

## Electrochemical Fabrication of Cadmium Chalcogenide Microdiode Arrays

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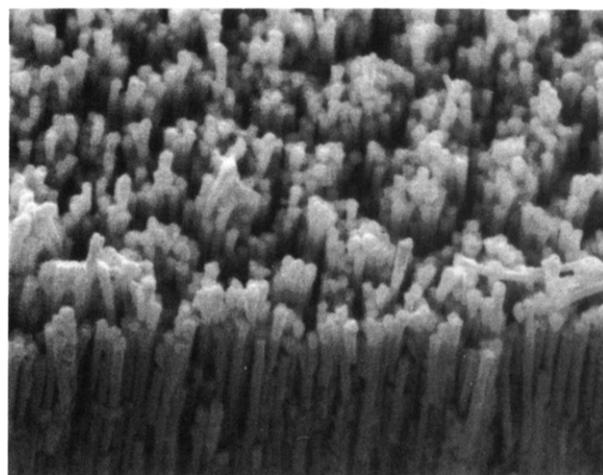
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Organic and metal microfibrils and microtubules have been synthesized using the pores of microporous membranes as geometric templates.<sup>1-6</sup> The membranes employed have linear, cylindrical pores of uniform diameter, and so the microfibrils and microtubules obtained have highly monodisperse dimensions. These novel microstructures have potential applications in optical and electronic devices, sensors, and drug delivery systems.<sup>7,8</sup> In this work, we have developed the chemistry for fabricating the II-VI semiconductors CdSe and CdTe within template membranes of this type; arrays of semiconductor microcylinders are obtained.<sup>9,10</sup> Unlike the elegant precipitation techniques developed to fabricate semiconductors within glass,<sup>11-15</sup> polymer,<sup>16-18</sup> micelle,<sup>19,20</sup> or zeolitic matrices,<sup>21-24</sup> the present technique employs electrodeposition, which has been shown to provide very precise control of both the dimensions and composition



5  $\mu\text{m}$

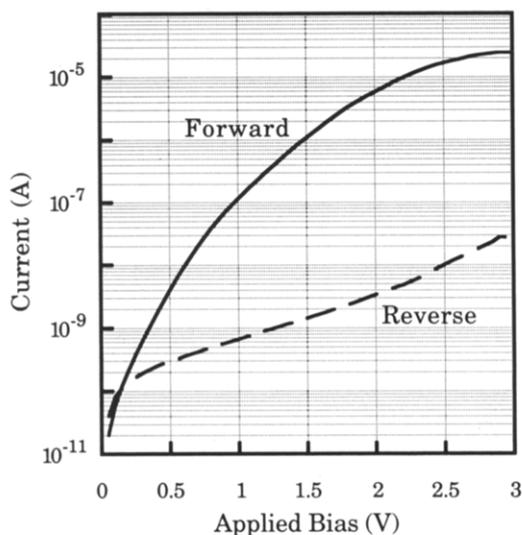
**Figure 1.** Scanning electron microscope image (20 keV, secondary electron image) of a CdSe diode array electrodeposited on a Ni substrate, using an Anopore membrane template. The Anopore membrane has been removed by soaking the electrode in 1 M NaOH.

of the semiconductor material.<sup>25-32</sup> The results represent the first synthesis of very large ( $>10^9$ ) semiconductor diode arrays. In addition, the restricted dimensions of the membrane templates are found to eliminate the fractal-like cauliflower morphology often observed in electrodeposited II-VI materials.<sup>33-36</sup> These results may be important for the fabrication of high-resolution optical detectors, solar cells, or high-definition displays.

Anopore membranes obtained from Anotech Separations, Ltd. were used as templates for the electrodeposition of the II-VI semiconductors. The membranes are ca. 50- $\mu\text{m}$  thick and contain tightly placed 2000- $\text{\AA}$ -diameter pores. A 300- $\text{\AA}$  layer of Au was sputter-coated onto one side of the Anopore membrane in order to form a conductive surface. A Ni substrate layer was then electrochemically plated (nickel "S" sulfamate electroplating solution, Technic Inc., Providence, RI) on top of the Au. The Ni completely covered one side of the Anopore membrane, and partially filled the pores. The membrane was then separated into squares of approximately 1  $\text{cm}^2$  area and the Ni-coated side of each was attached to a wire using

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**Figure 2.** Forward (solid) and reverse-biased (dashed) current-voltage curves of a CdSe diode array. The contact area corresponds to between  $10^5$  and  $10^6$  individual CdSe rods.

conductive Ag paint (Micro-Circuits Co.). The wire contacts and edges of the membranes were completely sealed in epoxy (Hysol 1C epoxy patch kit) or with a Teflon gasket. Electrolyte solutions were prepared using 18 MΩ DI water and the following reagents:  $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$  (98%),  $\text{TeO}_2$  (99.995%), and  $\text{SeO}_2$  (99.999%) (Aldrich Chemicals), ultrahigh-purity  $\text{H}_2\text{SO}_4$  (Baker Ultrex II, Baker Chemicals), and reagent grade HCl (Fisher Scientific). It should be noted that exposure to cadmium, selenium, and tellurium has been determined to be hazardous and all precautions should be taken to avoid contact with the solutions.

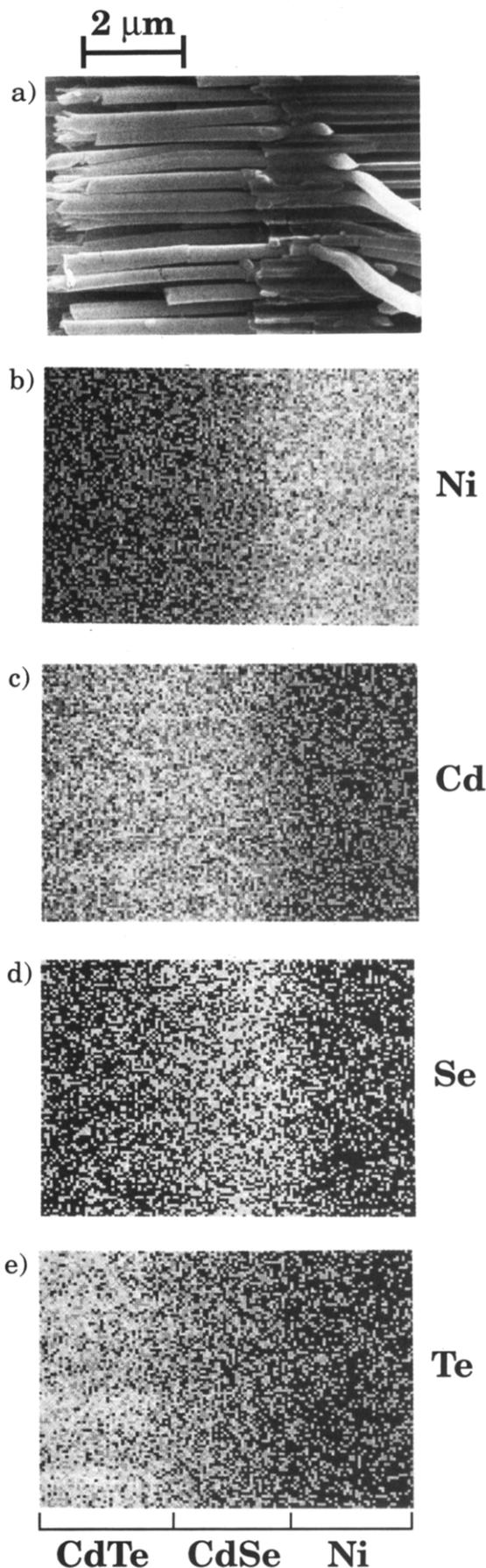
Cadmium selenide was then electrochemically deposited into the membrane using a previously developed ac electrodeposition technique.<sup>37</sup> The deposition bath typically contained 0.3 M  $\text{CdSO}_4$ , 0.25 M  $\text{H}_2\text{SO}_4$ , and 0.7 mM  $\text{SeO}_2$  or  $\text{TeO}_2$ . If lower concentrations of chalcogen were used, elemental analysis (semiquantitative electron beam-induced X-ray fluorescence, EDX) revealed that the microcylinders contained excess Cd. At 0.7 mM concentrations of chalcogen, the electrodeposited materials showed near 1:1 stoichiometry by EDX, based on comparison with authentic bulk samples. All solutions were stirred during deposition. It was found that the electrodeposition tended to be more homogeneous when carried out in the absence of light.

Cross-sectional SEM images of the electrodeposited CdSe (Figure 1) reveal that the cauliflower growth morphology, typical of electrodeposited CdSe and CdTe,<sup>37</sup> is suppressed by the Anopore membrane. Thus template restriction of the growth dimensions can improve the overall morphology of these electrodeposited materials. As was observed in our work on electrodeposited thin films, the X-ray powder diffraction peaks are broad, and show the CdSe to be primarily the zincblende phase.<sup>37</sup> Analysis of the width of the peaks using the Debye-Scherrer relationship<sup>38,39</sup> indicates that the crystallite size in this material is on the order of 200–300 nm.

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**Figure 3.** Cross-sectional scanning electron microscope image and X-ray element maps of a CdSe/CdTe heterojunction array. (a) secondary electron image, 20 keV; (b) Ni map; (c) Cd map; (d) Se map; (e) Te map.

Current-voltage data on the Ni/CdSe structure (Figure 2) was obtained by placing a tungsten carbide probe tip on the top of the CdSe layer after the Anopore layer had been removed (soaked in 1 M NaOH solution for 30 min, rinsed with 18 MΩ H<sub>2</sub>O, dried at 100 °C for 1 h). Hot-probe measurement of CdSe thin films electrodeposited on a Ni plate (i.e., without using the Anopore template) showed that the as-formed CdSe is n-type (typical for electrodeposited CdSe<sup>40</sup>), and point-contact current-voltage curves taken on these flat samples were similar to the curves of Figure 2. The current-voltage data thus indicate that the CdSe/Ni interface is rectifying. The rectification characteristics of the CdSe cylinders are poor (relative to commercial Schottky junction diodes), with a forward-to-reverse bias rectification ratio of 1000 at ±2 V. The current-voltage curves were nonexponential, probably indicative of high series resistances in the devices. Current-voltage data from some points exhibited lower rectification ratios, presumably due to large shunting currents from direct contact between the probe tip and some of the underlying Ni substrate rods. The contacting method precludes determination of the exact area of the electronically active region, although using the surface area of the probe tip (radius 0.005 cm) as an upper estimate of the active area gives a minimum saturation current density ( $J_0$ ) of  $3 \times 10^{-8}$  A/cm<sup>2</sup>, or  $10^{-17}$  A/cylinder.

Thermal annealing would undoubtedly improve the electronic properties of these CdSe microcylinders.<sup>33,41-44</sup> However, we have found that annealing (400 °C) the materials results in loss of contact at the CdSe/Ni interface. We are currently exploring this problem further.

Graded CdSe/CdTe heterojunctions were prepared by initially depositing a predetermined amount of CdSe within the Anopore template, as described above. The electrodes were removed from the electrolyte solution, placed in the CdSO<sub>4</sub>/TeO<sub>2</sub> solution, and an equal amount (as determined by coulometer) of CdTe was deposited.

Scanning electron microscope elemental X-ray maps (Figure 3) confirm the presence of Cd and Se in the lower section of the cylinder and Cd and Te in the top, while the transition region contains all three elements.<sup>45</sup> The length of the transition region is on the order of the resolution of the mapping technique, and so a more quantitative analysis cannot be made.

Diffraction peaks for the CdTe layer were not observed in X-ray powder diffraction data on the CdSe/CdTe arrays. This is consistent with previous CdTe electrodeposition results,<sup>34,46</sup> and indicates that the as-deposited CdTe is noncrystalline. Current-voltage data obtained from the heterojunctions were comparable to the Ni/CdSe junctions.

Template-restricted growth provides an improved morphology of electrodeposited semiconductors, although it does not yield enhanced electronic properties. It is interesting to point out that electron micrograph images of the billions of parallel, thin semiconductor cylinders in this work appear remarkably similar to retinal rod cells, the photoreceptors in the human eye.<sup>47</sup> The semiconductor rods are about a factor of 5 smaller in diameter than retinal rod cells. For these semiconductor "rods" to detect light analogous to the way the retina "sees", they will have to be made independently addressable and will have to convert light into electric signals with reasonable efficiency. Both of these properties have yet to be demonstrated for the semiconductor microcolumn arrays.

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