifying contact with the solution for reduction reactions.^{21,22} The spike in the oscillations, then, may be due to the build-up and breakdown of a thin rectifying film of Cu₂O. In agreement with this mechanism, the oscillations stop if the electrode is irradiated with light during the deposition. Light will generate electron-hole pairs in the cuprous oxide and lower the rectifying barrier at the semiconductor/solution interface. Figure 2 shows the effect of 240 mW/cm² light from a tungsten-halogen lamp back-irradiated through a transparent ITO substrate. The oscillations stop when the light is on and resume when the light is turned off.

Due to the layered structure of the films, the electrical properties depend strongly on whether transport is measured parallel with or perpendicular to the layers. Figure 3 shows the parallel resistivity of films grown at pH 9.0 at a series of current densities. The phase composition of the films was determined by X-ray diffraction. The resistivity varies over 10 orders of magnitude from approximately 10⁻⁴ Ω-cm at high Cu contents to greater than 10⁶ Ω-cm at low Cu contents. There is an abrupt decrease in resistivity at Cu contents exceeding 9.8 vol %. The curve drawn through the data is a fit to the data using percolation theory.²³

Parallel transport is rigorously ohmic at all of the compositions shown in Figure 3. That is, plots of current versus applied bias are linear. It is interesting that the resistivity of a film grown at a current density of 1.5 mA/cm² at pH 9.0 is 1.4 × 10⁻⁴ Ω-cm when measured parallel with the layers, but 4.3 × 10⁵ Ω-cm when measured perpendicular to the layers. Hence, the film is three billion times more conductive along the layers than perpendicular to the layers. The parallel resistivity approaches the perpendicular resistivity at copper contents below the percolation threshold.

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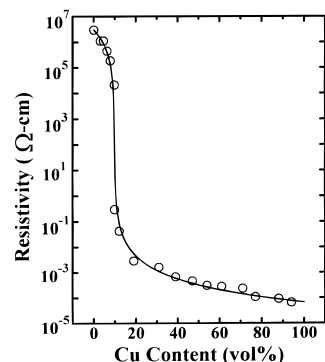


Figure 3. Parallel resistivity versus Cu content for a series of Cu/Cu₂O films. The Cu content was controlled by varying the applied current density at a solution pH of 9.0. The solid line is a fit to the data using percolation theory, with a percolation threshold of 9.8 vol % Cu.

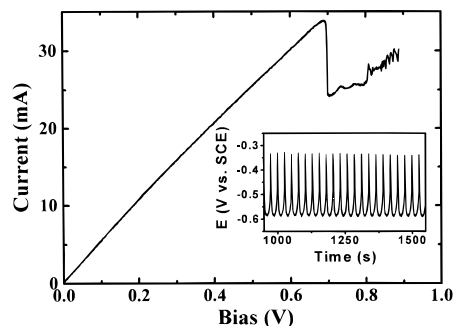


Figure 4. Perpendicular transport at 77 K through a Cu/Cu₂O film with 410 layers. The film consists of 7 nm thick layers of Cu₂O sandwiched between 12 nm thick layers of a composite that is nearly pure Cu. The inset shows potential oscillations observed during the deposition of the film.

In contrast to the ohmic behavior observed parallel with the layers, transport perpendicular to the layers showed negative differential resistance, suggestive of resonant tunneling. Figure 4 shows a plot of current versus applied bias for perpendicular transport through a film grown at a current density of 1.5 mA/cm² at a pH of 9.0. The multilayer film had 410 alternating layers of Cu and Cu₂O that were 12 and 7 nm thick, respectively. The *i*-*V* curve in Figure 4 was run at 77 K by making a point contact to the Cu/Cu₂O multilayer. Notice that the *i*-*V* curve looks nearly ohmic at low bias but shows a sharp negative differential resistance feature at a bias of 0.7 V. In future work, we plan to determine whether the bias at which negative differential resistance is observed is a function of the thickness of the Cu₂O layer.

We have found that layered nanostructures of copper and cuprous oxide can be self-assembled in aqueous solution by a very simple and inexpensive electrochemical method. The phase composition, layer thicknesses, and resistivity of the films can be tuned by varying the applied current density or the solution pH. The Cu₂O layers in the solids are only a few nanometers thick. Although the confinement dimension is small, the films can be deposited over areas of several square centimeters. The nanostructured films act as percolation solids when measured parallel with the layers and as tunnel devices when measured perpendicular to the layers.

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