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--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE59909R1
Full Title:	Fabrication of robust nanoscale contact between a silver nanowire electrode and CdS buffer layer in Cu(In,Ga)Se2 thin-film solar cells
Keywords:	Transparent conducting electrodes; Silver nanowires; solar cell; Cu(In,Ga)Se2; Nanoscale metal-semiconductor contact; Metal-semiconductor coreshell nanowire
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TITLE:

Fabrication of Robust Nanoscale Contact between a Silver Nanowire Electrode and CdS Buffer Layer in Cu(In,Ga)Se_2 Thin-Film Solar Cells

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KEYWORDS:

Transparent conducting electrodes; Silver nanowires; Solar cell; Cu(In,Ga)Se_2; Nanoscale metal-semiconductor contact; Metal-semiconductor coreshell nanowire

SUMMARY:

In this protocol, we describe the detailed experimental procedure for the fabrication of a robust nanoscale contact between a silver nanowire network and CdS buffer layer in a CIGS thin-film solar cell.

ABSTRACT:

Silver nanowire transparent electrodes have been employed as window layers for Cu(In,Ga)Se_2 thin-film solar cells. Bare silver nanowire electrodes normally result in very poor cell performance. Embedding or sandwiching silver nanowires using moderately conductive transparent materials, such as indium tin oxide or zinc oxide, can improve cell performance. However, the solution-processed matrix layers can cause a significant number of interfacial defects between transparent electrodes and the CdS buffer, which can eventually result in low

cell performance. This manuscript describes how to fabricate robust electrical contact between a silver nanowire electrode and the underlying CdS buffer layer in a $Cu(In,Ga)Se_2$ solar cell, enabling high cell performance using matrix-free silver nanowire transparent electrodes. The matrix-free silver nanowire electrode fabricated by our method proves that the charge-carrier collection capability of silver nanowire electrode-based cells is as good as that of standard cells with sputtered ZnO:Al/i-ZnO as long as the silver nanowires and CdS have high-quality electrical contact. The high-quality electrical contact was achieved by depositing an additional CdS layer as thin as 10 nm onto the silver nanowire surface.

INTRODUCTION:

Silver nanowire (AgNW) networks have been extensively studied as an alternative to indium tin oxide (ITO) transparent conducting thin films due to their advantages over conventional transparent conducting oxides (TCOs) in terms of lower processing cost and better mechanical flexibility. Solution-processed AgNW network transparent conducting electrodes (TCEs) have thus been employed in $Cu(In,Ga)Se_2$ (CIGS) thin-film solar cells[1–6]. Solution-processed AgNW TCEs are normally fabricated in the form of embedded-AgNW or sandwich-AgNW structures in a conductive matrix such as PEDOT:PSS, ITO, ZnO, etc.[7–11] The matrix layers can enhance that the collection of the charge carriers present in the empty spaces of the AgNW network.

However, the matrix layers can generate interfacial defects between the matrix layer and underlying CdS buffer layer in CIGS thin-film solar cells[12,13]. The interfacial defects often cause a kink in the current density-voltage (J-V) curve, resulting in a low fill factor (FF) in the cell, which is detrimental to solar cell performance. We previously reported a method to resolve this issue by selectively depositing an additional thin CdS layer (2^{nd} CdS layer) between the AgNWs and the CdS buffer layer[14]. The incorporation of an additional CdS layer enhanced the contact properties in the junction between the AgNW and CdS layers. Consequently, the carrier collection in the AgNW network was greatly improved, and the cell performance was enhanced. In this protocol, we describe the experimental procedure to fabricate robust electrical contact between the AgNW network and the CdS buffer layer using a 2^{nd} CdS layer in a CIGS thin-film solar cell.

PROTOCOL:

1. Preparation of Mo-coated glass by DC magnetron sputtering

1.1. Load cleaned glass substrates into a DC magnetron and pump down to below 4×10^{-6} Torr.

1.2. Flow Ar gas and set the working pressure to 20 mTorr.

1.3. Turn on plasma and increase the DC output power to 3 kW.

1.4. After pre-sputtering of 3 min for target cleaning, begin the Mo deposition until the Mo film thickness reaches approximately 350 nm.

1.5. Set the working pressure to 15 mTorr while maintaining the same output power (i.e., 3 kW).

1.6. Resume the Mo deposition until the total thickness of Mo reaches approximately 750 nm.

2. CIGS absorber layer deposition by means of a three-stage coevaporation

2.1. Load Mo-coated glass into a preheated co-evaporator under a vacuum lower than 5×10^{-6} Torr.

2.2. Set the temperatures of In, Ga, and Se effusion cells yielding deposition rates of 2.5 Å/s, 1.3 Å/s, and 15 Å/s, respectively.

2.2.1. Check the deposition rates using the quartz crystal microbalance (QCM) technique. The deposition rates are dependent on the set temperature of effusion cells and the amount of materials in the effusion cells.

2.3. Begin to supply In, Ga and Se onto the Mo-coated glass to form a 1 μm-thick $(In,Ga)_xSe_y$ precursor layer at the substrate temperature of 450 °C. The deposition time is 15 min (namely, 1st stage).

2.4. Stop the In and Ga supplies and increase the substrate temperature to 550 °C.

2.5. Begin to supply Cu (deposition rate: 1.5 Å/s) onto the $(In,Ga)_xSe_y$ precursor and continue until the Cu/(In + Ga) compositional ratio of the film reaches 1.15. Note that the Se deposition rate is maintained at 15 Å/s through the 2nd stage (namely, 2nd stage).

2.6. Stop supplying Cu and evaporate In and Ga again with the same deposition rates as the 1st stage to finally form an approximately 2 μm-thick CIGS film with Cu/(In+Ga) compositional ratio of 0.9. Maintain the Se deposition rate and substrate temperature at 15 Å/s and 550 °C, respectively. The deposition time of this stage is 4 min (namely 3rd stage).

2.7. In order to ensure a complete reaction, anneal the deposited CIGS film under ambient Se (15 Å/s) for 5 min at the substrate temperature of 550 °C.

2.8. Cool down the substrate temperature to 450 °C under ambient Se (15 Å/s) and then unload the CIGS-deposited substrate when the substrate temperature is below 250 °C.

3. Growth of the CdS buffer layer on the CIGS absorber layer using a chemical bath deposition (CBD) method

3.1. Prepare the CdS reaction bath solution in a 250 mL beaker by adding 97 mL of DI water, 0.079 g of $Cd(CH_3COO)_2 \cdot 2H_2O$, 0.041 g of NH_2CSNH_2, and 0.155 g of CH_3COONH_4. Stir the solution for several minutes to mix. Make sure that all added solutes are completely dissolved.

3.2. Add 3 mL of NH_4OH (28% NH_3) into the bath solution and stir the solution for 2 min. **Figure**

1 shows the experimental setup of CBD for CdS.

3.3. Put the CIGS sample into the reaction bath solution using a Teflon sample holder.

3.4. Put the reaction bath into the water-heat bath maintained at 65 °C and stir the reaction bath solution at 200 rpm using a magnetic bar during the deposition process.

3.5. React for 20 min to generate an approximately 70 to 80 nm CdS buffer layer on the CIGS.

3.6. After the reaction, remove the sample from the reaction bath, wash with a flow of DI water, and dry with N_2 gas.

3.7. Anneal the sample at 120 °C for 30 min on a hot plate.

4. Fabrication of the AgNW TCE network

4.1. Prepare a diluted AgNW dispersion (1 mg/mL) by mixing 19 mL of ethanol with 1 mL of a purchased ethanol-based AgNW dispersion (20 mg/mL).

4.2. Pour 0.2 mL of the diluted AgNW dispersion onto a CdS/CIGS sample (2.5 cm x 2.5 cm) to cover the whole surface of the sample and rotate the sample with 1,000 rpm for 30 s.

4.3. Repeat step 4.2 as needed to achieve the desired optical and electrical properties. Spin-coat the AgNWs 3x. A scanning electron microscopy (SEM) image of spin-coated AgNW TCE is shown in **Figure 2**.

4.4. After spin-coating, anneal the sample at 120 °C for 5 min on a hot plate.

5. Deposition of the 2nd CdS layer

5.1. Prepare a new CdS reaction bath solution as described in step 3.1.

5.2. Deposit CdS as in section 3, except change the reaction time as necessary.

NOTE: We optimized the reaction time, and 10 min resulted in the CIGS device with the best performance. The effect of 2nd CdS deposition time on a CIGS thin film solar cell device performance can be found in our previous work[14].

6. Characterization techniques

6.1. Characterize the surface and cross-sectional morphology of AgNWs and CdS-coated AgNWs by field emission SEM and transmission electron microscopy (TEM).

6.2. Measure solar cell performance using a current-voltage source equipped with a solar

simulator (1,000 W/m^2, AM1.5G).

REPRESENTATIVE RESULTS

The layer structures of the CIGS solar cells with (a) standard ZnO:Al/i-ZnO and (b) AgNW TCE are shown in **Figure 3**. The surface morphology of CIGS is rough, and a nanoscale gap can form between the AgNW layer and the underlying CdS buffer layer. As highlighted in **Figure 3A**, the 2nd CdS layer can be selectively deposited onto the nanoscale gap to create a stable electrical contact. The detailed explanation on the formation of electrical contact and enhancement of electrical properties and device performance can be found in the reference 14. The structural analysis of AgNW and CdS junction including cross sectional SEM and TEM, and corresponding elemental mapping can also be found in the reference 14.

Figure 4 shows the cross-sectional TEM images (a) along the 2nd CdS layer deposited on the AgNW network on the CdS/CIGS structure and (b) across the 2nd CdS layer deposited on the AgNW network. The CdS/CIGS structure shows a rugged surface morphology due to the granular structure of CIGS. Hence, bare AgNWs are suspended in air, and stable electrical contact with the CdS buffer layer cannot be expected. The 2nd CdS layer is uniformly deposited on the surface of the AgNWs, and the CdS layer on the core-shell AgNW (Ag@CdS NW) structure is produced as shown in **Figure 4B**. Furthermore, the 2nd CdS layer fills the air gaps between the CdS buffer layer and the AgNW layer, as shown in the inset of **Figure 4A**, and stable electrical contact is achieved.

Figure 5 and **Table 1** show the device performance of a CIGS thin-film solar cell with bare AgNW and Ag@CdS NW TCEs. Due to unstable electrical contact, the cell with bare AgNWs has poor device performance. Deposition of a 2nd CdS layer greatly enhances the cell performance, as shown in the J-V characteristics in **Figure 5**. The cell with the Ag@CdS NW TCE showed a greater than 50% increase in device efficiency and FF compared to the bare AgNW TCE.

FIGURE AND TABLE LEGENDS:

Figure 1: Chemical bath deposition setup. An image of the experimental setup for chemical bath deposition of CdS on CIGS.

Figure 2: An SEM image of the AgNW TCE. The SEM image shows the spin-coated AgNW TCE on the CdS/CIGS/Mo structure.

Figure 3: Schematic diagram of CIGS thin-film solar cells. Layer structure of a CIGS thin-film solar cell with (**A**) ZnO:Al/i-ZnO TCO and (**B**) AgNW TCE with a 2nd CdS layer.

Figure 4: Structural analysis of Ag@CdS NW. (**A**) Cross-sectional TEM image along a Ag@CdS NW on a CdS/CIGS structure and (**B**) high-resolution TEM image across a Ag@CdS NW.

Figure 5: Device performance comparison. J-V characteristics of CIGS thin-film solar cells with bare AgNW and Ag@CdS NW TCEs.

Table 1: Device performance data. A summary of the device performance derived from the J-V curves.

DISCUSSION:

Note that the deposition time of the 2nd CdS layer must be optimized to achieve the optimal cell performance. As the deposition time increases, the thickness of the 2nd CdS layer increases, and consequently, the electrical contact will improve. However, further deposition of the 2nd CdS layer will result in a thicker layer that reduces light absorption, and the device efficiency will decrease. We achieved the best cell performance with 10 min of deposition time for the 2nd CdS layer and determined that the cell efficiency decreased with longer deposition times.

To evaluate our method, we compared the device performance of the Ag@CdS NW-based CIGS solar cell with that of a standard CIGS solar cell with a sputtered ZnO:Al/i-ZnOl TCO, as described in **Figure 3A**[14]. The J-V characteristics were nearly equal, and the overall device performances were very similar. This result proves that our solution process method can produce a high-performance thin-film solar cell.

Various methods have been applied to enhance the electrical properties of AgNW TCE including the incorporation of conducive matrix. The method described in this protocol is simple and effective to enhance the electrical contact property between AgNWs and underlying CdS buffer layer in CIGS thin film solar cell. Due to the enhanced contact property, the solar cell performance is greatly improved. The method is designed to apply to the CdS/CIGS system but is not limited to the CdS/CIGS system. When an appropriate CBD method is created, our method can be applied to create high-quality electrical contact between AgNWs and the buffer layer in chalcogenide thin-film solar cells.

ACKNOWLEDGMENTS:

This research was supported by the In-House Research and Development Program of the Korea Institute of Energy Research (KIER) (B9-2411) and the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant NRF-2016R1D1A1B03934840).

DISCLOSURES:

The authors declare that they have no competing financial interests.

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Figure

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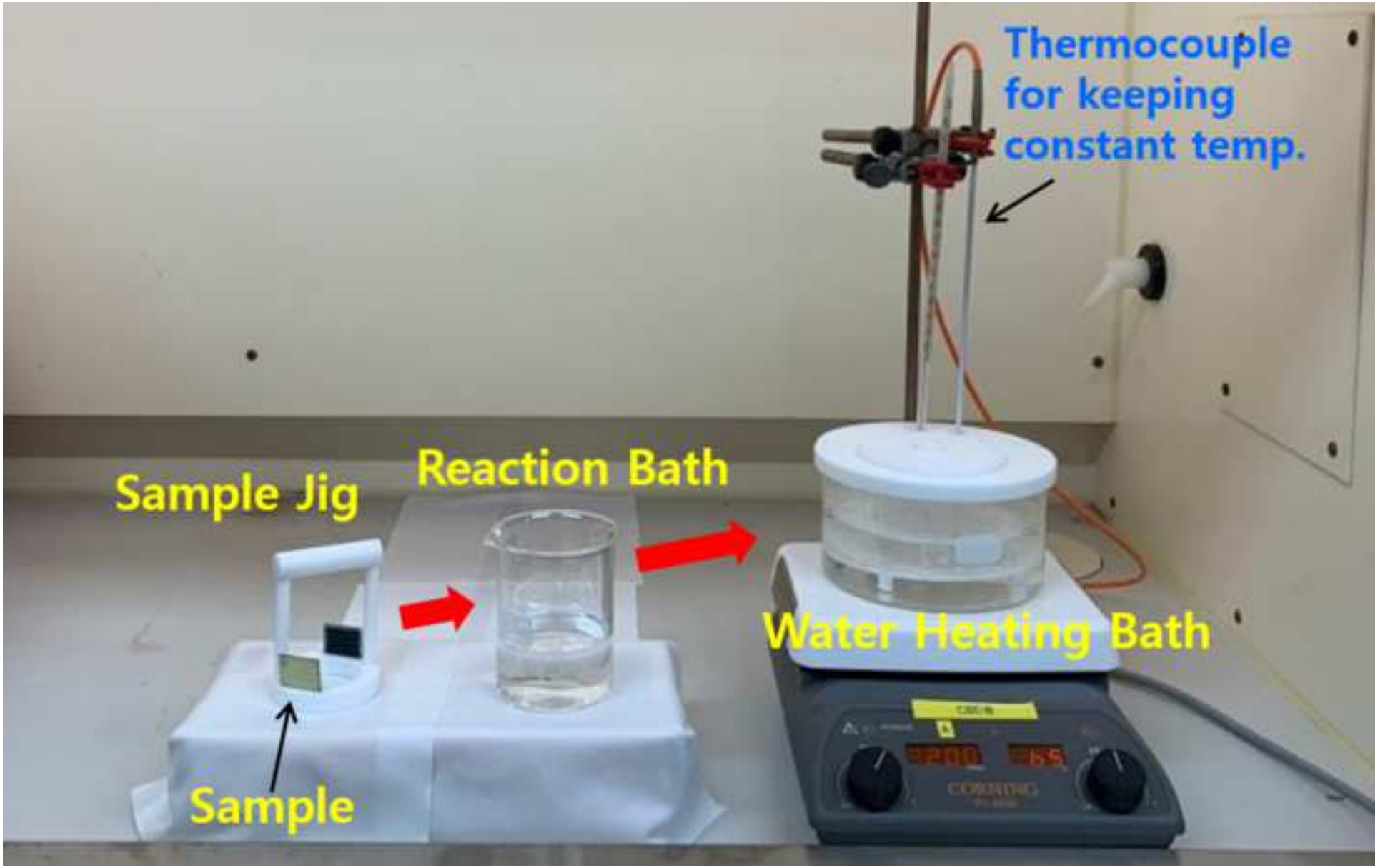

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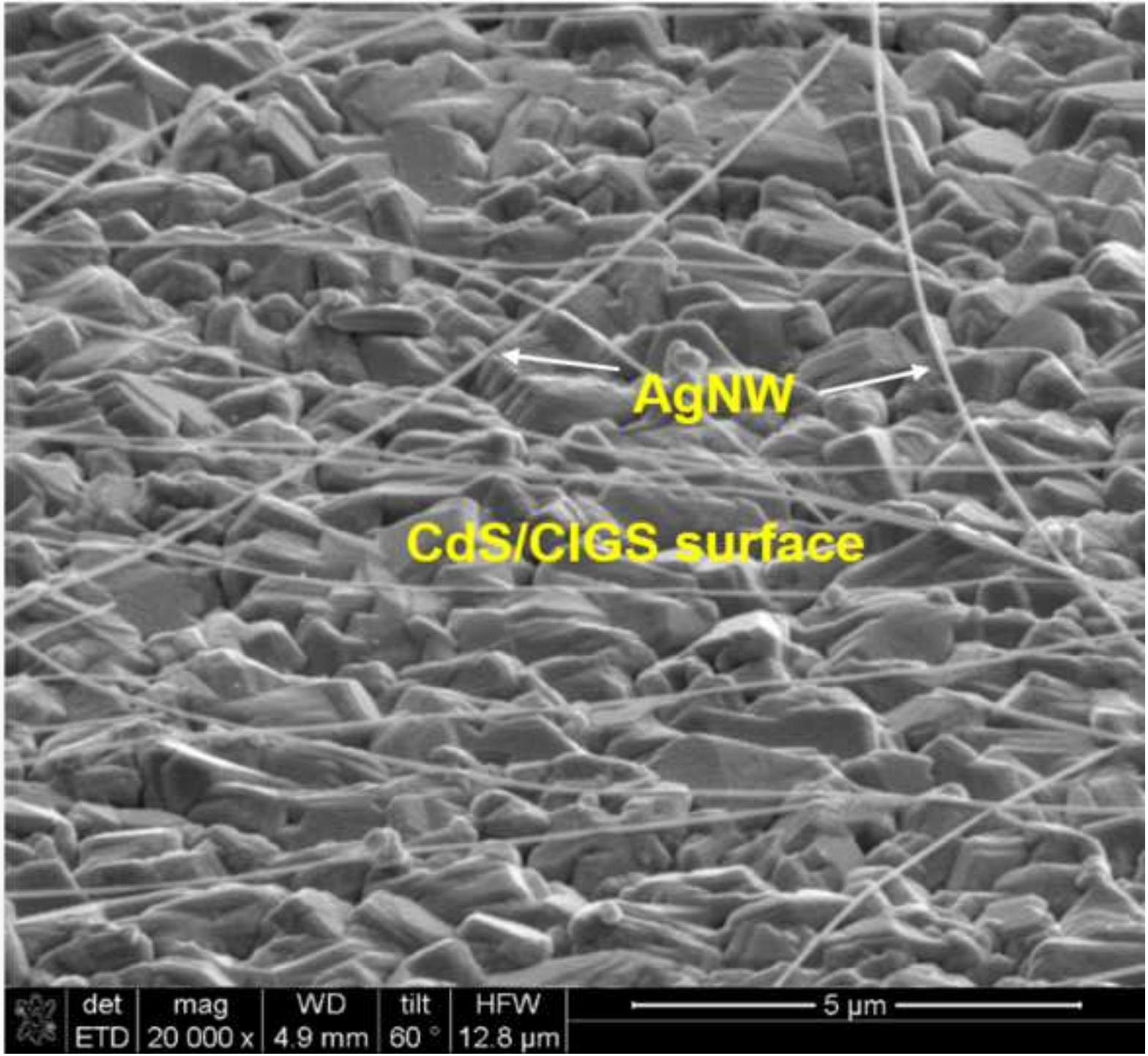

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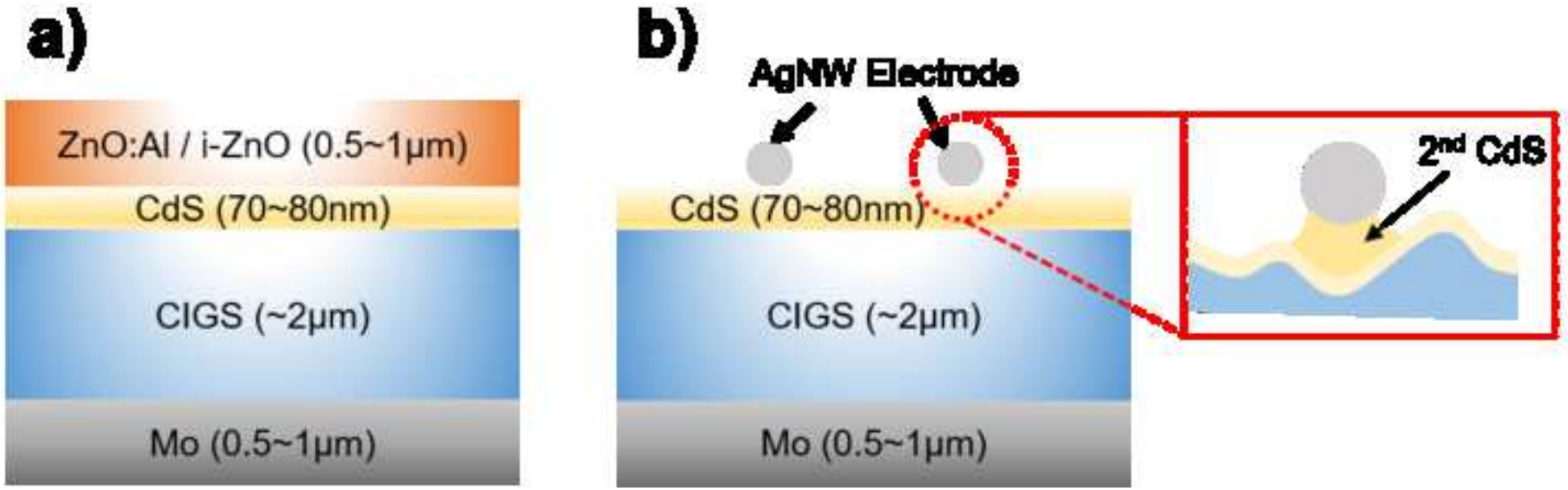

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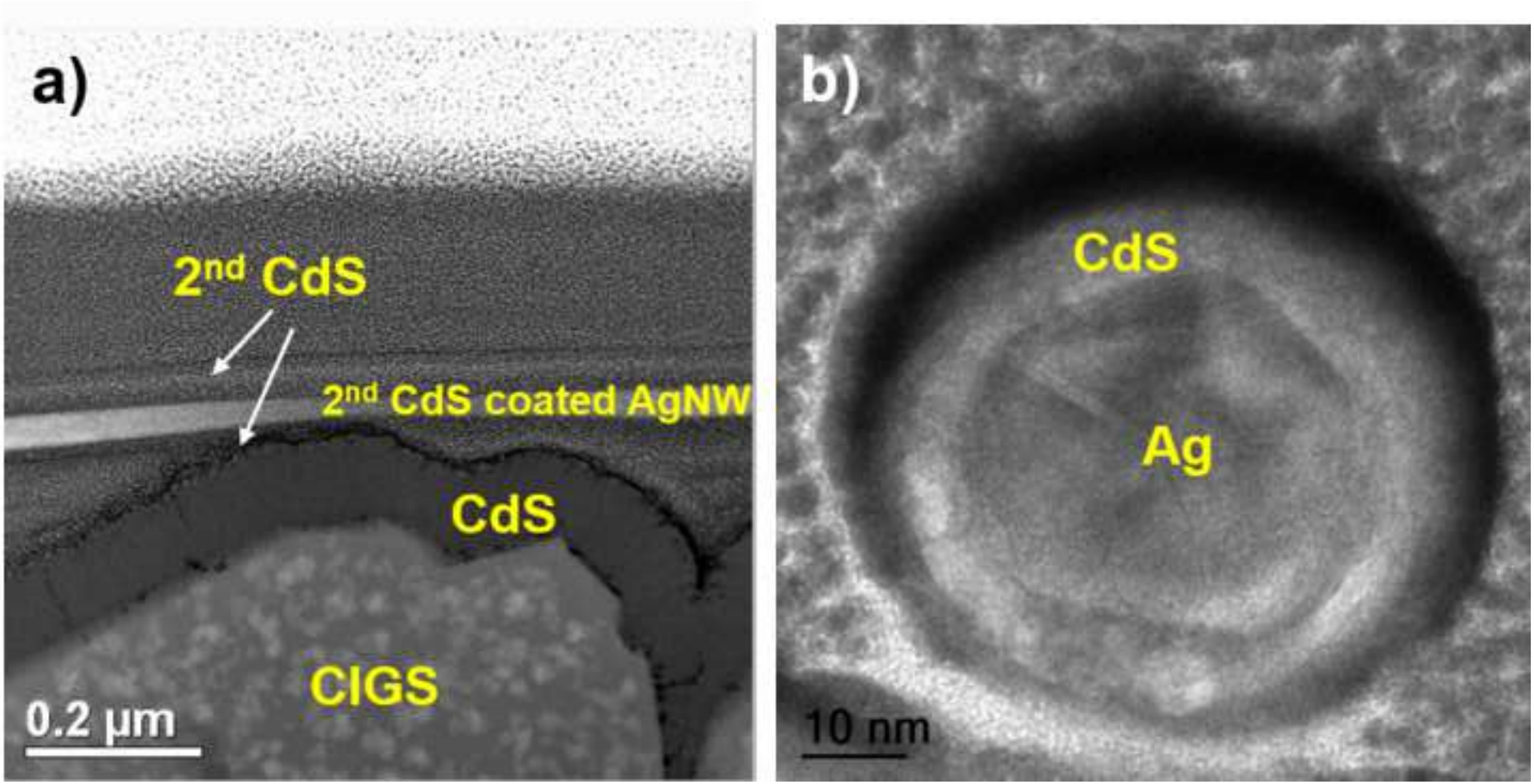

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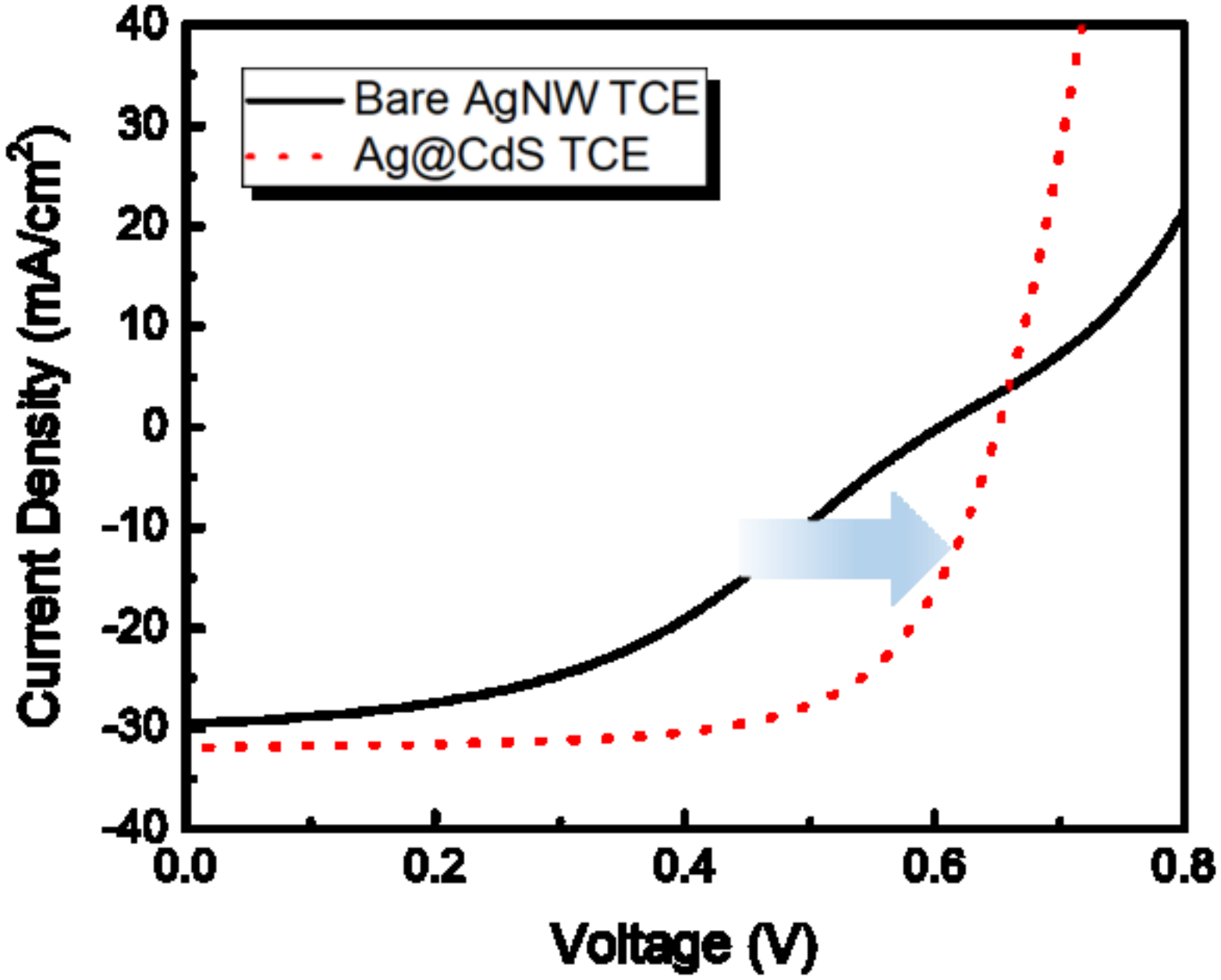

Table

Cell	V_{OC} (V)	J_{SC} (mA/cm^2)	Efficiency (%)	FF (%)
Bare AgNW TCE	0.60	29.5	7.9	44
Ag@CdS TCE	0.65	32.3	14.2	67.2

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Mo	Materion	Purity: 3N5	Mo sputtering
Cu	5N Plus	Purity: 4N7	CIGS deposition
In	5N Plus	Purity: 5N	CIGS deposition
Ga	5N Plus	Purity: 5N	CIGS deposition
Se	5N Plus	Purity: 5N	CIGS deposition
Ammonium acetate	Alfa Aesar	11599	CdS reaction solution
Ammonium hydroxide	Alfa Aesar	L13168	CdS reaction solution
Cadmium acetate dihydrate	Sigma-Aldrich	289159	CdS reaction solution
Thiourea	Sigma-Aldrich	T8656	CdS reaction solution
Silver Nanowire	ACSMaterial	AgNW-L30	AgNW dispersion

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April 19, 2019

Editor: Dr. Phillip Steindel
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Re: JoVE59909

Dear Editor:

We have attached the revised manuscript entitled "Fabrication of robust nanoscale contact between a sliver nanowire electrode and CdS buffer layer in Cu(In,Ga)Se_2 thin-film solar cells" for consideration for publication in JoVE. We appreciate the valuable suggestions from the referee, and we have addressed all of the reviewer's concerns and revised the manuscript according to the referee's suggestions. We have listed our response to the reviewers' comments, item by item, in the following pages of this cover letter. Our response to referee comments is highlighted in bold text for clarity, and the main text of manuscript highlighted in revised parts is attached to the end of cover letter.

Finally, please do not hesitate to contact me if you have further questions or need more information.

Yours Sincerely,
Choong-Heui Chung
E-mail: choong@hanbat.ac.kr

Our response to editorial comments:

General:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

We double checked the spelling and grammar.

2. Please include email addresses for all authors in the manuscript.

Author e-mail address are listed in the manuscript.

3. JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or reagent. Please limit the use of commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents.

For example: Sigma Aldrich, Alfa Aesar, etc.

All the company names are removed from manuscript and the company names are listed in the Table of Materials.

Protocol:

1. Please add more details to your protocol steps. Please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. If revisions cause a step to have more than 2-3 actions and 4 sentences per step, please split into separate steps or substeps.

We found out a typo in protocol of 5.3 Deposition of the 2nd CdS layer in the manuscript. We revised the 2nd CdS deposition time from 8 min to 10 min.

Specific Protocol steps:

1. 1.1: The Mo-coated glass is not in the Table of Materials-how is it made?

We revised the manuscript to describe how to make the Mo-coated glass in detail as following:

"1. Preparation of Mo-coated glass by DC magnetron sputtering

1. Load cleaned glass substrates into a DC magnetron sputter and pump down to below 4 x 10^{-6} Torr.

2. Flow Ar gas and set the working pressure to 20 mTorr.

3. Turn on plasma and increase the DC output power to 3 KW.

4. After pre-sputtering of 3 min for target cleaning, begin the Mo deposition until the Mo film thickness reaches approximately 350 nm.

5. Set the working pressure to 15 mTorr while maintaining the same output power (i.e.,3 KW).

6. Resume the Mo deposition until the total thickness of Mo reaches approximately 750 nm."

We also revised the material table to include the sputter target.

2. 1.2, 1.5: How do you determine and set these temperatures, exactly?
We describe the temperature control procedure more in detail for process 1.2 and 1.5 manuscript as following:
"The deposition rates were checked by the quartz crystal microbalance (QCM) technique. The deposition rates are dependent on the set temperature of effusion cells and the amount of materials in the effusion cells"

3. 5: Please include references for these procedures.
Section 5 refer to SEM/TEM characterization and J-V measurement. For clarity, we refer to the reference [Lee, S. et al. Robust nanoscale contact of silver nanowire electrodes to semiconductors to achieve high performance chalcogenide thin film solar cells. *Nano Energy*. 53, 675–682 (2018).], which is the reference 14 of the manuscript.

Figures, Tables, and Figure Legends:
1. Please upload each Figure individually to your Editorial Manager account as a .png, .tiff, or .pdf file. Please combine all panels of one figure into a single image file.
We will upload the image files (png format).

2. Please remove 'Figure 1' etc. from the figures themselves.
We removed.

3. Please remove the embedded figures and tables from the manuscript. Please upload Table 1 as a .xlsx file in your revision.
We removed figure images and table from the manuscript. We will upload Excel file of the table 1.

Discussion:
1. Discussion: As we are a methods journal, please revise the Discussion to explicitly cover the following in detail in 3–6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique
We added the paragraph describing a) – e) in the last part of discussion as following:

“Various methods have been applied to enhance the electrical properties of AgNW TCE including the incorporation of conducive matrix. The method described in this protocol is simple and effective to enhance the electrical contact property between AgNWs and underlying CdS buffer layer in CIGS thin film solar cell. Due to the enhanced contact property, the solar cell performance is greatly improved. The method is designed to apply to the CdS/CIGS system but is not limited to the CdS/CIGS system. When an appropriate CBD method is created, our method can be applied to create high-quality electrical contact between AgNWs and the buffer layer in chalcogenide thin-film solar cells”

Table of Materials:

1. Please ensure the Table of Materials has information on all materials and equipment used, especially those mentioned in the Protocol.

We confirmed.

Our response to reviewer #1:

Reviewer #1: The present MS describes embedding of silver nanowires into a CdS buffer layer of CIGS solar cell using a solution process method. AgNW being transparent do not impose any restriction in light transportation to solar cell and improves the electrical contacts as well. The results demonstrate the fact.

We thank the referee for a thorough evaluation of our manuscript. The comments were extremely helpful in revising our manuscript

Comment 1: In general the method of making electrical contact is novel, simple and easily viable. However, the author should explain the following facts i) how the electrical contacts to AgNW's embedded in CdS was made and ii) the SEM image of Cu(In,Ga)Se2 layer explaining rough morphology be incorporated in MS.

Our protocol is describing the detailed experimental method that we performed in our pervious paper [Lee, S. et al. Robust nanoscale contact of silver nanowire electrodes to semiconductors to achieve high performance chalcogenide thin film solar cells. *Nano Energy.* 53, 675–682 (2018).], which is the reference 14 of the manuscript. The formation of electrical contact are well explained and cross sectional SEM/TEM images were displayed in the paper. To clarify comment i) and ii) of reviewer, we revised our manuscript in the first paragraph of representative results as following:

"The detailed explanation on the formation of electrical contact and enhancement of electrical properties and device performance can be found in the reference 14. The structural analysis of AgNW and CdS junction including cross sectional SEM and TEM, and corresponding elemental mapping can also be found in the reference 14."

Our response to reviewer #2:

Reviewer #2: The authors have carried out an interesting experiment to enhance the efficiency of CIGS thin film solar cell by improving the electrical contact between the underlying Ag nanowire and the bulk CIGS thin film. However, the authors would need to provide additional data to support the efficacy of their claim.

We thank the referee for a thorough evaluation of our manuscript. The comments were extremely helpful in revising our manuscript

Comment 1: As expected, an additional layer of CdS on top of Ag nanowire enhanced the electrical contact between Ag and CdS, presumably by eliminating the "nanogaps" between Ag nanowire and the layer beneath it.

However, a key point that was mentioned in the manuscript but neither elaborated on nor supported by data was that "We optimized the reaction time, and 8 min resulted in the CIGS device with the best performance". As one would expect, too thin the additional CdS layer would not make good enough contact with Ag nanowire. On the other hand, too thick the additional CdS layer would reduce the overall conductivity and potentially increase the number of defect sites.

I would suggest the authors to add data, most likely JV curves, to show the effect of the second CdS thickness device performance. It would also be helpful if the authors could include SEM images of the corresponding films after the second CdS layer deposition.

We performed the J-V measurement and investigated the effect of 2nd CdS layer deposition time on the device performance in CIGS thin film sola cell including FF, V_{oc}, and Efficiency in our previous paper [Lee, S. et al. Robust nanoscale contact of silver nanowire electrodes to semiconductors to achieve high performance chalcogenide thin film solar cells. *Nano Energy.* 53, 675–682 (2018).], which is the reference 14 of the manuscript.

Additionally, we found out a typo in protocol of 5.3 Deposition of the 2nd CdS layer in the manuscript. We revised the 2nd CdS deposition time from 8 min to 10 min.

Figure 2 of reference 14:

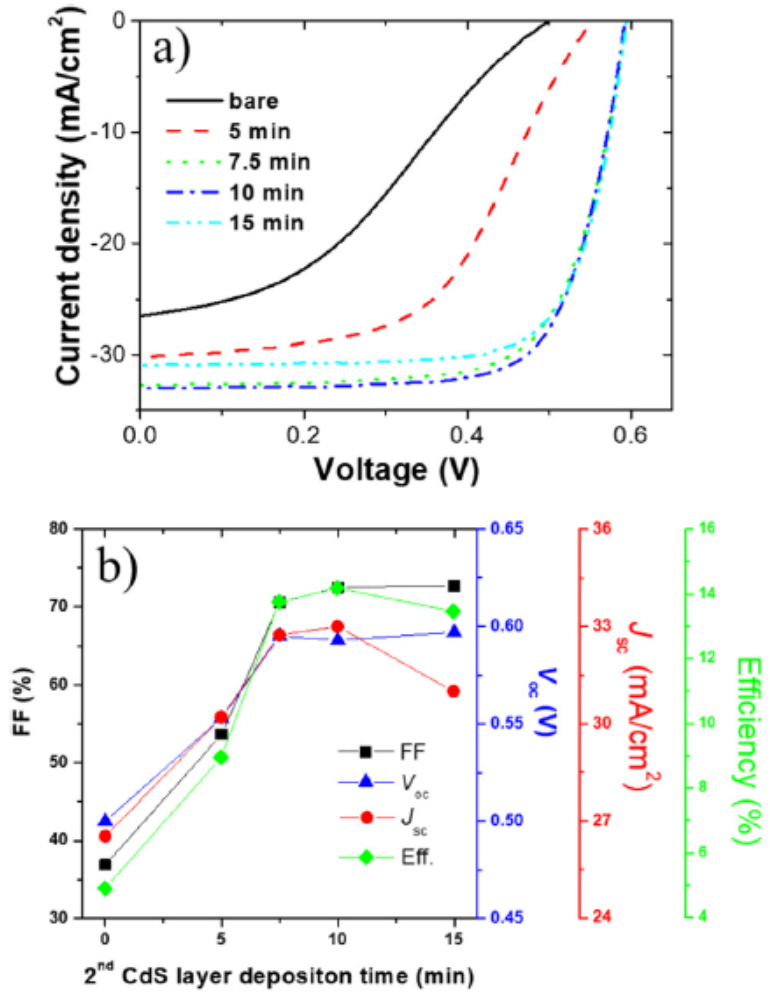

Fig. 2. Device performance measured under white-light (AM1.5G) illumination as a function of the deposition time of the 2nd CdS layer. (a) *J-V* characteristics of the Ag@CdS NW electrode-based CIGS thin films solar cells with varying deposition times of the 2nd CdS layer. (b) FF, V_{oc}, J_{sc}, and efficiency of the cells as a function of the deposition of time of the 2nd CdS layer.

To clarify the reviewer's suggestion, we added the comments on the effect of 2nd CdS deposition time on the device performance as following:

"The effect of 2nd CdS deposition time on a CIGS thin film solar cell device performance can be found in the reference 14."

Our response to reviewer #3:

Reviewer #3: it's a good protocol for the fabrication of a robust nanoscale contact between a silver nanowire network and CdS buffer layer in a CIGS thin-film solar cell.

We thank the referee for a thorough evaluation of our manuscript. The comments were extremely helpful in revising our manuscript

Comment 1: need SEM EDX data to demonstrate the chemical composition for each layer.

We performed the detailed structural analysis of 2nd CdS/AgNW junction in our previous paper [Lee, S. et al. Robust nanoscale contact of silver nanowire electrodes to semiconductors to achieve high performance chalcogenide thin film solar cells. *Nano Energy*. 53, 675–682 (2018).], which is the reference 14 of the manuscript. We revised our manuscript as following:

"The structural analysis of AgNW and CdS junction including cross sectional SEM and TEM, and corresponding elemental mapping can also be found in the reference 14."

Revised manuscript:

ABSTRACT:

Silver nanowire transparent electrodes have been employed as window layers for $Cu(In,Ga)Se_2$ thin-film solar cells. Bare silver nanowire electrodes normally result in very poor cell performance. Embedding or sandwiching silver nanowires using moderately conductive transparent materials, such as indium tin oxide or zinc oxide, can improve cell performance. However, the solution-processed matrix layers can cause a significant number of interfacial defects between transparent electrodes and the CdS buffer, which can eventually result in low cell performance. This manuscript describes how to fabricate robust electrical contact between a silver nanowire electrode and the underlying CdS buffer layer in a $Cu(In,Ga)Se_2$ solar cell, enabling high cell performance using matrix-free silver nanowire transparent electrodes. The matrix-free silver nanowire electrode fabricated by our method proves that the charge-carrier collection capability of silver nanowire electrode-based cells is as good as that of standard cells with sputtered ZnO:Al/i-ZnO as long as the silver nanowires and CdS have high-quality electrical contact. The high-quality electrical contact was achieved by depositing an additional CdS layer as thin as 10 nm onto the silver nanowire surface.

INTRODUCTION:

Silver nanowire (AgNW) networks have been extensively studied as an alternative to indium tin oxide (ITO) transparent conducting thin films due to their advantages over conventional transparent conducting oxides (TCOs) in terms of lower processing cost and better mechanical flexibility. Solution-processed AgNW network transparent conducting electrodes (TCEs) have thus been employed in $Cu(In,Ga)Se_2$ (CIGS) thin-film solar cells[1–6]. Solution-processed AgNW TCEs are normally fabricated in the form of embedded-AgNW or sandwich-AgNW structures in a conductive matrix such as PEDOT:PSS, ITO, ZnO, etc[7–11]. The matrix layers have been reported that the collection of the charge carriers present in the empty spaces of the AgNW network can be enhanced.

However, the matrix layer can generate interfacial defects between the matrix layer and underlying CdS buffer layer in CIGS thin-film solar cells[12,13]. The interfacial defects often cause a kink in the current density-voltage (J-V) curve, resulting in a low fill factor (FF) in the cell, which is detrimental to solar cell performance. We previously reported a method to resolve this issue by selectively depositing an additional thin CdS layer (2^{nd} CdS layer) between the AgNWs and the CdS buffer layer[14]. The incorporation of an additional CdS layer enhanced the contact properties in the junction between the AgNW and CdS layers. Consequently, the carrier collection in the AgNW network was greatly improved, and the cell performance was enhanced. In this protocol, we describe the experimental procedure to fabricate robust electrical contact between the AgNW network and the CdS buffer layer using a 2^{nd} CdS layer in a CIGS thin-film solar cell.

PROTOCOL:

1. Preparation of Mo-coated glass by DC magnetron sputtering

1. Load cleaned glass substrates into a DC magnetron sputter and pump down to below 4 x 10^{-6} Torr.

2. Flow Ar gas and set the working pressure to 20 mTorr.

3. Turn on plasma and increase the DC output power to 3 KW.

4. After pre-sputtering of 3 min for target cleaning, begin the Mo deposition until the Mo film thickness reaches approximately 350 nm.

5. Set the working pressure to 15 mTorr while maintaining the same output power (i.e.,3 KW).

6. Resume the Mo deposition until the total thickness of Mo reaches approximately 750 nm.

2. CIGS absorber layer deposition by means of a three-stage coevaporation

1. Mo-coated glass is loaded into a preheated co-evaporator of which vacuum should be lower than 5 x 10^{-6} Torr.

2. Set the temperatures of In, Ga, and Se effusion cells yielding deposition rates of 2.5 Å/s, 1.3 Å/s, and 15 Å/s, respectively. The deposition rates were checked by the quartz crystal microbalance (QCM) technique. The deposition rates are dependent on the set temperature of effusion cells and the amount of materials in the effusion cells.

3. Begin to supply In, Ga and Se onto the Mo-coated glass to form a 1 µm-thick $(In,Ga)_xSe_y$ precursor layer at the substrate temperature of 450 °C. The deposition time is 15 min. (namely, 1st stage)

4. Stop the In and Ga supplies and increase the substrate temperature to 550 °C.

5. Begin to supply Cu (deposition rate: 1.5 Å/s) onto the $(In,Ga)_xSe_y$ precursor and keep this procedure until the Cu/(In + Ga) compositional ratio of the film reaches to 1.15. Note that the Se deposition rate is maintained at 15 Å/s through the 2nd stage. (namely, 2nd stage)

6. Stop supplying Cu and evaporate In and Ga again with the same deposition rates as the 1st stage to finally form an approximately 2 μm-thick CIGS film with Cu/(In+Ga) compositional ratio of 0.9. The Se deposition rate and substrate temperature are maintained at 15 Å/s and 550 °C, respectively. The deposition time of this stage is 4 min. (namely 3rd stage)

7. In order to ensure a complete reaction, the deposited CIGS film is annealed under Se ambient (15 Å/s) for 5 min at the substrate temperature of 550 °C.

8. Cool down the substrate temperature to 450 °C under Se ambient (15 Å/s) and then unload the CIGS-deposited substrate when the substrate temperature is below 250 °C.

3. Growth of the CdS buffer layer on the CIGS absorber layer using a chemical bath deposition (CBD) method:

1. Prepare the CdS reaction bath solution in a 250 ml beaker by adding 97 ml of DI water, 0.079 g of $Cd(CH_3COO)_2 \cdot 2H_2O$, 0.041 g of NH_2CSNH_2, and 0.155 g of CH_3COONH_4 and then stir the solution for several minutes to mix. Make sure that all added solutes are completely dissolved.

2. Add 3 ml of NH_4OH (28% NH_3) into the bath solution and stir the solution for 2 min (Figure 1 shows the experimental setup of CBD for CdS).

3. Put the CIGS sample into the reaction bath solution using a Teflon sample holder.

4. Put the reaction bath into the water-heat bath maintained at 65 °C and stir the reaction bath solution with 200 rpm using a magnetic bar during deposition process.

5. Reacting for 20 min generates an approximately 70 to 80 nm CdS buffer layer on the CIGS.

6. After the reaction, remove the sample from the reaction bath, wash with a flow of DI water, and dry with N_2 gas.

7. Anneal the sample at 120°C for 30 min on a hot plate.

4. Fabrication of the AgNW TCE network:

1. Prepare a diluted AgNW dispersion (1 mg/ml) by mixing 19 ml of ethanol with 1 ml of a purchased ethanol-based AgNW dispersion (20 mg/ml).

2. Pour 0.2 ml of the diluted AgNW dispersion onto a CdS/CIGS sample (2.5 cm x 2.5 cm) to cover the whole surface of the sample and rotate the sample with 1000 rpm for 30 s.

3. Repeat the step 2 to achieve the desired optical and electrical properties. We spin-coated the AgNWs three times. A scanning electron microscopy (SEM) image of spin-coated AgNW TCE is shown in Figure 2.

4. After spin-coating, the sample was annealed at 120°C for 5 min on a hot plate.

5. Deposition of the 2nd CdS layer:

1. Prepare a new CdS reaction bath solution as previously described.

2. The CdS deposition process is the same as that reported in section 1, except the reaction time is different.

3. We optimized the reaction time, and 10 min resulted in the CIGS device with the best performance. The effect of 2nd CdS deposition time on a CIGS thin film solar cell device performance can be found in the reference 14.

6. Characterization techniques:

1. The surface and cross-sectional morphology of AgNWs and CdS-coated AgNWs were characterized by field emission SEM and transmission electron microscopy (TEM).

2. Solar cell performance was measured using a current-voltage source equipped with a solar simulator (1000 W/m^2, AM1.5G).

REPRESENTATIVE RESULTS

The layer structures of the CIGS solar cells with (a) standard ZnO:Al/i-ZnO and (b) AgNW TCE are shown in Figure 3. The surface morphology of CIGS is rough, and a nanoscale gap can form between the AgNW layer and the underlying CdS buffer layer. As highlighted in Figure 3(A), the 2nd CdS layer can be selectively deposited onto the nanoscale gap to create a stable electrical contact. The detailed explanation on the formation of electrical contact and enhancement of electrical properties and device performance can be found in the reference 14. The structural analysis of AgNW and CdS junction including cross sectional SEM and TEM, and corresponding elemental mapping can also be found in the reference 14.

Figure 4 shows the cross-sectional TEM images (a) along the 2nd CdS layer deposited on the AgNW network on the CdS/CIGS structure and (b) across the 2nd CdS layer deposited on the AgNW network. The CdS/CIGS structure shows a rugged surface morphology due to the granular structure of CIGS. Hence, bare AgNWs are suspended in air, and stable electrical contact with the CdS buffer layer cannot be expected. The 2nd CdS layer is uniformly deposited on the surface of the AgNWs, and the CdS layer on the core-shell AgNW (Ag@CdS NW) structure is produced as shown in Figure 4(B). Furthermore, the 2nd CdS layer fills the air gaps between the CdS buffer layer and the AgNW layer, as shown in the inset of Figure 4(A), and stable electrical contact is achieved.

Figure 5 and Table 1 show the device performance of a CIGS thin-film solar cell with bare AgNW and Ag@CdS NW TCEs. Due to unstable electrical contact, the cell with bare AgNWs has poor device performance. Deposition of a 2nd CdS layer greatly enhances the cell performance, as shown in the J-V characteristics in Figure 5. The cell with the Ag@CdS NW TCE showed a greater than 50% increase in device efficiency and FF compared to the bare AgNW TCE.

FIGURE AND TABLE LEGENDS:

Figure 1: Chemical bath deposition setup. An image of the experimental setup for chemical bath deposition of CdS on GIGS.

Figure 2: An SEM image of the AgNW TCE. The SEM image shows the spin-coated AgNW TCE on the CdS/GIGS/Mo structure.

Figure 3: Schematic diagram of CIGS thin-film solar cells. Layer structure of a CIGS thin-film solar cell with (**A**) ZnO:Al/i-ZnO TCO and (**B**) AgNW TCE with a 2nd CdS layer.

Figure 4: Structural analysis of Ag@CdS NW. (**A**) Cross-sectional TEM image along a Ag@CdS NW on a CdS/CIGS structure and (**B**) high-resolution TEM image across a Ag@CdS NW.

Figure 5: Device performance comparison. J-V characteristics of CIGS thin-film solar cells with bare AgNW and Ag@CdS NW TCEs.

Table 1: Device performance data. A summary of the device performance derived from the J-V curves.

DISCUSSION:

Note that the deposition time of the 2nd CdS layer must be optimized to achieve the optimal cell performance. As the deposition time increases, the thickness of the 2nd CdS layer increases, and consequently, the electrical contact will improve. However, further deposition of the 2nd CdS layer will result in a thicker layer that reduces light absorption, and the device efficiency will decrease. We achieved the best cell performance with 10 min of deposition time for the 2nd CdS layer and determined that the cell efficiency decreased with longer deposition times.

To evaluate our method, we compared the device performance of the Ag@CdS NW-based CIGS solar cell with that of a standard CIGS solar cell with a sputtered ZnO:Al/i-ZnOl TCO, as described in Figure 3(A)[14]. The J-V characteristics were nearly equal, and the overall device performances were very similar. This result proves that our solution process method can produce a high-performance thin-film solar cell.

Various methods have been applied to enhance the electrical properties of AgNW TCE including the incorporation of conducive matrix. The method described in this protocol is simple and effective to enhance the electrical contact property between AgNWs and underlying CdS buffer layer in CIGS thin film solar cell. Due to the enhanced contact property, the solar cell performance is greatly improved. The method is designed to apply to the CdS/CIGS system but is not limited to the CdS/CIGS system. When an appropriate CBD method is created, our method can be applied to create high-quality electrical contact between AgNWs and the buffer layer in chalcogenide thin-film solar cells.

ACKNOWLEDGMENTS:
This research was supported by the In-House Research and Development Program of the Korea Institute of Energy Research (KIER) (B9-2411) and the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant NRF-2016R1D1A1B03934840).

DISCLOSURES:

The authors declare that they have no competing financial interests.

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