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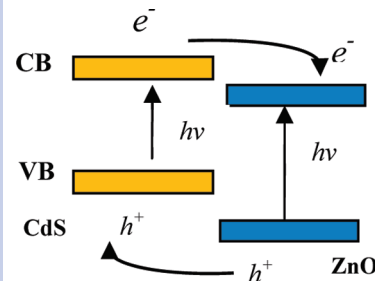
# Enhanced Photoresponse of Inkjet-Printed ZnO Thin Films Capped with CdS Nanoparticles

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**ABSTRACT** Composite semiconductors provide routes for realizing high-performance electronic devices, but for many applications of such devices, low-cost manufacturing techniques are desirable. We have engineered a 3 orders of magnitude enhancement of the ultraviolet photoresponse of ZnO thin films, fabricated “in situ” by drop-on-demand inkjet printing, and then capped with CdS nanoparticles by dip coating. As a consequence, the decay time of the photoresponse is reduced to about 4 ms. Thus, capping with CdS not only suppresses the detrimental passivation layer of ZnO thin films, but also generates an interfacial carrier transport layer to reduce the probability of carrier recombination.

**SECTION** Electron Transport, Optical and Electronic Devices, Hard Matter



Zinc oxide is a versatile technologically important material for developing optical and electronic components, especially in the emerging area of transparent electronics. Availability of more advanced facilities to synthesize and characterize materials at a nanoscale has revived interest to exploit the photoconductive properties of ZnO, especially in the UV regime, although such studies have been in progress for a long time since the 1950s.<sup>1</sup> The intrinsic UV properties of ZnO are very useful for developing nanoscale optoelectronic devices, because it is a wide bandgap semiconductor with good carrier mobility and can be doped to become both n-, and p-type.<sup>2,3</sup> However, it is difficult to obtain high UV conductivity from ZnO because of the existence of surface states that give rise to a high surface recombination velocity and thereby reduce the photocurrent generation and decreases the sensitivity.<sup>4–6</sup> One route to effectively passivate the unwanted surface states is to develop a second semiconductor layer. From this point of view, there are as of late a few studies on charge transfer at the interface between ZnO and the surrounding ambience in composites like CdS/ZnO,<sup>7–9</sup> SiO<sub>2</sub>/ZnO,<sup>10,11</sup> ZnO/PVK,<sup>12</sup> In<sub>2</sub>O<sub>3</sub>/SnO<sub>2</sub>/ZnO,<sup>13</sup> PVP/ZnO<sup>14</sup> mainly to understand the photoelectrochemical properties of such systems. Recently Fang et al.<sup>8</sup> have found that a CdS-cap layer acts as a passivating layer to suppress the detrimental surface states of ZnO nanowalls, which affects the intersurface carrier transport layer and thereby enhances the UV photoconductivity at the nanowalls. We have studied this phenomenon in inkjetted ZnO films with controlled porosity and film thickness.

For cost-effective fabrication of device components, inkjet printing has emerged as an attractive direct patterning technique, especially for integrated circuit applications, because of its versatility of delivering picoliter volumes of solutions or suspensions in well-defined patterns with high spatial

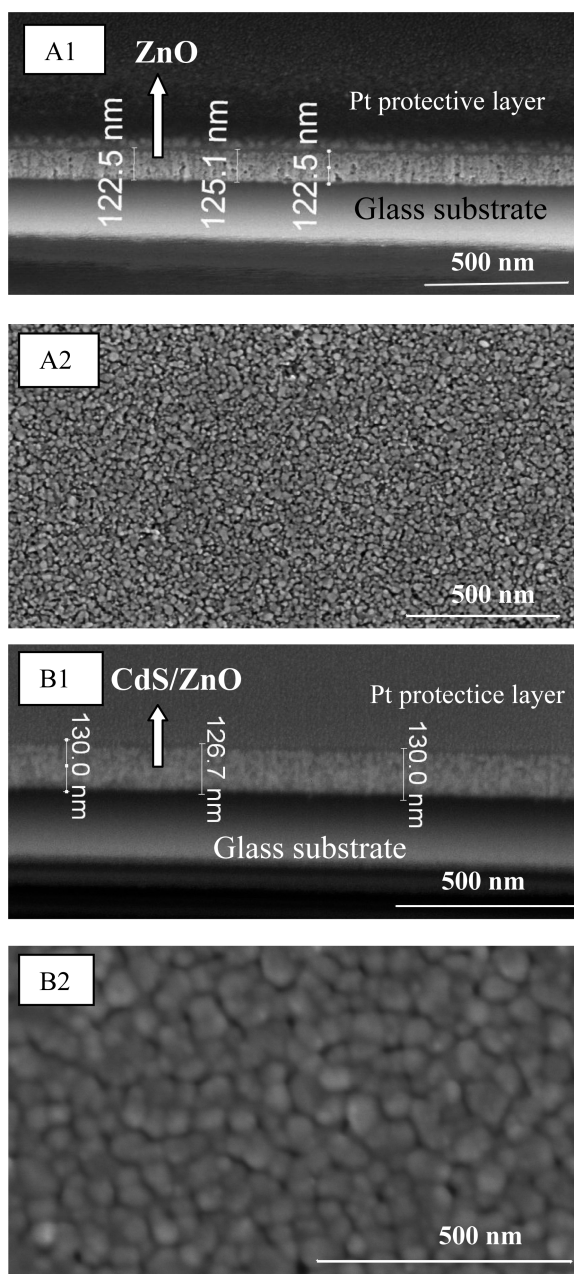
accuracy and noncontact deposition.<sup>15–17</sup> Recent reports on a few studies of inkjet-printed ZnO-based nanowire field-effect-transistors, indicate a promising future for inkjet printing to develop device applications.<sup>18,19</sup> On the basis of our earlier work,<sup>20</sup> in this letter, we demonstrate the possibility to engineer enhanced photoconductivity of ZnO-based composite semiconductor thin films, synthesized “in situ” by inkjet printing and coupled by dip coating CdS nanoparticles (NPs).

As-prepared ZnO films usually show significant n-type conductivity; consequently, the cadmium ions generated in the solution would have a tendency to be captured on the surface of ZnO. The absorbed cadmium ions on the ZnO nanostructure provide the initial nucleation sites for the surface growth of CdS NPs.<sup>21</sup> With this in mind, we deposited by in situ syntheses ZnO films, and then via dip coating introduced a thin layer of CdS as described below.

Figure 1 shows the high resolution SEM images of the pure ZnO and CdS NP/ZnO thin films. The morphology changes of the CdS NP/ZnO composite films were investigated after the CdS deposition process of various concentrations, and deposition times. For pure ZnO, the film (125 nm thickness) (Figure 1A1) is porous across the surface and the cross section, and all the particles from the top surface present island-type morphology from Figure 1A2. After coating the CdS NP, in a precursor of 0.0125 M (mol/liter) concentration for 5 dip cycles, the film remains homogeneous without any indication of a separated second layer (Figure 1B1). It becomes denser, and the thickness increases to ~130 nm, and the top-view image shows a distribution of spherical particles around 20–50 nm on the surface (Figure 1B2). When the dip-cycles

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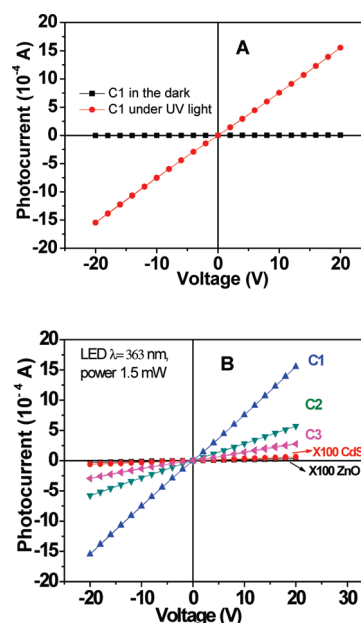
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**Figure 1.** Cross-section and top-view morphologies of the ZnO (A1, A2) and CdS/ZnO (B1, B2) thin film coated with 0.0125 M precursor concentrations for 5 dip cycles, respectively.

and the concentrations are increased, the average size of the particles increases as well.

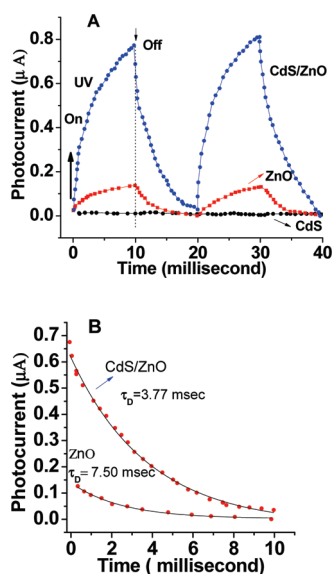
In Figure 2, the photocurrent generated versus the bias voltage is shown for ZnO, CdS, and the three dip-coated films. All the current–voltage characteristics were found to be linear. The increase of the UV-driven photocurrent under bias voltage indicates the light absorption and photocarrier generation in CdS/ZnO composite. The photocurrent of the CdS/ZnO composite thin film produced by dip coating under the illumination increased to  $7.66 \times 10^{-4}$  A at 10 V bias voltage, 400 times larger than in



**Figure 2.** *I*–*V* characteristics of CdS/ZnO films dip-coated with the precursor concentrations 0.0125 M for 5 cycles (C1), 10 cycles (C2), and 0.05 M for 5 cycles (C3), respectively, under UV light irradiation.

dark (Sample C1, Figure 2A). This enhancement of the current is more than 3 orders of magnitude compared with that of the pure ZnO thin film ( $1.72 \times 10^{-7}$  A). Sequential increase of the deposition cycles and the concentrations is found to result in the photocurrent rapidly decreasing with thicker CdS layers. For films obtained from 0.125 M (Sample C1) to 0.05 M (Sample C3) precursor concentrations, with the same five-dip cycle, the UV response value reduces by a factor of almost 30, decreasing from  $7.66$  to  $0.23 \times 10^{-5}$  A/V. The above results clearly demonstrate that the interface of the CdS NP/ZnO composite thin films have a significant effect for the photo-response, which is consistent with the reports on the effect of quantum-sized PdS, CdS, Ag<sub>2</sub>S, as sensitizers for wide band gap semiconductors.<sup>22</sup> We find that the thinnest continuous CdS coating with the concentration of 0.0125 M for 5 deposition cycles has the highest photocurrent responsivity for UV. The CdS nanoclusters prepared by dip coating of Cd<sup>2+</sup> with Na<sub>2</sub>S precursor solution in CdS/ZnO composite are smaller than the ZnO particles. The particles diameter of the CdS NPs is around 5 nm. Thus the CdS nanoclusters that surround the surfaces of ZnO particles are essentially composed of ultra-small CdS nanoclusters. A similar observation has also been made earlier by Alivisatos in the study with CdS/HgS composite semiconductor nanoclusters.<sup>23</sup> These observations suggest that only the particles that establish interparticle interaction cause the changes in the photophysical behavior of the composites. Therefore, we propose that the wider distribution of the CdS NP size and the weakened contact between the CdS and ZnO could lead to the decrease of the interfacial charge-transfer, resulting in the observed low responsivity for the thicker deposition CdS NP.

The transient photoresponse (the rise and decay time curves) of CdS, pure ZnO, and CdS/ZnO is shown in Figure 3.



**Figure 3.** (A) Photoresponse versus time for the UV irradiation “on”, and “off” conditions in ZnO and CdS/ZnO thin films. (B) Theoretical fit (continuous line) to the data for the photocurrent decay process.

As seen in Figure 3A, the photocurrent in CdS/ZnO is found to increase from  $0.02 \mu\text{A}$  to  $0.76 \mu\text{A}$  within 10 ms under the UV “on” condition, and increases gradually toward saturation due to the slow charge transfer process across the grain boundaries;<sup>24</sup> whereas, for ZnO, the current slowly increases to  $0.13 \mu\text{A}$  for the same irradiation time. When the UV light is turned “off”, the current decreases to reach its initial state within 8 ms (Figure 3B). Compared to pure ZnO, the decay time constant  $\tau_D$  of CdS/ZnO was estimated to be reduced from 7.50 to 3.77 ms by fitting the curve to the well-known relation<sup>25</sup>  $I = I_0 \exp(-t/\tau_D)$ , where  $I$  and  $I_0$  are the photocurrent with and without UV illumination, respectively. The photoresponse of CdS-coated ZnO visibly demonstrates the enhancement of photocurrent compared with that observed for pure ZnO. All the samples studied demonstrated similar behavior of a significant increase in the photocurrent and decrease in the decay time constant upon capping with CdS. It has been reported<sup>4</sup> earlier that oxygen physically absorbed on the surface of ZnO plays an important role that could possibly explain the change in the photoconductivity transient when ZnO is coated with CdS. We suggest that the enhancement of the photocurrent of the composite CdS/ZnO could be attributed to the interfacial charge transfer<sup>26–28</sup> as well as the passivation of the surface of ZnO.<sup>7–9</sup>

In summary, by dip coating, chemically capped CdS NPs have been homogeneously embedded in porous ZnO thin film deposited by inkjet printing. The electrical conductivity under UV irradiation is found to be enhanced by more than three orders of magnitude compared with that observed for pure ZnO. This enhancement can be explained qualitatively to arise from interfacial charge transfer as well as the surface passivation. Also the decay time of photoresponse of the ZnO film after capping with CdS is reduced to about 4 ms.

ZnO precursor ink was prepared for inkjet printing as our earlier method,<sup>20</sup> 0.2 M ZnO precursor solution was prepared by dissolving zinc acetate dihydrate in isopropanol solvent with ethanolamine as the stabilizer. The precursor was then inkjet printed on glass substrates, and the final as-deposited films were calcinated at  $400^\circ\text{C}$  to obtain polycrystalline zinc oxide films. To obtain tunable capping of CdS, we first dip-coated the ZnO films with different concentrations (0.0125 or 0.05 M) of cadmium sulfate aqueous solution for 10 s, then rinsed the samples in deionized water for 3 s. The rinsed samples were sequentially put into the sodium sulfide aqueous solution with the same concentration as cadmium sulfate solution for 20 s. Finally the films were rinsed in deionized water for 30 s to complete one cycle. The crystallinity of the films was determined by an X-ray diffractometer (Siemens D5000) with Cu K $\alpha$  radiation source. The morphologies and the chemical composition of the CdS/ZnO composite films were analyzed by a high-resolution scanning electron microscope with X-ray energy dispersive spectroscopy. Accurate film thickness determination was carried out in our Dual Beam FIB/SEM (Nova 600 Nanolab by FEI) facility from the cross-section analysis. The electrical properties were measured by a two-probe technique with copper contacts as electrodes in a coplanar gap configuration using a Keithley integrated instrument. The UV response measurements were performed using a synthesized functional analyzer and a high-resolution oscilloscope.

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