Uniform Coating of Light-Absorbing Semiconductors by Chemical Bath Deposition on Sulfide-Treated ZnO Nanorods

6 AUTHORS, INCLUDING:

Eran Edri
Lawrence Berkeley National Laboratory
23 PUBLICATIONS **794** CITATIONS

SEE PROFILE

Elena Rabinovich
Weizmann Institute of Science
4 PUBLICATIONS **359** CITATIONS

SEE PROFILE

Olivia Niitsoo
City College of New York
20 PUBLICATIONS **654** CITATIONS

SEE PROFILE

Uniform Coating of Light-Absorbing Semiconductors by Chemical Bath Deposition on Sulfide-Treated ZnO Nanorods

Eran Edri,[†,‡] Elena Rabinovich,[†,‡] Olivia Niitsoo,[†,§] Hagai Cohen,[⊥] Tatyana Bendikov,[⊥] and Gary Hodes*,[†]

Department of Materials and Interfaces and Department of Chemical Research Support, Weizmann Institute of Science, Rehovot 76100, Israel

ZnO nanorod films are increasingly used as an alternative to nanoporous TiO$_2$ as the electron conductor in semiconductor-sensitized nanoporous solar cells (SSSCs). Semiconductor light absorbers deposited onto ZnO by chemical bath deposition (CBD) tend to form poorly covering deposits of isolated clusters. We show how a short solution pretreatment of the ZnO nanorod films with a sulfide solution, which forms a thin ZnS film at the ZnO surface, results in a very large improvement of the coverage and uniformity of the CBD semiconductor coatings. These composite films give large improvements in solar cell efficiency. Several factors can be responsible for this improvement: better coverage of the ZnO nanorods, less shorting between hole conductor and conducting substrate, and the formation of a ZnS buffer layer.

1. Introduction

Nanoporous solar cells are based on high surface area metal oxides as (most commonly) electron conductors, on which is deposited a solar-absorbing material, followed by deposition of a hole-conducting phase. The solar-absorbing material is commonly a molecular dye, as in the dye-sensitized solar cell (DSC), but can also be a semiconductor as in the semiconductor-sensitized solar cell (SSSC). The hole-conducting phase can be a liquid electrolyte or a solid hole conductor.

While the most common oxide used is nanoporous TiO$_2$, ZnO is being increasingly investigated as an alternative, and has shown recent success in solid state SSSCs (or Extremely Thin Absorber-ETA cells).[1−3] The common (and most thermodynamically stable) crystallographic wurtzite structure of ZnO is built from a hexagonally close-packed lattice structure, where the oxygen and zinc ions are both tetrahedrally coordinated and their planes are alternately packed. This, on a larger length scale, develops to the anisotropic, rod-like structure that commonly forms when ZnO is deposited by certain techniques, especially CBD.[4] This nanorod morphology increases the surface area of the ZnO film by typically 10 to some tens of times compared to a planar film, depending on nanorod diameter, length, and spacing. This feature makes ZnO a potentially suitable candidate for nanoporous cells, and particularly for SSSCs, where the semiconductor thickness can be considerably thicker (typically several tens of nanometers) compared to the molecular thickness in a DSC, which requires a much larger surface-area enhancement.

For the SSSC, the light-absorbing semiconductor is deposited on the ZnO. Ideally, the semiconductor coating on the ZnO should be as conformal as possible in order to exploit as much of the ZnO surface as possible and to prevent direct contact between the oxide and the hole conductor (although this

additional contact may or may not be detrimental to the cell function, it does complicate understanding of the cell). There are a number of commonly used methods for depositing this semiconductor onto the porous oxide. Solution techniques, such as electrodeposition, SILAR (also known as dip method), chemical bath deposition (CBD), and spray, are the most common methods used.

Among the semiconductors deposited on ZnO in the literature, CdS is one of the most common. It was found that using sequential dipping of the ZnO substrate in Cd^{2+} solution and Na$_2$S solution (the SILAR method[5]) resulted in full coverage of the surface with small crystallites of CdS.[6] However, poor coverage with CdS clusters was obtained with CBD, in particular when the commonly used thiourea/ammonia bath for CdS was employed.[7] In ref 7 apparently good coverage could be obtained by using very dilute deposition solutions, but in this case, the amount of CdS deposited was very small, as seen by the absorbance spectrum. Use of a (probably neutral or slightly acidic) thioacetamide bath for CdS was shown to give good coverage of the ZnO nanorods in one paper[8] and heterogeneous cluster coverage in another.[9] An unusual nonaqueous bath (almost all CBD baths are aqueous) with thiourea was also found to give good coverage.[10]

We have noted that in depositing CdS onto ZnO nanorods by CBD from a thiourea solution (the most common S precursor used for CdS deposition), the coverage of the ZnO is poor and the CdS tends to cluster and leave most of the ZnO uncovered. This is in contrast to nanoporous TiO$_2$ where good coverage is obtained by the same method. However, by converting the surface of the ZnO to ZnS with an alkaline sulfide solution treatment, a much more uniform coating of CdS is obtained with complete coverage of the ZnO and virtually conformal CdS coating for CdS thicknesses of ≥10 nm. A comparable effect is also obtained for CdSe coating of ZnO. We also show preliminary results of ETA cells made using CdS-coated ZnO and with a CuSCN hole-conducting layer, which show greatly improved cell performance as a result of the surface treatment.

---

* To whom correspondence should be addressed. E-mail: gary.hodes@weizmann.ac.il.
† Department of Materials and Interfaces.
‡ Both these authors contributed equally to the research.
§ Present address: Department of Chemical Engineering, City College of New York, 140th St. at Convent Avenue, New York, NY 10031.
⊥ Department of Chemical Research Support.

Sulfide-Treated ZnO Nanorods

J. Phys. Chem. C, Vol. 114, No. 30, 2010 **13093**

2. Experimental Section

ZnO Film Deposition. The films were deposited on fluorine-doped tin oxide glass (FTO) or on soda lime glass microscope slide substrates. The substrates were cleaned by sonication in Alconox detergent solution for several minutes and thoroughly rinsed with Millipore deionized water.

The ZnO nanorod films were deposited mainly by chemical bath deposition (CBD) from an ammonia-based bath on $KMnO_4$-activated substrates.[11] For the surface activation, the substrates were immersed in closed vials containing 20 mL of 0.5 mM freshly prepared $KMnO_4$ solution with two or three drops of *n*-butanol. The vials were then placed in a preheated bath (90 °C) for 30 min. To remove loosely adhering Mn−O species the activated substrates were very extensively rinsed with deionized water (see ref 11 for further details of the activation).

ZnO nanowire arrays were deposited on the activated substrates from deposition solutions containing 0.1 M $Zn(CH_3COO)_2$, 1.7 M (10% v/v) ethanolamine, and 0.6 M ammonium hydroxide. Each substrate was immersed tilted in the deposition solution in a closed vial and heated to 90 °C in a preheated bath for 45 min. After deposition, the films were rinsed with distilled water and dried in a flow of N_2.

In specified experiments, ZnO was electrochemically (cathodically) deposited on FTO glass from a solution of 0.05 M zinc nitrate, at 70 °C. A standard three-electrode setup was used with a Ag/AgCl reference electrode and a Pt foil counter electrode. A potential of −0.9 V and a typical deposition duration of 90 min were used.

ZnO Surface Treatment. For the typical surface treatment, ZnO films were immersed in a solution of 0.1 M Na_2S (pH ca. 13) at room temperature for specific durations (see text). In some cases, the ZnO was treated with solutions of 0.5 M ammonium sulfide (pH ca. 9.5), 0.1 M potassium hydroxide, 0.1 M thioacetamide (40 min), or 1 M thiourea (40 min). After treatment, the samples were rinsed thoroughly with deionized water.

CdS Deposition. CdS was deposited by three different chemical bath deposition solutions: thiourea/ethylenediamine bath (0.025 M $CdAc_2$, 0.1 M ethylenediamine, and 0.1 M thiourea at room temperature for 30−180 min), which was the mostly used standard method; thiourea/ammonia bath (0.002 M $CdSO_4$, 0.01 M thiourea, and 1 M ammonia), where the solution was heated to 60 °C for 100 min;[7] and thioacetamide bath (0.01 M $Cd(NO_3)_2$ and 0.01 M thioacetamide at room temperature for 40 min).[8] After CdS deposition the samples were rinsed with deionized water and dried in a N_2 flow.

CdSe Deposition. CdSe deposition was carried out by CBD as described elsewhere.[12] In short, stock solutions of 0.5 M $CdSO_4$, 0.7 M $N(CH_2COOK)_3$ (NTA), and 0.2 M Na_2SeSO_3 (prepared by stirring 0.2 M elemental Se with 0.5 M Na_2SO_3 for ∼6−8 h at 70 °C) were used. The final solution composition was 80:80:160 mM Cd:Na_2SeSO_3:NTA, respectively. pH was adjusted to 8.5 with KOH prior to addition of selenosulfate, and the final pH was 10.3. The samples were placed in a stirred water bath at 80 °C for 30 min and subsequently were rinsed with deionized water and dried in a N_2 flow.

CuSCN Deposition and Solar Cell Fabrication. To complete the photovoltaic device, a CuSCN hole conductor layer and gold contact were deposited on the samples as described before.[13]

In brief, a saturated solution of CuSCN in dipropyl sulfide was prepared in advance by stirring the solution overnight and allowing it to settle for several days. This solution was diluted with dipropyl sulfide in 1:1 ratio to form 0.16 M CuSCN
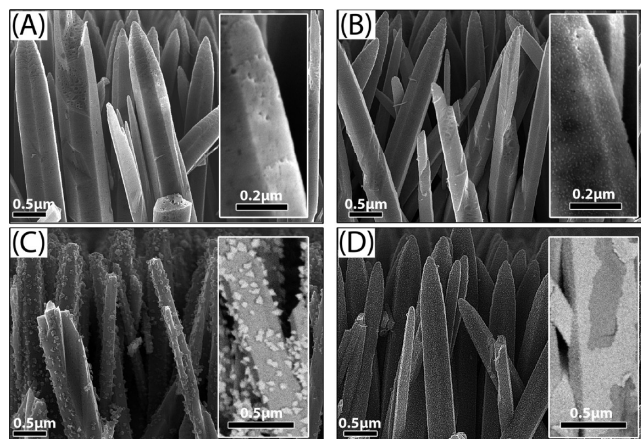

Figure 1. SEM images showing the effect of sulfide treatment on ZnO surface coverage by CdS: (A) ZnO nanorods; (B) sulfide-treated (0.1 M Na_2S, 10 min room temperature) ZnO; (C) CdS (deposited from an ethylenediamine/thiourea bath) on untreated ZnO; and (D) as 1C, but CdS deposited on treated ZnO. The insets show higher magnification images (C and D) using backscattered images to increase the contrast between the light atomic weight ZnO (dark) and heavier CdS (light). In the inset of 1D (as well as in some other subsequent images in this paper), a region where the CdS has partially peeled off (probably due to the cross-section fracture) was deliberately chosen to show the difference between ZnO and CdS.

solution concentration just before use. The samples were dipped in an aqueous solution of 0.5 M LiSCN for 5 min at room temperature and the excess solution was gently wiped with a tissue from the surface.[14] The samples were then heated on a hot plate to 65−75 °C and kept at this temperature during the deposition. CuSCN deposition was carried out in a homemade apparatus using a movable syringe needle, sealed at the end and with four 0.3 mm diameter holes, spaced 3 mm apart, drilled in the side of the needle.[15] Typically 0.3−0.4 mL of solution was used for a sample area of 3 cm², resulting in a CuSCN layer 1−2 μm thick above the ZnO nanorods thus preventing contact between ZnO and the Au back contact. Gold contacts 60 nm thick were deposited on top of the CuSCN layer by electron beam evaporation.

Film and Cell Characterization. The morphology of the samples was observed by a SEM, Leo Ultra 55 scanning electron microscope, in most cases using 2 kV accelerating voltage.

XPS measurements were carried out on a Kratos AXIS ULTRA system, using a monocromatized Al Kα X-ray source at 75 W and detection pass energies ranging between 20 and 80 eV.

The photovoltaic response of the cells was measured by using a white-light LED lamp calibrated to give the same short circuit current as natural sunlight, and normalized to full sun (100 mW·cm⁻²) with an Eppley pyranometer to measure the sunlight. Current−voltage (I−V) measurements were made with a Keithley 230 programmable voltage source and a Keithley 2000 multimeter. A defined area of 0.91 cm² was scribed around the gold contact to delineate the cell size.

3. Results and Discussion

The CBD ZnO rods have well-defined side faces with a rather smooth surface (Figure 1A). Attempts to grow CdS on ZnO by a thiourea-based bath for CdS (the most common type used for this technique) resulted in clustering of the CdS and poor coverage of the ZnO (Figure 1C). If, however, the ZnO is treated with a Na_2S solution, which converts the ZnO nanorod surface to ZnS (Figure 1B; more details on

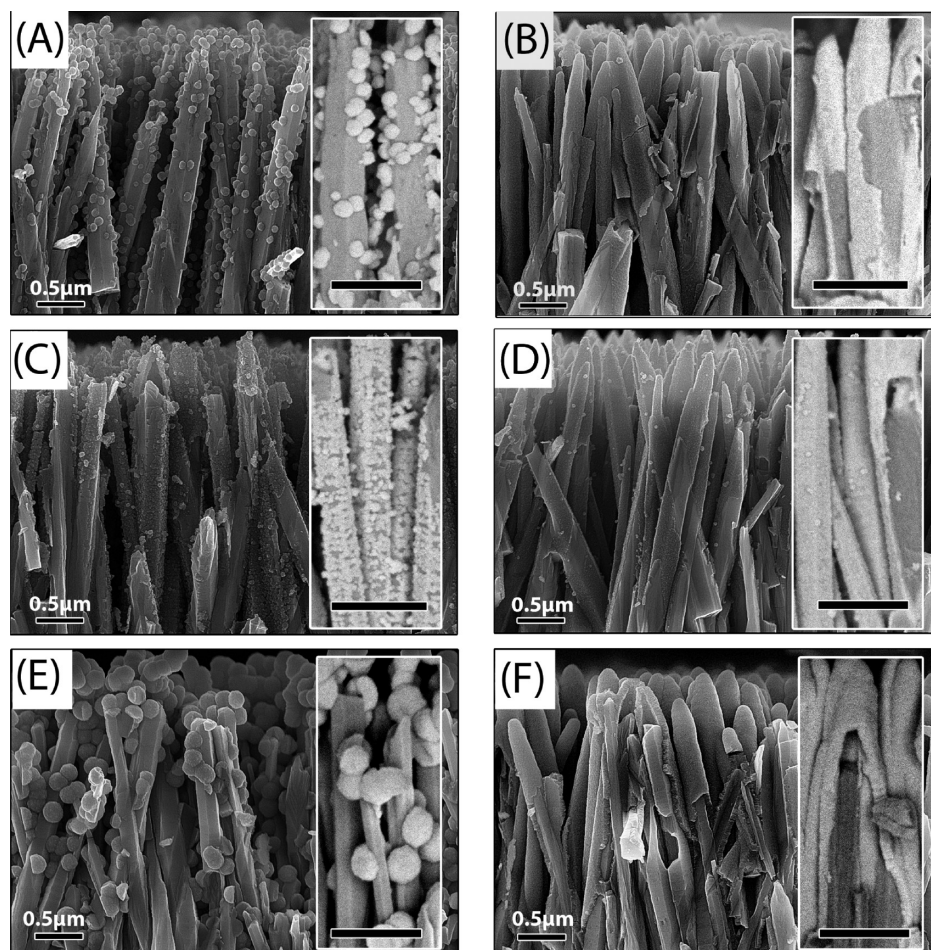**13094** *J. Phys. Chem. C, Vol. 114, No. 30, 2010*

Edri et al.

Figure 2. SEM images showing the effect of sulfide treatment on ZnO surface coverage by (A, B) CdS from ammonia/thiourea bath, (C, D) CdS from a thioacetamide bath, and (E, F) CBD CdSe. Left column images (A, C, E) are nontreated ZnO rods, right column images (B, D, F) show sulfide-treated ZnO rods. The insets are higher magnification backscattered images; scale bars for the insets are all 0.5 μm.

this reaction below), a much more even and conformal coating by the CdS is obtained (Figure 1D).

The method used to deposit the CdS is important. Deposition from a more commonly used bath (ammonia-complexed instead of ethylenediamine) shows the same general features as in Figure 1—poor coverage on untreated ZnO and excellent coverage on the treated ZnO (Figure 2A,B). Deposition of CdS on ZnO from a slightly acidic thioacetamide bath has been described with good coverage found.[8] In our hands, this bath gave much better coverage on untreated ZnO than did the alkaline baths (Figure 2C), but a much better uniformity was obtained from the same bath when the ZnO was Na_2S treated (Figure 2D). We note that the CdS coatings in ref 8 were relatively rough compared with those deposited by the same method on treated ZnO (Figure 2D). The effect of the ZnO treatment is not limited to CdS: CBD CdSe shows the same behavior, possibly even to a higher degree, with extensive clustering and poor coverage for the untreated ZnO (Figure 2E) and very uniform coating for the treated ZnO (2F).

The difference between thioacetamide and thiourea baths in terms of their covering power for untreated ZnO is not obvious. Cd ions are expected to react with both S sources faster than Zn ions (e.g., it was shown[16] for thioacetamide at pH >3 to neutral that the reaction to form CdS had a rate constant double that for ZnS formation). The reaction of metal ions with thioacetamide to metal sulfide at pH >3 to about neutral is believed to proceed by direct reaction of the metal ion and thioacetamide, rather than by hydrolysis of the thioacetamide

to free sulfide.[16,17] Attempts to carry out the reaction in thioacetamide under alkaline conditions, to separate effects of pH from thioacetamide/thiourea chemistry, resulted in almost immediate precipitation of CdS rather than controlled deposition. It appears that, under the conditions used for the thioacetamide CdS deposition, some partial degree of exchange of ZnO occurs to ZnS, explaining why the coverage of ZnO with CdS is better—although still inferior to coverage of the treated ZnO—than the alkaline thiourea deposition.

We should mention a related deposition method for CdS on ZnO—SILAR (Successive Ionic Layer And Reaction).[5] This method involves successive immersion of the ZnO in solutions of sulfide and Cd ions, rinsing between dips, and repeating this process to obtain thicker films. Regardless of whether the first immersion is in sulfide or Cd ions, the sulfide immersion will convert the ZnO surface to ZnS. The result will therefore be similar to CBD on a treated ZnO surface. This explains why the SILAR method gives a good coverage of "untreated" ZnO, in contrast to CBD in general.

We also investigated the effect of the sulfide treatment on differently prepared ZnO. We used electrodeposited ZnO for this purpose. Figure 3 shows CdS deposited by CBD on untreated (Figure 3A) and treated (Figure 3B) electrodeposited ZnO. Again, the effect of the treatment on the coverage of the ZnO is very pronounced.

The time of treatment of the ZnO by the Na_2S solution is not critical for obtaining good coverage. Even 30 s of treatment is enough for this purpose. However, it is of interest to know how
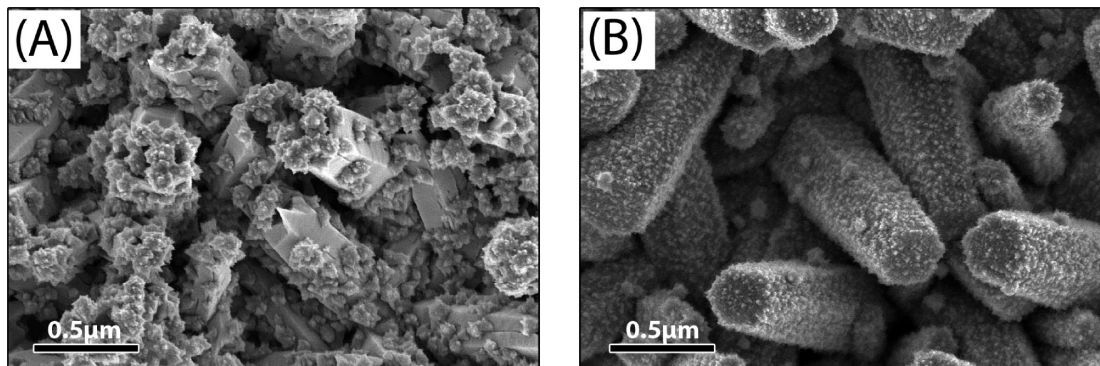
Sulfide-Treated ZnO Nanorods

J. Phys. Chem. C, Vol. 114, No. 30, 2010 **13095**

Figure 3. CBD CdS on untreated (A) and treated (B) electrodeposited ZnO.

TABLE 1: ZnS Effective Thickness on ZnO As a Result of Treatment with 0.1M Na$_2$S at Room Temperature for Various Times[a]

time [min]	thickness [Å]
0.5	3.4
1	4.0
2	5.2
5	8.2
10	12.3
20	19.5

[a] Layer thickness values were derived assuming a homogeneous and uniform layered structure. Because of the nanorod geometry, we assume that these calculations give upper limits for the thickness values.

thick the ZnS layer is, as this might be important for other purposes. For example, the ZnS, with its high bandgap and low electron affinity (therefore high-lying conduction band), might be a good buffer layer for solar cells using ZnO. Estimation of the effective ZnS thickness as a function of treatment time was made from a combination of XPS elemental analyses and SEM images. The XPS-derived average thickness values of the ZnS layer, shown in Table 1, were calculated by using the following expression (suited for a planar, uniform coating):

$$d = \lambda \ln(1 + I_{ZnS}/I_{ZnO})$$

where d is the thickness of the ZnS layer, λ is the photoelctron inelastic mean free path (chosen to be 2.5 nm), and I_{ZnS} and I_{ZnO} are the intensities measured for ZnS and ZnO, respectively (see the Supporting Information for more details and limits on the thickness estimation).

Apart from the initial rapid increase in measured thickness (and this could be due to a strong adsorption of sulfide from Na$_2$S that is not rinsed off), the increase in ZnS thickness is almost linear with treatment time up to at least 20 min. As seen from a sample with 24 h treatment (ca. 5 nm ZnS, Figure 4), the ZnS thickness does level off.

The CdS films on treated ZnO appear to be relatively conformal, although less smooth than the untreated ZnO itself, as indeed is the treated ZnO (see the gradual roughening of the surface as the sulfide treatment time increases in Figure 4). Deposition of thin CdS layers provides more information on the degree of coverage of the treated ZnO early in the deposition process. Since standard CdS films shown above were typically deposited for 150 min, we also looked at 10 and 30 min deposition times. The results are shown in Figure 5, where two important conclusions can be drawn. The first is that, for small deposition times (i.e., relatively small amounts of CdS depos-
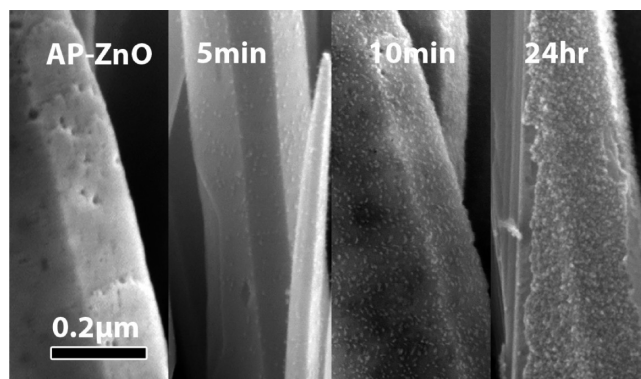

Figure 4. The development of the ZnS film on ZnO by treating in Na$_2$S for different durations. The smooth ZnO surface is uniformly covered with crystallites of ZnS until after 24 h a film of ca. 5 nm thick ZnS covers the nanorods. Noticeable roughening develops for the thicker films, but the coverage remains excellent (we deliberately choose regions where the film has been "broken" in the process of cross-section sample preparation to be able to measure the thickness).

ited), the CdS coating is not uniform, but rather heterogeneous. As the deposition time increases from 10 min (top row in Figure, 5) to 30 min (bottom row), the coverage increases, as might be expected.

The second conclusion is that the coverage increases as the sulfide treatment time increases for the same CdS deposition time (Figure 5 going from left with no treatment, to right with 30 min of treatment). In the absence of any treatment, no CdS deposit is seen after 10 min (top left image) and only very isolated deposits after 30 min CdS (bottom left image). In contrast, even 1 min sulfide treatment is enough to improve the CdS coating drastically for both CdS deposition times (second left images), and the coverage improves as the sulfide treatment time increases. Thus the ZnS layer in the treated layer not only improves uniformity, but also catalyzes the CdS deposition.

The sulfidation is most rapidly carried out by a sulfide solution. Other sulfiding agents have the same effect, although slower. For good CdS coverage from 0.1 M Na$_2$S, 30 s is sufficient, as already noted. However, in a 0.1 M solution of thioacetamide, 40 min is required to give a comparable effect, while for thiourea (1 M), a 40 min treatment decidedly improves the surface coverage, but to a much lesser extent than the other treatments. (Of course, these times will be pH dependent since the rate of hydrolysis of the S precursors will increase with increasing pH.) We find that thioacetamide reacts much faster with Cd^{2+} under alkaline conditions than does thiourea and assume the same for Zn. Thus, as suggested earlier, the better coverage with thioacetamide (even under the mild acidic
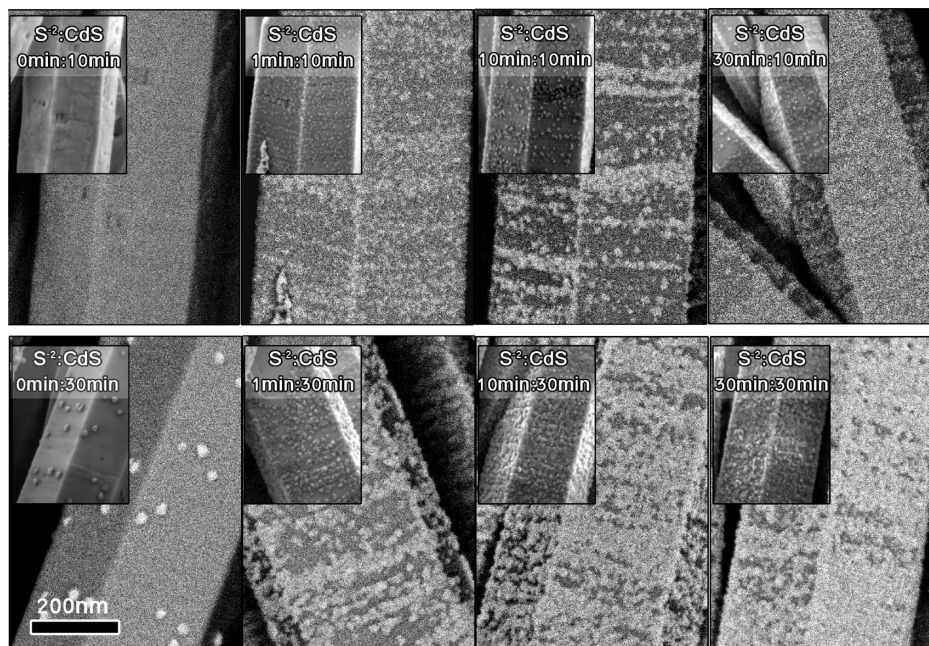
Figure 5. Effect of duration of sulfide treatment on ZnO surface coverage by CdS. Top row: 10 min CdS deposition after 0, 1, 10, and 30 min (left to right, respectively) of sulfide treatment. Bottom row: the same as the top row but with 30 min of CdS CBD. Main images: Backscattered SEM. Insets: Secondary electron images of the same regions. Scale bar (lower left image) is for all main images; for insets, the same bar represents 400 nm. The insets all show the duration of sulfide treatment (S) and CdS deposition (CdS).

conditions used) as S source instead of thiourea could be explained by partial sulfidation of the ZnO by the thioacetamide. Ammonium sulfide (0.5 M for 10 min) also gave comparable results, if somewhat slower, to those of Na$_2$S. Since the pH of this solution is ca. 9.5 compared to ca. 13 for the Na$_2$S solution, this indicates that the pH of the sulfiding solution is not critical.

The surface treatment process is at least partially reversible. When ZnO rods are treated with Na$_2$S and then annealed in air at 350 °C, the rods are (rather uniformly) covered with small particles, presumably due to partial (back) oxidation and slight roughening of the sulfidized surface. Nonetheless, after 30 min of annealing, the surface coverage by CBD CdS is better than that without the sulfide treatment (results not shown), although not as good as unannealed, sulfided ZnO. We also note that the effect did not result from simply cleaning of the ZnO surface by the basic sulfide solution. Treating the ZnO in KOH solution (up to 0.5 M) instead of Na$_2$S, which is expected to etch the ZnO, was not found to improve the surface coverage by CdS.

While the conversion of the ZnO surface to ZnS is clearly the reason for the much-improved coverage by CdS or CdSe, there are a number of questions that arise from our results.

One is: What is the mechanism of the exchange? That the exchange occurs is well-known and expected from simple thermodynamical reasoning. The solubility of ZnS is ∼7 orders of magnitude smaller than that of ZnO.[18] Since we can expect exposed surface oxide to convert very rapidly to ZnS (essentially immediately on any time scale involved in the experiments in this paper), a logical mechanism is one involving ionic diffusion (Zn^{2+} being the obvious choice) through the growing ZnS layer. The observation that the increase in ZnS thickness with reaction time decreases greatly above a few nanometers is in accord with this mechanism. Dissolution of ZnO and immediate reprecipitation of ZnS may also play a role, although this mechanism is most likely during the early stages of the exchange, where there is still surface oxide.

Another question to be considered is: Why does the CdS(e) coverage improve when the ZnO surface is converted to ZnS?

The simplest and intuitive answer is "like-to-like": A sulfide (or selenide, telluride) is in general expected to grow more readily on a substrate of similar chemistry (in particular, that has S atoms at the surface, which can bond to Cd^{2+} cations). Another possibility that we considered is that the alkaline sulfide solution "cleans" the surface. Our observation that a (non-S-containing) alkaline solution, which actually etches the ZnO, has no effect on the metal Cd chalcogenide coating of the ZnO, strongly implies that this is *not* the reason in our case. Since the ZnS catalyzes the CdS deposition as noted above, the ZnS is clearly a better nucleation initiator than ZnO for CdS. Figure 5 shows that the nucleation of CdS on the ZnS/ZnO is not homogeneous, but occurs preferentially as bands perpendicular to the growth axes. One possibility for this could be a similar morphology of the ZnS itself. A close look at the ZnS/ZnO SEM images (Figure 4) shows a slight tendency for such striation of morphology for the 5 min treatment, but none for the 10 min treatment. Since clear striation of the CdS occurs for the 10 min treated ZnO, this suggests that the preferential nucleation is not a roughness or other ZnS morphology-related issue. Other possible explanations are connected with the atomic level structure of the underlying ZnO (the prismatic face contains alternating Zn and S atoms) or structural defects in the nanorods.

The ability to obtain a more conformal coverage of metal chalcogenides on ZnO rods could have a significant impact on nanoporous solar cells. Here, a good contact between each crystal of the light-absorbing semiconductor and the ZnO (electron conductor) is important; clustering of the light absorber crystals will increase the chances of electron−hole recombination[19] and will also prevent direct contact between the hole and electron conductors (which may or may not cause a problem).

To illustrate the importance of the sulfide treatment on the behavior of ZnO-based solar cells, we show preliminary results of the photovoltaic response from ZnO (CBD nanorod morphology)/CdS/CuSCN cells (see the Experimental Section for details) comparing two cells differing only in whether the ZnO was sulfide-treated or not (Figure 6).
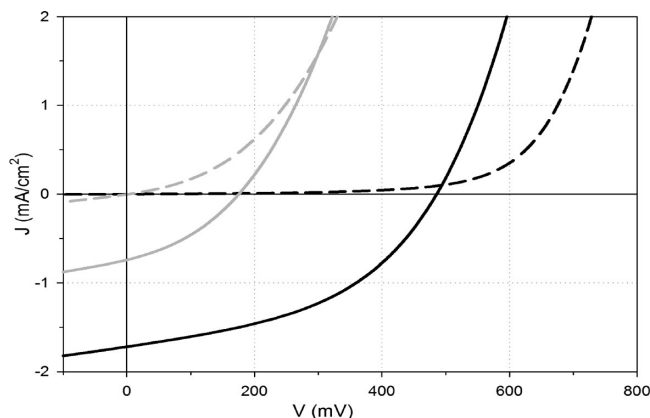
Sulfide-Treated ZnO Nanorods

J. Phys. Chem. C, Vol. 114, No. 30, 2010 **13097**

Figure 6. The best $J-V$ curves of sulfide treated (black) and nontreated (gray) ZnO|CdS|CuSCN cells in the dark (dashed lines) and under 1 sun illumination conditions (full lines). For these cells, the ZnO deposition solution was modified, mainly by addition of a low concentration of an antimony salt to the deposition bath, in order to obtain a better blocking layer under the ZnO nanorods (submitted to Crystal Growth and Design). The modified deposition solution contained: 70 mM Zn(Ac)$_2$; 0.1 mM antimony tartrate; 0.52 M ammonium hydroxide and 1.7 M ethanolamine.

The effect of the sulfide treatment on the performance of the cell is very pronounced. All cell parameters are improved. In parallel with the photovoltaic behavior, the dark diode behavior of the device is improved by this treatment, as seen by the improved rectification characteristics (the dashed lines in Figure 6). The short circuit current is increased from 0.7 to 1.7 mA/cm^2, and the open circuit voltage is increased from 180 to 490 mV. Also, the fill factor is improved from 34% to 44% and consequently the efficiency is increased from 0.05% to 0.37%.

Besides the better coverage of ZnO with the absorber, there are two other factors that can be favorable for photovoltaic cells. We believe that the most important one is related to the role of the dense ZnO layer under the ZnO nanorods. This dense underlayer is necessary for both ZnO and TiO$_2$ based ETA cells to prevent shorting between the conducting glass and the solid hole conductor.[20] We usually find such a dense underlayer to form in situ during deposition of ZnO by our technique.[11] However, this apparently dense layer is usually not good enough to prevent electrical shorting, even though it appears to be structurally dense under SEM imaging; this is probably due to very small cracks or pinholes in this dense layer. The sulfide treatment will allow coverage of these defects by the CBD absorber, in contrast to the poor coverage of untreated ZnO; this can therefore block these defects and thus suppress shorting. This point can explain our common observation that cells made with untreated ZnO vary widely in performance, particularly in V_{OC}, which will be most strongly affected by shorting, while cells made with treated ZnO are much more reproducible with a much narrower spread in performance, particularly in V_{OC}.

A second potential effect of the treatment is the action of the thin ZnS as a buffer layer. Buffer layers are often used in these cells between absorber and oxide to reduce recombination.[20] While their specific role is not well-defined, likely reasons include reduction of recombination of electrons in the ZnO with holes in the absorber or hole conductor by increasing electron hole separation and/or introduction of a potential barrier.

We note that photovoltaic cells (planar ZnO/organic polymer) were described where (NH$_4$)$_2$S treatment of ZnO was used.[21]

In these cells, the sulfide treatment either reduced the cell efficiency drastically (on single crystal ZnO) or even resulted in no appreciable photovoltaic activity at all (on planar sol–gel films). These cells were very different from the cells described here, and it is likely (although not certain) that the coverage of the ZnO by the polymer was not an important issue.

4. Conclusions

We have shown that through a simple room temperature chemical method, a uniform coverage of ZnO by chemical bath deposited CdS and CdSe can be achieved. Dipping the ZnO substrate in a sulfide containing solution results in partial conversion of ZnO to ZnS, which in turn results in a uniform, almost conformal layer of the chalcogenide film. The ZnS promotes nucleation of CdS compared to ZnO. This treatment has a remarkable impact on the performance of a photovoltaic device (ZnO|CdS|CuSCN solar cell). Preliminary results show an order of magnitude improvement in solar cell efficiency.

Supporting Information Available: Details of the XPS analyses of the ZnS thickness. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Levy-Clement, C.; Tena-Zaera, R.; Ryan, M. A.; Katty, A.; Hodes, G. *Adv. Mater.* **2005**, *17*, 1512.
(2) Dittrich, T.; Kieven, D.; Rusu, M.; Belaidi, A.; Tornow, J.; Schwarzburg, K.; Lux-Steiner, M. *Appl. Phys. Lett.* **2008**, *93*, 053113–3.
(3) Krunks, M.; Katerski, A.; Dedova, T.; Oja Acik, I.; Mere, A. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1016.
(4) Govender, K.; Boyle, D. S.; Kenway, P. B.; O'Brien, P. *J. Mater. Chem.* **2004**, *14*, 2575.
(5) Nicolau, Y. *Appl. Surf. Sci.* **1985**, *22–23*, 1061.
(6) Tak, Y.; Hong, S. J.; Lee, J. S.; Yong, K. *J. Mater. Chem.* **2009**, *19*, 5945.
(7) Tak, Y.; Hong, S. J.; Lee, J. S.; Yong, K. *Cryst. Growth Des.* **2009**, *9*, 2627.
(8) Spoerke, E. D.; Lloyd, M. T.; Lee, Y.; Lambert, T. N.; McKenzie, B. B.; Jiang, Y.; Olson, D. C.; Sounart, T. L.; Hsu, J. W. P.; Voigt, J. A. *J. Phys. Chem. C* **2009**, *113*, 16329.
(9) Wang, G.; Yang, X.; Qian, F.; Zhang, J. Z.; Li, Y. *Nano Lett.* **2010**, *10*, 1088.
(10) Lee, W.; Min, S. K.; Dhas, V.; Ogale, S. B.; Han, S. *Electrochem. Commun.* **2009**, *11*, 103.
(11) Kokotov, M.; Hodes, G. *J. Mater. Chem.* **2009**, *19*, 3847.
(12) Gorer, S.; Hodes, G. *J. Phys. Chem.* **1994**, *98*, 5338.
(13) O'Regan, B.; Lenzmann, F.; Muis, R.; Wienke, J. *Chem. Mater.* **2002**, *14*, 5023.
(14) Larramona, G.; Chone, C.; Jacob, A.; Sakakura, D.; Delatouche, B.; Pere, D.; Cieren, X.; Nagino, M.; Bayon, R. *Chem. Mater.* **2006**, *18*, 1688.
(15) O'Regan, B. C.; Lenzmann, F. *J. Phys. Chem. B* **2004**, *108*, 4342.
(16) Bowersox, D.; Smith, D.; Swift, E. *Talanta* **1960**, *3*, 282.
(17) Peeters, O. M.; Blaton, N. M.; Ranter, C. J. D. *J. Chem. Soc., Perkin Trans. 2* **1978**, 23.
(18) Chaparro, A. M. *Chem. Mater.* **2005**, *17*, 4118.
(19) Hodes, G. *J. Phys. Chem. C* **2008**, *112*, 17778.
(20) Lévy-Clément, C. In *Nanostructured Materials for Solar Energy Conversion*; Elsevier: Amsterdam, The Netherlands, 2006; pp 447–484.
(21) Uhlrich, J. J.; Franking, R.; Hamers, R. J.; Kuech, T. F. *J. Phys. Chem. C* **2009**, *113*, 21147.