Electrodeposited Nanophotonics

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ABSTRACT: Prior work involving the detection and emission of light from semiconductor nanostructures has involved single crystalline nanomaterials. Here we review the use of electrodeposited, polycrystalline (pc), cadmium selenide (CdSe) in nanowires and nanogap device structures for photonics. The photodetectors and photon emitters we describe are symmetrical metal–semiconductor–metal (M-S-M) devices prepared either by the evaporation of two gold contacts onto linear arrays of pc-CdSe nanowires prepared using lithographically patterned nanowires electrodeposition (LPNE), or by the electrodeposition of pc-CdSe directly onto gold nanogaps. The properties of these devices for detecting light using photocconductivity, and for generating light by electroluminescence, are described.

1. INTRODUCTION

The phrase “nanophotonics” pertains to the manipulation, detection, and emission of light from nanometer-scale devices. Lieber et al. described the first light-emitting devices based upon semiconductor nanowires in 2001. More recent work has explored the properties for light emission of single nanowires and arrays of nanowires, core–shell heterostructures, and nanowire arrays interfaced to films. Nanowire photoconductors for the detection of light were first demonstrated by Yang and co-workers using nanowires of both zinc oxide and tin dioxide. In addition to those two materials, subsequently studied by many, other materials that were investigated included gallium nitride (GaN), and cadmium sulphide (CdS).

All of this prior research focused on devices that are based upon single crystalline semiconductor nanowires (for recent reviews, see refs:10,16,18,52,53). The case for employing single crystalline nanowires rather than polycrystalline nanowires in photonics devices is based upon prior work with both nanowires and films. If we consider photoc conductivity, for example, the photocurrent, \( I_p \), is given by

\[
I_p = \frac{q P_p}{h \nu} \left( \frac{\mu t \tau_{\text{eff}} E}{L} \right)
\]

where \( q \) is the elementary charge, \( P_p \) is the incident optical power, \( \eta \) is the quantum yield, \( \nu \) is the frequency of the incident light, \( \mu \) is the carrier mobility, \( \tau_{\text{eff}} \) is the effective minority carrier lifetime, \( E \) is the electric field (the applied voltage, \( V_{\text{app}}/L \)), and \( L \) is the distance between electrical contacts. Both \( \mu \) and \( \tau_{\text{eff}} \) are depressed by grain boundaries in polycrystalline semiconductor materials. Polycrystalline nanowires and films have carrier mobilities that are a factor of \( 10^{-5} \) lower than for single crystalline versions of the same material. Studies on silicon have shown that \( \tau_{\text{eff}} \) is directly proportional to the mean grain diameter, across 5 orders of magnitude in both variables. \( \tau_{\text{eff}} \) is reduced significantly even in single crystalline silicon nanowires derived from the anisotropic etching of crystalline silicon wafers, highlighting the importance of carrier trapping and recombination at surface states. Qualitatively, the same behavior is seen in compound semiconductor materials. Although no data that we are aware of describes light emission from polycrystalline nanowires, researchers comparing single crystalline and polycrystalline films in light-emitting diodes have concluded that a reduction in the emission intensity by a factor of 100 is typical for polycrystalline films.

In spite of the deficiencies outlined above, there are two motivations for investigating polycrystalline (pc) nanomaterials for photonics. The first is speed. \( \tau_{\text{eff}} \) approximates the photocurrent decay time in the dark:

\[
I_p(t) = I_p,0 \exp \left( \frac{-t}{\tau_{\text{eff}}} \right)
\]

where \( I_p,0 \) is the dark current at a particular applied bias. The 3 dB bandwidth of the photoconductor, \( f_{\text{3dB}} \), is inversely proportional to \( \tau_{\text{eff}} \):

\[
f_{\text{3dB}} = \frac{1}{2 \pi \tau_{\text{eff}}}
\]

Equation 3 predicts that the low values of \( \tau_{\text{eff}} \) that are characteristic of polycrystalline materials correlates with a more rapid photocconductivity response and recovery. Commensurate with this expectation, fast (microsecond to picosecond) photoconductors based upon pc-CdSe and pc-CdTe films have been reported. The response and recovery times for photocconductivity in these microscopic films are considerably faster.

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than most single crystalline nanowires, nanorods, etc. (Table 1).
It is reasonable to assume that reducing the carrier lifetime will
simultaneously make possible more rapid modulation of the
electroluminescence from these devices, but this has not yet been
investigated.

The second motivation involves the “nanowire integration
problem”. Incorporating single crystalline nanowires into elec-
trical circuits is not straightforward. Such nanowires are obtained
as orientationally disordered powders either from solution phase
synthetic methods, or as a consequence of the removal of orien-
ted nanowires from a surface as in vapor—liquid—solid (VLS)
growth.83−86 How are individual nanowires extracted from
these powders and positioned within an electrical circuit with the
attachment of electrical contacts? A desire to solve the nanowire
integration problem has brought about the development of new
and innovative methods including contact printing of nano-
structures,87 electro-erosion,88 and mechanical alignment.89,90 Each
of these processes provides a different strategy for positioning a
nanowire within a prefabricated electrical circuit.

Instead of making the circuit first and “plugging” nanowires
into it, an alternative is to synthesize polycrystalline nanowires
first, in a predetermined position and orientation on a dielec-
tric substrate, and then fabricate the circuit on top of them
(Figure 1). Lithographically patterned nanowire electrodeposi-
tion or LPNE,92−94 provides a means for doing this. LPNE can be
used to pattern arrays of thousands of CdSe nanowires, on glass,
and other dielectrics.59,93,96 In this article, I describe recent work
from our laboratory in which we probe the properties of pc-CdSe
nanowires and nanostructures for the detection and electrically
stimulated emission of light.91,95−100

### Table 1. Summary of Cadmium Chalcogenide-Based Photodetector Performance

<table>
<thead>
<tr>
<th>absorber</th>
<th>(t_{\text{resp}})</th>
<th>(I_{\text{phot}})</th>
<th>photosensitivity (S)</th>
<th>absorber and gap dimensions</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe film</td>
<td>1.0 ms</td>
<td>1.5 ms</td>
<td>(10^{-10})</td>
<td>(40 \mu m(gap) \times 2.2 \text{ mm}(w) \times 700 \text{ nm}(h))</td>
<td>136</td>
</tr>
<tr>
<td>CdSe film</td>
<td>1.6 ms</td>
<td>1.6 ms</td>
<td>1</td>
<td>(0.5 \text{ cm}(gap) \times 2.0 \text{ cm}(w) \times 750 \text{ nm}(h))</td>
<td>137</td>
</tr>
<tr>
<td>CdSe film</td>
<td>1.0 ms</td>
<td>0.2 ms</td>
<td>(10^{6})</td>
<td>(35 \mu m(gap) \times 10 \mu m(w) \times 300 \text{ nm}(h))</td>
<td>72</td>
</tr>
<tr>
<td>CdSe film</td>
<td>1.3 ms</td>
<td>0.2 ms</td>
<td>n.r.</td>
<td>(1 \text{ cm}(A) \times 300 \text{ nm}(h))</td>
<td>73</td>
</tr>
<tr>
<td>CdSe film</td>
<td>2.00 ms</td>
<td>200 ms</td>
<td>(10^{5}−10^{6})</td>
<td>(5 \text{ mm}(gap) \times 5 \text{ mm}(w) \times 170 \text{ nm}(h))</td>
<td>138</td>
</tr>
<tr>
<td>CdS nw</td>
<td>~15 ms</td>
<td>~15 ms</td>
<td>39</td>
<td>(20 \mu m(gap) \times 200 \text{ nm}(dia.) \text{ array})</td>
<td>100</td>
</tr>
<tr>
<td>CdS nr</td>
<td>15 ms</td>
<td>15 ms</td>
<td>(1.5 \times 10^{5})</td>
<td>(200 \text{ nm}−5 \mu m(w) \times 40 \text{ nm}(h))</td>
<td>139</td>
</tr>
<tr>
<td>CdS nr</td>
<td>200 ms</td>
<td>500 ms</td>
<td>2</td>
<td>(25 \mu m(gap) \times 640 \text{ mm}(w) \times 50 \text{ nm}(h))</td>
<td>50</td>
</tr>
<tr>
<td>CdS nr</td>
<td>746 ms</td>
<td>794 μs</td>
<td>(9.2 \times 10^{5})</td>
<td>(18 \mu m(gap) \times 10−60 \mu m(w) \times 2−40 \text{ nm}(h))</td>
<td>105</td>
</tr>
<tr>
<td>CdS nr</td>
<td>551 μs</td>
<td>109 ms</td>
<td>(3.3 \times 10^{5})</td>
<td>(50 \text{ nm}(gap) \times 5−10 \mu m(w) \times 65 \text{ nm}(h))</td>
<td>81</td>
</tr>
<tr>
<td>CdS nr</td>
<td>137 μs</td>
<td>379 μs</td>
<td>(10^{5})</td>
<td>(13 \mu m(gap) \times 500 \text{ nm}(w))</td>
<td>140</td>
</tr>
<tr>
<td>CdTe nr</td>
<td>&gt;1 s</td>
<td>&gt;3 s</td>
<td>10</td>
<td>(2 \mu m(gap) \times 300 \text{ nm}(dia.) \text{ vertical array})</td>
<td>141</td>
</tr>
<tr>
<td>CdSe QD</td>
<td>~10 μs</td>
<td>100−6000</td>
<td>n.r.</td>
<td>(5 \mu m(gap))</td>
<td>142</td>
</tr>
<tr>
<td>CdSe/QdS QD</td>
<td>~10 μs</td>
<td>100−6000</td>
<td>n.r.</td>
<td>(~100 \text{ nm}(gap))</td>
<td>143</td>
</tr>
<tr>
<td>CdSe nr</td>
<td>15 μs</td>
<td>31 μs</td>
<td>100</td>
<td>(~2.5 \mu m(gap) \times 2−4 \mu m \times 50−100 \text{ nm})</td>
<td>144</td>
</tr>
<tr>
<td>CdSe nr</td>
<td>1 s</td>
<td>200 μs</td>
<td>15</td>
<td>(1−2 \mu m(gap) \times 350 \text{ or } 70 \text{ nm}(dia.))</td>
<td>101</td>
</tr>
<tr>
<td>CdSe nr</td>
<td>1.7 ms</td>
<td>6.7 ms</td>
<td>n.a.</td>
<td>(5 \mu m(gap) \times 5 \mu m(w) \times 60 \text{ nm}(h))</td>
<td>113</td>
</tr>
<tr>
<td>CdSe nw</td>
<td>700 ms</td>
<td>700 ms</td>
<td>40</td>
<td>(5 \mu m(gap) \times 60 \text{ nm}(dia.))</td>
<td>86</td>
</tr>
<tr>
<td>pc-CdSe on</td>
<td>~10 μs</td>
<td>10 μs</td>
<td>500</td>
<td>(5 \mu m(gap) \times 30−60 \text{ nm}(dia.))</td>
<td>102</td>
</tr>
<tr>
<td>carbon SWNTs</td>
<td>9 ms</td>
<td>3 ms</td>
<td>~2</td>
<td>(2.5 \mu m(gap) \times 973 \text{ nm}(w) \times 87 \text{ nm}(h))</td>
<td>144</td>
</tr>
<tr>
<td>CdSe nr</td>
<td>15 μs</td>
<td>27 μs</td>
<td>10−5×10^7</td>
<td>(5 \mu m(gap) \times 200 \text{ nm}(w) \times 60 \text{ nm}(h))</td>
<td>96</td>
</tr>
<tr>
<td>pc-CdSe nw</td>
<td>20 μs</td>
<td>30 μs</td>
<td>10−100</td>
<td>(5 \mu m(gap) \times 200 \text{ nm}(w) \times 60 \text{ nm}(h))</td>
<td>96</td>
</tr>
<tr>
<td>pc-CdSe ng</td>
<td>~10 μs</td>
<td>10 μs</td>
<td>100</td>
<td>(5−20 \mu m(gap) \times 1 \mu m(w))</td>
<td>98</td>
</tr>
</tbody>
</table>

Abbreviations: QD = quantum dot; nw = nanowire; nr = nanoribbon; ng = nanogap; n.r. = not reported. Response and recovery times as reported by the authors.

**Figure 1.** Schematic diagram depicting the fabrication of light-emitting M-S-M junctions starting with an array of pc-CdSe nanowires prepared using lithographically patterned nanowire electrodeposition (LPNE). Reprinted with permission of reference 91, copyright 2013, American Chemical Society.

Although polycrystalline nanomaterials have the potential to exhibit performance and device fabrication advantages relative to single crystalline materials, these advantages have been realized in few investigations to date. Mallouk and Keating et al.101 were the first to study photoconductivity in pc-CdSe nanowires. In that work, gold−CdSe−gold segmented nanowires were prepared using template electrodeposition, and these structures showed a strong photoconductive response. Joselevich and co-workers102 used carbon single-walled nanotubes to nucleate CdSe electrodeposi-
tion, forming pc-CdSe nanowires 134−174 nm in diam-
eter. These structures showed rapid, sub-10 ms, response and recovery of their photoconductivity to light. We are aware of no other work in this area, aside from that of our own research group described below.

### 2. Electrodeposition of pc-CdSe Nanowires and Nanogap Structures

CdSe has been intensively studied for photonics applications. It is a direct band gap semiconductor with a band gap in the visible region of the spectrum \(E_g = 1.75 \text{ eV}, T = 298 \text{ K}\).
Prior work includes applications of CdSe to field-effect transistors, solar photovoltaics, photodetectors, and light-emitting diodes. pc-CdSe nanowires were synthesized using the lithographically patterned nanowire electrodeposition or LPNE method (Figure 2a,b).

The process flow for the LPNE synthesis of CdSe is as follows: A nickel layer is first evaporated on a glass surface, and photoresist is deposited onto the nickel surface (Figure 2a,b step (i)). The nickel layer thickness will dictate the thickness of the CdSe nanowires that is electrodeposited. This photoresist is then patterned using a contact mask (Figure 2a,b step (ii)), and the exposed nickel is removed by etching in nitric acid (Figure 2a,b step (iii)). The etching time is adjusted during this process to expose nickel is removed by etching in nitric acid (Figure 2a,b step (iv)). Near stoichiometric pc-CdSe nanowires are obtained using the scanning electrodeposition/stripping method pioneered by Sailor et al. Typical cyclic voltammograms (Figure 2c, orange trace) show a single, broad reduction wave that encompasses the formation of elemental cadmium and selenium and the formation of CdSe as the potential is scanned negatively from −0.20 V vs SCE to −0.90 V. On the ensuing positive scan, an oxidation wave signals the removal of excess cadmium from the nascent deposit. Elemental selenium is not removed within this potential window, and for this reason, a highly skewed Cd:Se molar ratio of 100:1, typically, is used in the plating solution to promote the conversion of selenium to CdSe instead of elemental selenium. By scanning the potential across this window multiple times, a pc-CdSe nanowire of the desired width is produced (e.g., Figure 2c,f).

The stoichiometry of the CdSe electrodeposited prepared using the electrodeposition/stripping procedure was investigated by X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray analysis (EDX) for CdSe nanowires prepared on graphite. The molar ratio Se:Cd = 1.5−1.7 under the conditions shown in Figure 2c, but it is reduced to ~1.1 if the nanowire is thermally annealed at 300 °C × 30 min in N2.

After electrodeposition of the CdSe, two modes for thermal processing can be applied to achieve the desired dave value (Figure 3): Heating the plating solution during the electrodeposition/stripping method pioneered by Sailor et al.117

Figure 3. Schematic depiction of the influence of thermal processing on the mean grain diameter of pc-CdSe nanowires prepared using LPNE. Represented here is the cross section of nanowires with a height of 60 nm, taken perpendicular to the surface. Reprinted with permission of reference 96, copyright 2011, American Chemical Society.

deposition of CdSe, and thermal postprocessing of nanowires in an inert gas environment in an oven. The combination of these two processes provides the means for adjusting dave from 5 nm up to 100 nm for pc-CdSe nanowires, as shown schematically in Figure 3. The structure of the nanowires prepared by LPNE can be characterized using grazing incidence X-ray diffraction (GIXRD). GIXRD data are acquired using surfaces on which linear arrays of thousands of nanowires are deposited at an interwire pitch of 5 μm (e.g., Figure 2d). An estimate of the mean grain diameter, dave is obtained from the GIXRD patterns using the line-width of the most intense (e.g., (111) for cubic CdSe) reflection according to the Scherrer eq.119

\[
d_{ave} = \frac{\lambda}{B \cos \theta}
\]

where dave is the mean grain diameter, \( \lambda \) is the X-ray wavelength, B is the full width of the peak measured at half-height, and \( \theta \) is the diffraction angle. In typical GIXRD patterns of pc-CdSe

Figure 2. Synthesis of pc-CdSe nanowires: (a,b) Schematic diagram showing the five-step process flow for the synthesis by lithographically patterned nanowire electrodeposition (LPNE) of pc-CdSe nanowires - (i) a nickel layer and a (+)-photore sist (PR) layer are both deposited on a glass surface, (ii) the PR layer is patterned with a contact mask, (iii) nickel is etched from the patterned surface using nitric acid, (iv) pc-CdSe is electrodeposited from an aqueous solution containing both SeO3 and Cd2+. CdSe is deposited at the nickel electrodes - within the horizontal trench delineated on three sides by the PR, the glass surface, and the nickel electrodes. (v) PR and nickel are selectively removed to expose the exposed nickel is removed by etching in nitric acid (Figure 2a,b step (iv)). Near stoichiometric pc-CdSe nanowires are obtained using the scanning electrodeposition/stripping method pioneered by Sailor et al.117 Typical cyclic voltammograms (Figure 2c, orange trace) show a single, broad reduction wave that encompasses the formation of elemental cadmium and selenium and the formation of CdSe as the potential is scanned negatively from −0.20 V vs SCE to −0.90 V. On the ensuing positive scan, an oxidation wave signals the removal of excess cadmium from the nascent deposit. Elemental selenium is not removed within this potential window, and for this reason, a highly skewed Cd:Se molar ratio of 100:1, typically, is used in the plating solution to promote the conversion of selenium to CdSe instead of elemental selenium. By scanning the potential across this window multiple times, a pc-CdSe nanowire of the desired width is produced (e.g., Figure 2c,f).
nanowires deposited on glass surfaces (Figure 4a), the broad peak centered at 25° is contributed by diffuse reflection of X-rays from the amorphous glass surface. Narrower lines superimposed on this background are produced by reflections from CdSe. Two different crystal structures are achieved for the CdSe nanowires probed in Figure 4a: Trace (i) shows reflections for wurtzite phase CdSe nanowires while traces (ii–iii) all show patterns characteristic of cubic phase CdSe. The phase transition from cubic to wurtzite is induced by exposure of the CdSe nanowires to CdCl₂ in methanol prior to heating at 300 °C in N₂ for 4 h (Figure 5). Raman spectra, not shown here, provide information on the short-range structure of pc-CdSe nanowires that is also diagnostic of the crystallinity and the crystal structure.⁹¹,⁹₈

Electrodeposited pc-CdSe shows strong, band-edge photoluminescence at 1.75–1.80 eV (298 °C) and no perceptible trap state emission at lower energies. Neither the line width of this emission nor the peak energy is influenced significantly by the thermal processing described above.⁹₅,⁹₆,⁹₈

In the photonics devices constructed from these nanowires, the electrical contacts are separated by 0.5–5.0 μm, typically. Nanogap structures allow the influence of narrower spacings for the electrical contacts, making possible higher electrical fields, to be investigated. Thus, in addition to pc-CdSe nanowires, we have also prepared gold nanogap structures in which a nanometer-scale gap is formed in a gold film either by electromigration⁹₈ or by focused ion beam (FIB) milling (Figure 6).⁹₇ This gap, which can range in width from 5 nm in the case of electromigration⁹₈ to 200 nm,⁹₇ can then be bridged with electrodeposited pc-CdSe using the same electrodeposition procedure described in Figure 2c for nanowire growth (Figure 7).⁹₇,⁹₈ The thermal annealing of gold nanogap structures is not possible, however, because of the instability of these nanogaps at the temperatures required for CdSe grain growth.⁹₇,⁹₈ It should be noted that the photonic properties of all devices were characterized in a laboratory air ambient (typically 20 °C and RH ≈ 55%). We did not systematically investigate the issue of stability, but device instability usually coincided with thermal damage caused by joule heating, sometimes culminating in the fracturing of the glass substrate on which the device was deposited. The use of substrates with higher thermal conductivities, such as crystalline silicon, might mitigate this issue.

Figure 4. (a) Grazing incidence (incident angle = 0.3°) X-ray diffraction pattern (GIXRD) for arrays of pc-CdSe nanowires electrodeposited at 5 μm pitch on glass: (i) deposited at 25 °C, dipped in saturated CdCl₂:CH₃OH solution, and annealed (N₂, 300 °C, 4 h), (ii) deposited at 75 °C and annealed (N₂, 300 °C, 4 h), (iii) deposited at 75 °C; (iv) as-deposited at 25 °C. A broad reflection centered at ~25° in each pattern is derived from the amorphous glass surface. (b,c) Selected area electron diffraction patterns for (b) sample (i), and (c) sample (ii) showing the same principle reflections seen for these samples by XRD. The discontinuous diffraction rings seen in (b) are a consequence of the large grain dimensions in this sample. Reprinted with permission of reference 96, copyright 2011, American Chemical Society.

Figure 5. SEM images of: (a) an array of pc-CdSe nanowires and, at higher magnification, (b) pc-CdSe nanowires processed without, and, (c) with exposure to CdCl₂ in methanol. Reprinted with permission of reference 96, copyright 2011, American Chemical Society.

Figure 6. Fabrication of pc-CdSe filled, gold nanogap structures that function as light-emitting nanojunctions (LEnJs). (a) Schematic process flow for creating a nanogap and electrodeposition of pc-CdSe into it. (b) Photograph of a 2.5 cm × 2.5 cm glass slide showing six × twelve-nanogap arrays. (c) Optical micrograph of the six × twelve-nanogap arrays. (d) Scanning electron micrograph of a twelve-nanogap device characterized by 5 μm gold fingers after the fabrication by FIB of 200–250 nm nanogaps. Reprinted with permission of reference 97, copyright 2013, American Chemical Society.
3. PHOTODETECTORS BASED UPON PHOTOCONDUCTIVITY

Following the pioneering work of Mallouk and Keating et al., our research group began studying the photoconductivity of ensembles of pc-CdS wires in 2004. Micro- and nanowires of CdS were obtained by first electrodepositing cadmium metal nanowires at the step edges present on a highly oriented pyrolytic graphite electrode, and then converting these cadmium nanowires to CdS by annealing in H2S at 300°C for 30 min. Ensembles of 10–100 pc-CdS nanowires prepared in this way were then transferred from the graphite surface to a dielectric, such as glass, and electrical contacts were prepared. This process, called electrochemical step edge decoration (ESED), enabled the preparation of ensembles of very long (>1 mm) nanowires. After transfer to glass surfaces, ensembles of pc-CdS nanowires showed a strong photoconductivity response, characterized by a photosensitivity, $S = (I_{\text{photo}} - I_{\text{dark}})/I_{\text{dark}}$, of 40 and a rapid photoconductivity response with rise and recovery times in the 15 ms range—competitive with other II–VI nanowire-based photodetectors prepared up until that time. Subsequently, stoichiometric pc-CdSe nanowires were prepared by ESED on graphite using an electrodeposition/stripping process that is similar to the process in use today (i.e., Figure 2c) but that the photoconductivity response of those nanowires were not investigated. However, the utility of ESED for device fabrication is limited both because of the requirement for nanowire transfer from the HOPG surface and because the arrangement of nanowires after transferring to a dielectric surface is dictated by the location of step edges on the graphite used for nanowire growth.

The deficiencies of the ESED process were addressed in 2006 by the development of a new process for electrochemical nanowire growth called lithographically patterned nanowire electrodeposition (LPNE). As already described above (Figure 2a), LPNE provides a means for patterning nanowires prepared by electrodeposition directly on dielectric surfaces. LPNE was applied to the synthesis of pc-CdSe nanowires in 2010.

Nanowires with lateral dimensions of 60 nm × 200 nm and millimeter scale lengths were prepared. These nanowires were close to stoichiometric and had a mean grain diameter of ~10 nm. We found that arrays of 350 such nanowires showed a strong photoconductivity response with $S$ in the range from 10 to 100 (Figure 8b), and response and recovery times of 20–40 μs.
distance between contacts. In contrast to $p-n$ or $p-i-n$ photodiodes, photoconductor-based photodetectors are capable of producing $G$ values that exceed one and can be as high as $10^5$. But $G$ values measured for these nanocrystalline $pc$-CdSe nanowires were in the range from 0.032 to 0.050. That is, the absorption of more than 20 photons was required to produce a signal of one electron in the measurement circuit.

Two strategies for increasing $G$ were tested in subsequent studies: First, the mean grain diameter, $d_{ave}$, of the $pc$-CdSe nanowires was increased using thermal annealing coupled with hot electrodeposition, as already described above (Figures 3, 4), and second, the distance between the electrical contacts was dramatically reduced from the 5 $\mu$m value seen in Figure 8a by using gold nanogap structures having gap dimensions in the range from 0.1 to 1 $\mu$m.
5–20 nm range. The rationale for these two strategies is easily understood with reference to eq 5: Increasing the mean grain diameter was intended to increase $\tau_{\text{eff}}$, which is proportional to $G$. The gap distance, on the other hand, is directly proportional to $\tau_p$ and therefore inversely proportional to $G$.

Both of these approaches enhance $G$ significantly. Increasing $d_{\text{ave}}$ from 5 to 100 nm increases $S$ from 8 to 300 and $G$ by a factor of ~30—from 0.02 to 6. However, the increase in $d_{\text{ave}}$ caused an even stronger increase in the photocurrent response and recovery times, both of which increased by factors of $10^3–10^6$ (see Figure 9). For example, the rise and recovery times for the $d_{\text{ave}} = 10$ nm nanowires are 8 $\mu$s, while that of $d_{\text{ave}} = 100$ nm nanowires are 8 s. These data show very clearly that $d_{\text{ave}}$ can be used to adjust the properties of pc-CdSe nanowires for detecting light, but the simultaneous optimization of bandwidth and gain is difficult. Increasing $\tau_{\text{eff}}$ increases both $I_p$ (eq 1) and $G$ (eq 5) but decreases $f_{3db}$ (eq 3).

However, eq 5 also suggests a way to circumvent this catch-22: reduce $f$ by employing nanogap structures instead of nanowires. Gold nanogaps with widths in the 5–20 nm range produced by electromigration (Figure 10a–d) were filled with electrodeposited pc-CdSe (Figure 10e) using the same procedure described in Figure 2. The photoconductivity of these devices was characterized by a $S = 500$, $G \approx 45$, and response/recovery times (limited by our measurement circuit) of $<2 \mu$s, corresponding to $f_{3db} \approx 175$ kHz (Figure 10f–h). Thus, nanogap structures allow a higher gain × bandwidth product to be accessed, allowing for the elevation of both $G$ and $f_{3db}$ simultaneously relative to the accessible $G$ and $f_{3db}$, for pc-CdSe nanowires.

The excellent photodetector performance obtained from pc-CdSe in both nanogaps and nanowires is surprising when it is considered that the grain boundaries present in pc-CdSe makes it a profoundly defective material that has, for example, low carrier mobilities, $\mu_{\text{eff}}$, in the $10^{-4}$–$10^{-5}$ cm$^2$/V s range, as compared with $\mu_{\text{eff}} = 650–800$ cm$^2$/V s at 298 K for bulk CdSe. However, these defects do not disqualify pc-CdSe for preparing efficient and fast photoconductive photodetectors. In fact, polycrystalline CdSe nanowires and filled nanogaps prepared by electrodeposition produce metrics for photodetection that rival or exceed those of single crystalline nanorods, nanowires, and nanoribbons (Table 1).

4. ELECTROLUMINESCENT NANOGAPS AND NANOWIRES

We are in the early stages of investigating the properties of electrodeposited pc-CdSe in symmetrical, metal–semiconductor–metal (M-S-M) junctions for generating light. The fabrication and evaluation of pc-CdSe-filled nanogap structures and pc-CdSe nanowires were both reported in 2013.

As already recounted above, the history of emissive nanowire devices dates to 2001. Emissive nanogap structures were first reported in 2002 by Dickson and coworkers who observed electroluminescence (EL) from silver and gold nanoclusters located within metal nanogaps. Subsequently, light emission was seen from metal nanogaps containing single CdSe nanocrystals, CdSe/ZnS (core/shell) nanocrystals, and CdSe/ZnS (core/shell) nanocrystals. The quantum efficiency, $\eta$, for light emission from M-S-M structures based upon cadmium chalcogenides, including nanogaps and nanowires is in the range from $\eta = 10^{-3}$ to $10^{-7}$, while the threshold voltage for light emission, $V_{\text{th}}$, is 5–15 V. However, all this prior work has involved investigations of single crystalline nanoparticles or nanowires, or ensembles of single crystalline nanostructures.

Our initial goals in studying light emission from pc-CdSe was to understand whether this defective material could compete with single crystalline nanomaterials in terms of the critical light emission metrics.

Initial devices consisting of pc-CdSe-filled nanogap structures, referred to as light-emitting nanojunctions or LE$n$Js, are depicted in Figure 6. Although gold nanogaps are not stable with respect to thermal annealing, LE$n$Js were prepared using two different electrodeposition temperatures, $T_{\text{dep}} = 20$ °C and 75 °C in order to evaluate the influence of mean grain diameter (Figures 11, 12).

![Figure 11](https://example.com/figure11.png)

Figure 11. Optical micrographs and intensity profiles for LE$n$Js. (a,b) Optical micrographs showing EL as a function of the applied voltage (indicated in white). Data for $T_{\text{dep}} = 20$ °C (a) and 75 °C (b) are shown. All images were acquired using an integration time of 10 s. The dotted yellow line in the 2.5 V image coincides with the location of the nano gaps in these images. (c,d) Intensity profiles for 20 °C (c) vs 75 °C (d) along above dashed lines at 2.5 V. (e,f) Magnified traces of emission spots reveal that the full width at half-maximum intensity of each peak is ≤1 μm. Reprinted with permission of reference 97 copyright 2013, American Chemical Society.

Optical micrographs of LE$n$Js arrays (Figure 11a,b) show 10 LE$n$Js prepared using $T_{\text{dep}} = 20$ °C (a) or 75 °C (b). A subset of the LE$n$Js in each image begins emitting at an applied voltage, $V_{\text{app}}$, near 2 V, and the number of emitting junctions as well as the light intensity increases with $V_{\text{app}}$. Light emission is concentrated at ~1 μm “hot spots” aligned along the length of the 10 μm LE$n$Js. LE$n$Js prepared using $T_{\text{dep}} = 75$ °C have a higher probability for light emission as compared with devices prepared at 20 °C. Moreover, while the light emission process and current—voltage
curves for these LEnJs are symmetrical with respect to the polarity of $E_{\text{app}}$ (Figure 12a–d), the current and the light intensity measured at a particular $E_{\text{app}}$ are both an order of magnitude higher for the 75 °C-deposited junctions. A preliminary conclusion is that light emission is promoted by the larger grain diameter of the pc-CdSe deposited at 75 °C ($d_{\text{ave}} = 11$ nm (75 °C) versus 6 nm (20 °C)).

A spectrum of the emitted light for a LEnJ prepared using $T_{\text{dep}} = 75$ °C (Figure 12e) shows a broad emission envelope centered at 750 nm ($\sim 1.65$ eV) at large values of $E_{\text{app}} > 2.5$ V, just below the 1.75 eV band gap of CdSe. However, a spectrum acquired at $E_{\text{app}} = 1.7$ V, near the threshold for light emission, is red-shifted to 890 nm (1.42 eV). This observation suggests that near the threshold voltage, light emission occurs from trapped electrons and holes, whereas for higher $E_{\text{app}}$ and currents, near-band edge recombination occurs across the entire band gap of the pc-CdSe.

Arrays of pc-CdSe nanowires (e.g., Figure 8a) behave similarly to LEnJs (Figure 13a–c). Although EL emission from M-S-M junctions has been attributed to a variety of mechanisms, several lines of evidence implicate Poole–Frenkel emission in the LEnJs and nanowire arrays described here. Poole–Frenkel emission involves the electric field-driven “untrapping” of electrons and holes from defects; a prominent feature of our polycrystalline materials. Once liberated from traps, recombination and EL light emission from electrons and holes can occur. Both LEnJs (Figure 12b, inset) and nanowire arrays (Figure 13b) show a linear dependence of $\ln(I)$ on $E_{\text{app}}^{1/2}$ qualitatively as expected for Poole–Frenkel emission:

$$I = I_0 \exp \left( \frac{\beta \mu V_{\text{FB}}^{1/2}}{kT d^{1/2}} \right)$$

Figure 12. Electrical and optical characterization of LEnJs. (a) Current versus applied bias for Au–CdSe–Au nanogap devices fabricated at 20 °C (blue) vs 75 °C (red). (b) The same $I$–$V$ data shown in (a) with rescaled current axes. Inset: Plot of $\ln I$ versus $V_{\text{FB}}^{1/2}$ for these data showing the linearity of these plots. (c,d) EL intensity (left axis) and current (right axis) versus applied forward bias at 20 °C (c) vs 75 °C (d). e) EL emission spectrum for a typical LEnJ prepared from $T_{\text{dep}} = 75$ °C plating solution. (f) Energy level diagram depicting the M-S-M at an applied bias equal to the flat-band potential of the device, $E_{\text{FB}}$ showing a reduction in the barrier for hole injection by $V_{\text{bi}}$. Depicted here are two radiative recombination processes for electrons and holes responsible for the EL emitted by these devices. Reprinted with permission from reference 97, copyright 2013, American Chemical Society.
where \( d \) is the thickness of the semiconductor layer, \( I_0 \) is the low-field current, and \( \beta_{pf} \) is the Poole–Frenkel field-lowering coefficient.\(^{54,134} \) In the case of nanowires, EL light emission is concentrated in the vicinity of electrical contacts where the electrical fields, directly measured using scanning Kelvin probe microscopy, are also the highest.\(^{91} \) While the contribution of

Table 2. Comparison of Device Metrics for Nanowire and Nanorod Light-Emitting Junctions and Diodes

<table>
<thead>
<tr>
<th>emissive element(^a)</th>
<th>device(^b)</th>
<th>device length(^c) (μm)</th>
<th>( V_{th} ) (V)</th>
<th>( \lambda ) (nm)</th>
<th>EQE (^f)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdSe nr</td>
<td>M-S-M</td>
<td>0.030</td>
<td>1.75</td>
<td>750–720</td>
<td>10(^{-3})</td>
<td>23</td>
</tr>
<tr>
<td>CdSe nw</td>
<td>M-S-M</td>
<td>2–6</td>
<td>4</td>
<td>730</td>
<td>(1–5) ( \times 10^{-6} )</td>
<td>22</td>
</tr>
<tr>
<td>CdSe nw + graphene</td>
<td>p–n</td>
<td>~2–3</td>
<td>4</td>
<td>705</td>
<td>n.r.</td>
<td>31</td>
</tr>
<tr>
<td>n-CdSe+p-Si nw</td>
<td>p–n</td>
<td>~1</td>
<td>n.a.</td>
<td>700</td>
<td>10(^{-3})–10(^{-2})</td>
<td>8</td>
</tr>
<tr>
<td>CdSe@ZnS nc’s</td>
<td>M-S-M (M = Au)</td>
<td>0.1–0.2</td>
<td>1.60</td>
<td>680–820</td>
<td>n.r.</td>
<td>128</td>
</tr>
<tr>
<td>in ng</td>
<td>M-S-M (M = Pt/In)</td>
<td>0.1–0.2</td>
<td>~11</td>
<td>620–650</td>
<td>n.r.</td>
<td>128</td>
</tr>
<tr>
<td>CdSe@ZnS nc’s</td>
<td>Si–S–Si</td>
<td>in STM</td>
<td>~17</td>
<td>500–750</td>
<td>n.r.</td>
<td>129</td>
</tr>
<tr>
<td>in STM</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-InP+p-InP nw</td>
<td>p–n</td>
<td>~2</td>
<td>1.7</td>
<td>680–820</td>
<td>10(^{-3})</td>
<td>19</td>
</tr>
<tr>
<td>InP superlattice nw</td>
<td>p–n</td>
<td>10(^{-3})</td>
<td>~1.0</td>
<td>n.r.</td>
<td>n.r.</td>
<td>145</td>
</tr>
<tr>
<td>GaN nw</td>
<td>n–i–n</td>
<td>n.a.</td>
<td>3</td>
<td>900</td>
<td>10(^{-4})</td>
<td>21</td>
</tr>
<tr>
<td>p-GaN + n-Si nw</td>
<td>p–n</td>
<td>10(^{-3})</td>
<td>6 (( V_g = 2 ) V)</td>
<td>350–450</td>
<td>10(^{-3})</td>
<td>8</td>
</tr>
<tr>
<td>GaN CMS nw</td>
<td>p–n</td>
<td>2–3</td>
<td>~4</td>
<td>tunable 380–650</td>
<td>0.039–0.058</td>
<td>11</td>
</tr>
</tbody>
</table>

\( ^{a} \text{Abbreviations: nc = nanocrystal, nr = nanorod, nw = nanowire, ng = nanogap.} \)

\( ^{b} \text{Abbreviations: MSM = metal-semiconductor-metal, } p-n = p-n \text{ junction photodiode.} \)

\( ^{c} \text{The distance across the emissive element between the electrical contacts.} \)

\( ^{d} \text{Threshold voltage for light emission.} \)

\( ^{e} \text{EQE = external quantum efficiency.} \)

Figure 13. (a–c) Current versus voltage data (a,b) and EL intensity versus voltage (c) for three light-emitting junctions. (d) Brightfield optical micrograph of an nc-CdSe nanowire array. (e) Series of image of the EL emission for an array acquired at currents (\( E_{app} \)) of 0.6 μA (20 V), 0.9 μA (28 V), 1.2 μA (37 V), 1.6 μA (45 V), 2.2 μA (56 V). (f) Plot of the percentage of emissive nanowire junctions as a function of \( E_{app} \). Reprinted with permission of reference 91, copyright 2013, American Chemical Society.
other mechanisms for light emission can not be discounted, our data suggests that Poole–Frenkel emission is a prominent mechanism for EL in these systems.

As in the case of LEnJs, individual pc-CdSe nanowires progressively begin to emit light with increasing $E_{\text{app}}$ (Figure 13d), contributing to EL intensities that increase quadratically with $E_{\text{app}}$ (Figure 13c). Doh et al. have reported similar intensity dependencies for single crystalline CdSe nanowires. This nanowire “turn on” process is documented by the photomicrographs (Figure 13e) showing part of a 350 nanowire device. Using data like that shown in Figure 13a and c, the external quantum efficiency (EQE) can be estimated

$$\text{EQE} = \frac{P_{\text{opt}}}{\nu I e}$$

where $P_{\text{opt}}$ is the measured optical power, $h$ is Planck’s constant, $\nu$ is the frequency of the emitted light, $I$ is the current, and $e$ is the elementary charge. For pc-CdSe nanowires and LEnJs, EQE values range from $(6-8) \times 10^{-7}$ to $1 \times 10^{-6}$. These values are certainly low, but they are virtually the same as EQEs measured for single crystalline CdSe nanowires and nanorods which produce values in the range from $10^{-3}$ to $10^{-2}$ (Table 2). In terms of maximizing the efficiency of light emission, tremendous opportunities exist for expanding our understanding and improving the performance of M-S-M devices based upon polycrystalline semiconductor materials.

5. SUMMARY

Electrodeposited polycrystalline CdSe is a versatile photonic material from which M-S-M devices can be obtained either by deposition into prefabricated metal nanogaps, or by nanowire formation using LPNE. These devices enable the detection of light by modulation of their photoconductivity, and the generation of light by electroluminescence. For the detection of light, the intrinsic defectiveness of pc-CdSe is actually an advantage, because it promotes rapid recombination of photoexcited carriers and a prompt return to the dark conductivity state from the photoconductive state of this material (eq 3). A bandwidth of up to 175 kHz has been measured for LEnJs coupled with S up to 500—metrics that are competitive with the current state-of-the-art (Table 1). Surprisingly, the defects associated with grain boundaries do not handicap pc-CdSe relative to single crystalline CdSe for EL emission—EQE values are approximately the same for these systems. We speculate that pc-CdSe works reasonably well for EL because a channel for light emission, Poole–Frenkel emission, is facilitated in pc-CdSe relative to single crystalline CdSe, but more investigation will be required in order to understand and further optimize EL emission from polycrystalline semiconducting materials.

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Notes

The authors declare no competing financial interest.

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Reginald Penner is Chancellor’s Professor in the Departments of Chemistry and Chemical Engineering and Materials Science at the University of California, Irvine. He received B.A. degrees in Chemistry and Biology at Gustavus Adolphus College in Minnesota, and a Ph.D. at Chemistry at Texas A&M University working with Professor Charles R. Martin. After a postdoctoral appointment with Professor Nathan S. Lewis at Stanford and Caltech, he joined the faculty at UC Irvine in 1990. His research group studies the electrodeposition of nanomaterials, and the applications of these materials in devices including chemical sensors, biosensors, optical sensors and light emitters, batteries and capacitors.

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