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LETTERS

Negative Differential Resistance in Electrochemically Self-Assembled Layered Nanostructures

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Resonant tunneling devices are used for ultrahigh-speed applications. In this work, tunnel junctions based on copper metal (Cu) and cuprous oxide (Cu_2O) are electrochemically self-assembled from aqueous solution in an oscillating system. The Cu_2O layer thickness (L) is tuned from 0.8 to 2.8 nm by simply changing the applied current density. The layered structures show sharp negative differential resistance (NDR) signatures at room temperature in perpendicular transport measurements, and the NDR maximum shifts to higher bias with a $1/L^2$ dependence as the Cu_2O layer is made thinner. The results are consistent with resonant tunneling from Cu into hole states in the valence band of quantum-confined Cu_2O through thin space−charge regions on each side of the Cu_2O.

Quantum mechanical tunneling can impair the performance of conventional electronic devices such as field effect transistors as the dimensions of the active regions approach the nanometer scale. If devices can be designed to be based on tunneling, they can be made both small and fast, because tunneling is not limited by carrier mobilities in the semiconductor. Resonant tunneling diodes based on group III−V semiconductors such as GaAs/GaAlAs and InAs/AlSb have been produced which operate at frequencies up to 712 GHz.[1,2] As the molecular limit in size is approached, single-electron effects such as Coulomb staircases can also be observed in electron transport through tunnel systems.[3,4] Tunnel devices have not found widespread application, however, due to their limited output power and because their performance is often diminished near room temperature. In this work, tunnel junctions based on copper metal (Cu) and cuprous oxide (Cu_2O) are electrochemically self-assembled from aqueous solution in an oscillating system. The layered nanostructures show sharp negative differential resistance (NDR) signatures *at room temperature* in perpendicular transport measurements, and current densities as high as 40000−50000 A/cm^2 have been observed. The results are consistent with resonant tunneling from Cu into hole states in the valence band of quantum-confined Cu_2O through thin space−charge regions on each side of the Cu_2O.

Negative differential resistance is observed in perpendicular transport through double-barrier tunnel junctions.[5−9] In addition to producing structures which can serve as high-speed amplifiers or high-frequency oscillators, the NDR feature also provides a direct measurement of the energy of discrete states in quantum-confined semiconductors. The maximum observed in current−voltage curves is caused by a maximum in the quantum mechanical tunneling probability due to strong overlap of the wave functions of the contact and discrete state when the two states are at the same energy. The energy of the discrete state is an eigenvalue of the Schrödinger wave equation using a simple particle-in-a-box treatment according to eq 1

$$E = \hbar^2\pi^2n^2/2mL^2 \quad (1)$$

where E is the energy (J) of the discrete state relative to the valence or conduction band edge, $\hbar$ is Planck's constant divided

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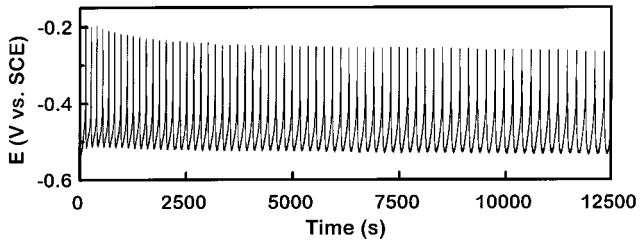

Figure 1. Spontaneous potential oscillations observed during the constant-current deposition of Cu/Cu_2O layered nanostructures. The film was deposited onto a 2 cm^2 Cu electrode at a current density of 0.15 mA/cm^2 in a stirred solution of 0.6 M Cu(II) and 3.0 M lactate ion at pH 8.3. The first Cu_2O layer is estimated to be 1.5 nm thick, and the oscillation period and layer thicknesses progressively increase as the deposition proceeds. The oscillation period increases from an initial value of 130 to 210 s after 10 000 s of deposition.

by 2π (1.0546×10^{-34} J s), n is the principal quantum number ($n = 1, 2, 3, ..., 4$), m is the mass of the confined electron or hole (kg), and L is the confinement dimension (m).

The system can be brought into resonance by applying an electrical bias to contacts on both sides of the double tunnel junction. The energies of the contacts relative to the Fermi energy are generally calculated from the applied bias according to eq 2

$$E = \pm eV/2 \tag{2}$$

where V is the applied bias (V) and e is the electron charge (1.6022×10^{-19} C). The tunneling probability increases as the bias is increased until the contact and discrete state energies are degenerate. The tunneling probability then decreases as the bias is increased past the resonance condition. The decrease in tunneling probability lowers the current at higher bias, giving a negative differential resistance. The NDR signature shifts to higher bias with a $1/L^2$ dependence, similar to the blue shift that is seen in the optical properties of mesoscopic semiconductors as the confinement dimension is made smaller.[10−12]

The emphasis of our research has been the room-temperature electrochemical processing of layered nanostructures of metal oxide semiconductors from aqueous solution. Superlattices of conducting metal oxides were previously deposited in a beaker by pulsing the applied potential or current,[13−15] and layered nanostructures of copper metal (Cu) and cuprous oxide (Cu_2O) have recently been self-assembled at constant applied current.[16−18] The electrode potential *spontaneously* oscillates during the deposition of the Cu/Cu_2O films when a constant current is applied to the cell. The Cu/Cu_2O layered nanostructures in this study were electrodeposited from an aqueous solution of 0.6 M Cu(II) and 3 M lactate ion at a pH between 8 and 9. Figure 1 shows an example of potential oscillations that are observed when a film is deposited at an applied current density of 0.15 mA/cm^2 at a pH of 8.3 onto a Cu substrate. The oscillation period progressively increases during growth, and the oscillations can persist for several days. We have also observed potential oscillations when the Cu/Cu_2O films are deposited onto Pt, Au, indium−tin-oxide, glassy carbon microelectrodes, and directly onto single-crystal Si.

We have demonstrated in earlier work by Auger depth profiling, scanning tunneling microscopy, and scanning electron microscopy that layered structures are formed when the electrode potential oscillates during constant-current deposition.[17,18] Here, we use the electrochemical quartz crystal microbalance (EQCM) to follow the deposition process in situ by monitoring the frequency response of the quartz oscillator during deposition. Decreases in frequency correspond to increases in the mass

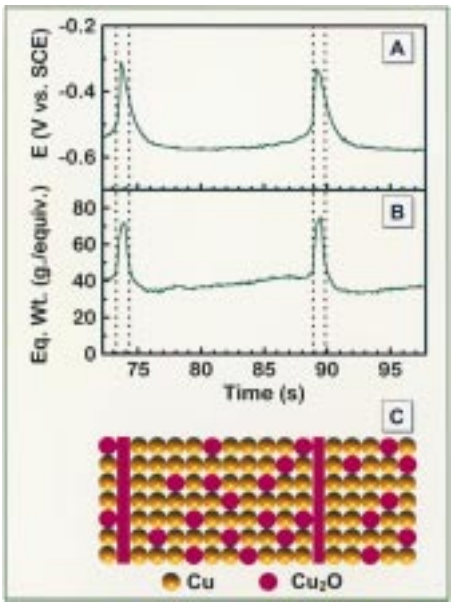

Figure 2. Real-time monitoring of the deposition process using the electrochemical quartz crystal microbalance (EQCM). (A) Potential oscillations that are observed during the deposition of a film at a current density of 2.0 mA/cm^2 at a pH of 9.0 directly onto a 0.2 cm^2 platinum-coated EQCM oscillator. (B) Equivalent weight of the deposit, calculated from the change in frequency of the quartz oscillator. (C) Proposed nanostructure for the film. The Cu_2O layer is estimated to be 2.5 nm thick, and the Cu/Cu_2O layer is estimated to be 15 nm thick and to consist of approximately 82 mol % Cu.

added to the electrode, allowing calculation of the equivalent weight of the material being deposited.[19] Figure 2 shows the oscillation in potential (A) and equivalent weight (B), and the proposed nanostructure (C) for a film that was deposited at pH 9 at a current density of 2.0 mA/cm^2. The Cu_2O layer is estimated to be 2.5 nm thick, and the Cu/Cu_2O layer is estimated to be 15 nm thick and to consist of approximately 82 mol % Cu. The Cu_2O layers can be made thinner by decreasing the applied current at fixed pH or by increasing the pH at fixed applied current.

Figure 3 shows the current−voltage curve for perpendicular transport at room temperature through a Cu/Cu_2O layered nanostructure with 554 layers. The sample was deposited onto a copper substrate, and a point contact with an area of approximately 1×10^{-5} cm^2 was made to the top surface. The thickness of the first Cu_2O layer was estimated to be 2.4 nm. A sharp NDR feature is observed on both the positive and negative scans at +0.17 and −0.18 V, respectively. The slope of the iV curve becomes negative at biases exceeding the NDR maximum, and the differential conductance and resistance are negative in this region. The current density flowing through the point contact on this sample is in the 40000−50000 A/cm^2 range.

The observation of NDR does not prove that the system is quantum confined. It is necessary to show that the position of the NDR maximum shifts with layer thickness as predicted by eqs 1 and 2. Figure 4 shows that the NDR signature shifts to higher bias as the Cu_2O layer thickness is decreased from 2.5 to 0.8 nm. The electrochemical assembly method described here is ideal for this type of study, since a large number of samples with different Cu_2O layer thicknesses can be produced by simply depositing the films at different current densities. The maximum in the NDR curve shifts with a $1/L^2$ dependence (Figure 5), consistent with quantum confinement. We have used the thickness of the first layer in every film for L, since the layer thickness progressively increases as the film grows. Deviation

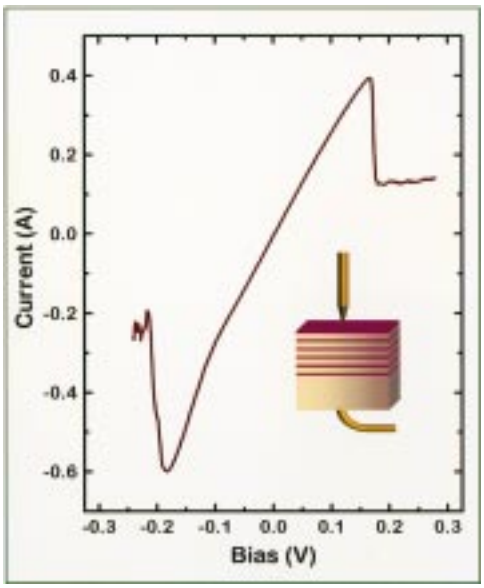

Figure 3. Perpendicular transport at room temperature through a Cu/Cu_2O film with 554 layers. The first Cu_2O layer is estimated to be 2.4 nm thick. The slope of the *iV* curve becomes negative at biases exceeding the NDR maximum, and the differential conductance and resistance are negative in this region. Inset cartoon shows the configuration used to make the perpendicular transport measurement. The point contact area is approximately 1×10^{-5} cm^2, so the current density is in the 40000−50000 A/cm^2 range.

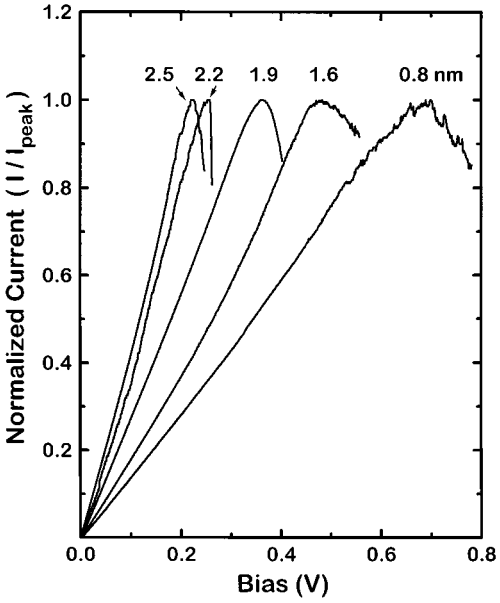

Figure 4. NDR curves for layered nanostructures as a function of the Cu_2O layer thickness. The NDR maximum shifts to higher applied bias for samples with thinner Cu_2O layers.

from linearity occurs for Cu_2O layers thinner than 1.5 nm and for applied biases larger than 0.50 V. The deviation may be due to incomplete confinement of carriers in the thinner layers. An effective mass for the confined carriers of $0.61m_o$ is calculated from the slope of the line in Figure 5, where m_o is the free electron mass (9.109×10^{-31} kg). Since the literature values[20] for the electron and hole effective masses in Cu_2O are $0.84m_o$ and $0.61m_o$, respectively, our measurements indicate that the confined carriers are holes in the valence band of nanometer-scale Cu_2O.

Band diagrams which are consistent with our observations are shown in Figure 6 for zero bias and a bias corresponding to resonance. The resonant condition in a multibarrier structure

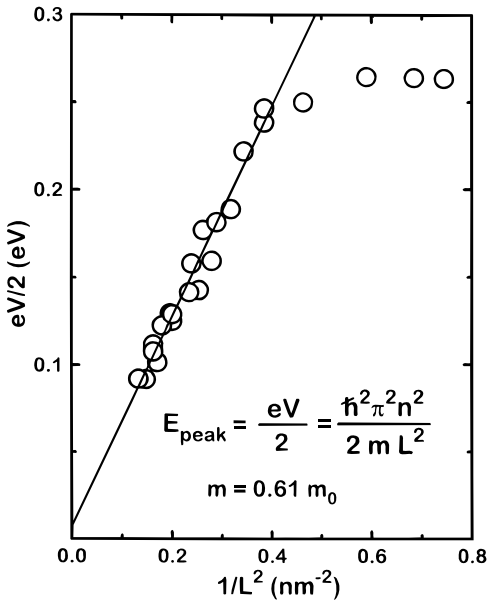

Figure 5. Demonstration that the NDR signature shifts with the Cu_2O layer thickness (L) with a $1/L^2$ dependence. The effective mass calculated from the slope of the line is $0.61m_o$, indicating that holes are the quantum-confined carriers.

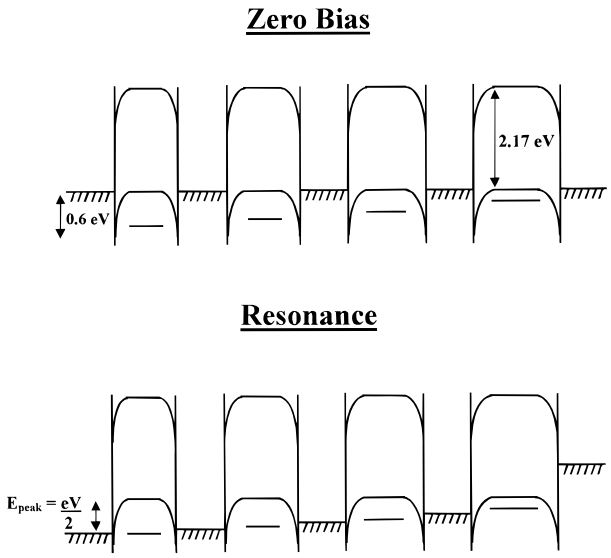

Figure 6. Proposed energy-level diagrams for the self-assembled Cu/Cu_2O tunnel junctions at zero bias and at resonance. The energy of the hole state, E_{peak}, moves down in the figure as the Cu_2O layer is made thinner, since hole energies increase in the downward direction. The NDR maximum occurs in perpendicular transport measurements when the applied bias brings the energies of the Cu-rich layer and E_{peak} to the same energy. The Cu_2O layers closest to the substrate have the greatest degree of quantum confinement and control the bias at which NDR is observed.

can be satisfied if the width of the quantum well is systematically varied across the structure or in weakly coupled quantum well structures by sequential tunneling, which is a combination of conventional tunneling and phonon-induced intrasubband decay. We believe that the former is occurring in this system. In conventional vapor processing of layered structures, it is necessary to program the deposition process to systematically vary the layer thicknesses. In this work, each subsequent layer grows to a greater thickness as the deposition proceeds, since the oscillation period increases (see Figure 1). The thin Cu_2O layers closest to the substrate have the greatest degree of quantum confinement and control the bias at which the NDR feature is

observed. Cuprous oxide is known to be a p-type semiconductor with a band gap of 2.17 eV.[21] It is also known to form a rectifying junction with Cu with a barrier height of approximately 0.6 eV.[22] We suggest that thin space−charge regions at each Cu/Cu_2O interface produce the double tunnel junctions and that tunneling occurs from the Cu-rich layers into hole states in the Cu_2O through these space−charge regions.

Layered architectures with hundreds of quantum-confined Cu_2O layers can be electrochemically self-assembled in a beaker. The resulting structures have NDR signatures at room temperature comparable to those of high-speed III−V semiconductor tunnel devices prepared by ultrahigh-vacuum techniques. The tunnel junctions in this study are based on metal oxide semiconductors, which may be the forerunners of future high-temperature, high-power electronic devices. Since there is growing interest in replacing aluminum with copper for integrated circuit (IC) interconnects, it may be possible to integrate these tunnel junctions directly into traditional silicon-based IC chips.

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