Final Report

Electrodeposited TCOs for Thin-Film and Future Solar Cells

DOE Grant No.: DE-EE0000577

Recipient: University of Texas at Arlington
Working Partner: HelioVolt Corporation

Principal Investigator: Prof. Meng Tao
Phone: 817-272-1353
Fax: 817-272-7458
Email: mtao@uta.edu

Executive Summary

Quoted from the Proposal: "The objective of this DOE SAI project is to demonstrate the feasibility of electrodeposited and solution-doped transparent conducting oxides (TCOs) such as zinc oxide with resistivity in the mid-10^{-4} Ω-cm range. The target application is an "on-top" TCO which can be deposited on semiconductors in thin-film and future solar cells including amorphous silicon, copper indium gallium selenide and emerging solar cells. There is no solution-prepared on-top TCO currently used in commercial solar cells. This project, if successful, will fill this gap…Our technical objectives include electrodeposited TCOs with 1) resistivity in the mid-10^{-4} Ω-cm range, 2) post-deposition annealing below 300°C and 3) no-vacuum processing or low-vacuum processing."

All the three research objectives listed above have been accomplished in the 14-month period from July 1, 2009 through September 30, 2010. The most noticeable accomplishments of this project are 1) identification of a terawatt-scale dopant for zinc oxide, i.e. yttrium, whose known reserve is enough for 60 peak terawatts of thin-film solar cells; 2) demonstration of a record-low resistivity, 6.3×10^{-5} Ω-cm, in solution-deposited zinc oxide with an abundant dopant; and 3) the record-low resistivity was accomplished with a maximum process temperature of 300°C and without vacuum annealing. Industrial applications of the new yttrium-doped zinc oxide are being pursued, including 1) green deposition of yttrium-doped zinc oxide to reduce water consumption during deposition and 2) search for an industrial partner to develop an electrochemical tool for large-area uniform deposition of yttrium-doped zinc oxide.

Table of Contents

1. Background to Present Research

All 2nd-generation thin-film solar cell technologies, including a-Si, CIGS and CdTe, employ TCOs as an integral part of the cell structure. It is expected that many 3rd-generation solar cell technologies will employ TCOs as well, such as organic solar cells. As the electrical contact and optical window in solar cells, two most important figures of merit for TCOs are low resistivity (low 10^{-4} Ω-cm) and high transmissivity (>80%) in the spectral range of interest to solar cells (350–1,200 nm). Low cost is equally important, which requires low-cost source materials and low-cost synthesis methods for TCOs. Additional requirements for "on-top" TCOs include refractive index around 2 for index matching in solar modules, low-temperature and gentle deposition to avoid temperature- or plasma-induced damage to the semiconductor underneath, and stability against interfacial reactions or diffusion at elevated temperatures during cell fabrication. Here "on-top" means the TCO layer is deposited on the semiconductor layer in solar cells, i.e. the substrate cells.

ZnO is an ideal TCO for solar cells. It meets many of the requirements listed above: high transmissivity, low-cost source materials, a refractive index of 2, and stability against interfacial reactions and diffusion. ZnO in commercial solar cells is typically deposited by vacuum-based sputter deposition, which is inherently more costly than solution-based deposition methods. Chemical bath deposition of ZnO has been reported, but the resistivity of solution-prepared ZnO is above high 10^{-4} Ω-cm, as compared to mid 10^{-4} Ω-cm from sputter-deposited ZnO. The most common commercial n-type dopant for ZnO is Al.

In this project we pursue electrodeposition of ZnO, with the objective to achieve resistivity at low 10^{-4} Ω-cm. Electrodeposition is a low-temperature gentle process, with low cost. More importantly, electrodeposition provides advantages other solution-based deposition methods do not offer including 1) electrodeposited TCOs are denser with lower resistivity and require lower post-deposition annealing temperatures and 2) electrodeposition provides precise and in-line control of film thickness. If successful, electrodeposited ZnO will bring down the cost of sputter-deposited ZnO in thin-film solar cells from the current \$0.18–0.28/W_p to \$0.08–0.10/W_p, i.e. a 3–5% reduction in module cost.

2. Comparison of Accomplishments and Objective

Our objective, as originally proposed, was to demonstrate the feasibility of electrodeposited ZnO with resistivity in the mid-10^{-4} Ω-cm range. This was intended to be accomplished with processing temperatures below 300°C, processing time on the order of a few minutes and without vacuum processing or with low-vacuum processing.

All the technical targets have been accomplished. The lowest resistivity demonstrated so far is 6.3×10^{-4} Ω-cm, which is a record. This resistivity was demonstrated with a maximum process temperature of 300°C and without vacuum annealing.

3. Research Tasks Performed

The technical tasks of this project, as originally proposed, include:

1) Development of an electrochemical process for the deposition of Al-doped ZnO;
2) Development of an electrochemical process for the deposition of F-doped ZnO;
3) Investigation of post-deposition annealing conditions to achieve resistivity in the mid-10^{-4} Ω-cm range;
4) Investigation of the structural and optical properties including microstructure, surface morphology, refractive index and transmissivity; and
5) Characterization and comparison of CIGS cells with electrodeposited and sputter-deposited ZnO.

All the technical tasks listed above have been carried out. In addition, we have identified yttrium as a more suitable dopant for ZnO and have demonstrated excellent performance from Y-doped ZnO. The following contains more details about the technical tasks we have carried out:

3.1 Al-Doped ZnO

1) Task 1: Electrodeposition of Al-Doped ZnO

This task has been successfully completed. The precursors for electrodepositing Al-doped ZnO are $Zn(NO_3)_2$ and $Al(NO_3)_3$. Cyclic voltammetry in an aqueous solution containing 0.1 M $Zn(NO_3)_2$ and 0.2 mM $Al(NO_3)_3$ at 70°C reveals the following reduction reaction:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad \text{(R1)}$$

in the potential range of -0.5 and -0.8 V vs. a Ag/AgCl reference electrode. The produced OH^- ions react with Zn^{2+} ions in the solution to form ZnO:

$$Zn^{2+} + 2OH^- \rightarrow ZnO\downarrow + H_2O \quad \text{(R2)}$$

and with Al^{3+} ions in the solution to form Al_2O_3, which co-precipitates with ZnO, leading to Al-doped ZnO:

$$2Al^{3+} + 6OH^- \rightarrow Al_2O_3\downarrow + 3H_2O \quad \text{(R3)}$$

In addition to Al, Ga has also been attempted as a n-type dopant in ZnO to achieve low resistivity. The precursor for Ga is $Ga(NO_3)_3$. The doping mechanism for Ga-doped ZnO is similar to that of Al-doped ZnO, by co-precipitation as revealed by cyclic voltammetry.

In both Al-doped and Ga-doped cases, detailed studies of the sheet resistance of the doped ZnO films as a function of $Al(NO_3)_3$ or $Ga(NO_3)_3$ concentration in the deposition solution are carried out, in an attempt to minimize the resistivity of the doped ZnO films.

2) Task 3: Post-Deposition Annealing

This task for Al-doped and Ga-doped ZnO has been successfully completed. The optimized post-deposition annealing conditions for Al-doped ZnO are found to be 200ºC for 3 hours in air. The minimum sheet resistance for Al-doped ZnO achieved is 13.8 Ω/□, which occurs with an Al^{3+}/Zn^{2+} ratio of 0.001 in the deposition solution. The corresponding resistivity for the Al-doped ZnO is 8×10^{-4} Ω-cm.

For Ga-doped ZnO, the optimum post-deposition annealing conditions are found to be 300ºC for 2 hours in vacuum (μTorr). The minimum sheet resistance for Ga -doped ZnO achieved is 7 Ω/□ and the corresponding resistivity of the Ga-doped ZnO is 3.8×10^{-4} Ω-cm. This meets the resistivity requirement for TCOs in solar cells. The sample is deposited in a solution with a Ga^{3+}/Zn^{2+} ratio of 0.0064.

3) Task 4: Investigation of Film Properties

Energy dispersion spectroscopy is carried out to determine the Al content in Al-doped ZnO as a function of Al^{3+}/Zn^{2+} ratio in the deposition solution. The Al/Zn ratio in the film corresponding to the minimum sheet resistance of 13.8 Ω/□ is 0.02. Optical characterization reveals high transmissivity (>80%) for Al-doped ZnO, which meets the transmissivity requirement for TCOs.

For Ga-doped ZnO, energy dispersion spectroscopy reveals the Ga/Zn ratio in the film corresponding to the minimum sheet resistance of 7 Ω/□ is 0.23. Optical characterization reveals high transmissivity (80%) for Ga-doped ZnO. X-ray diffraction confirms that Ga-doped ZnO deposited under the conditions described above is actually ZnO.

3.2 F-Doped ZnO

1) Task 2: Electrodeposition of F-Doped ZnO

This task has been completed. The deposition solution contains 0.5 M $Zn(NO_3)_2$ as the Zn precursor and 0.6 M NaF as the F precursor, which meet the solubility requirement. The complaxing agent used is EDTA ($C_{10}H_{16}N_2O_8$) at 0.5 M. The solution pH is adjusted to 7 by adding NaOH. It is found that 0.5-M EDTA allows the solution pH to be increased to ~10 without $Zn(OH)_2$ precipitation. The solution temperature is 80°C. Cyclic voltammetry reveals

that reaction R1 takes place at –1 V with respect to the Ag/AgCl reference electrode. Therefore –1 V is selected as the deposition potential for F-doped ZnO. With Zn^{2+}, OH^- and F^- ions in the solution, the following two precipitation reactions lead to F-doped ZnO:

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad \text{(R4)}$$

$$Zn^{2+} + 2F^- \rightarrow CuF_2 \quad \text{(R5)}$$

2) Task 4: Investigation of Film Properties

Current-voltage characterization and x-ray diffraction for F-doped ZnO are completed. Current-voltage characterization reveals that without F, the resistivity of undoped ZnO is 4.6×104 □-cm. With 0.6 M NaF in the solution, resistivity of ZnO is reduced to 10□7 -cm. X-ray diffraction reveals that the major peaks of F-doped ZnO are (100), (101) and (110). The resistivity of as-deposited F-doped ZnO is two orders of magnitude higher than that of as-deposited Al and Ga-doped ZnO, which made us to look into other dopants for ZnO.

3.3 Y-Doped ZnO

1) New Task: Electrodeposition of Y-Doped ZnO

This task was not in the original proposal, but initial experiments suggest it as a promising approach. The deposition solution contains 0.1 M $Zn(NO_3)_2$ as the Zn precursor and varying $Y(NO_3)_3$ as the Y precursor. Deposition temperature was 70°C. Cyclic voltammetry reveals that reaction R1 takes place at –0.65 V with respect to the Ag/AgCl reference electrode. Therefore –0.7 V was selected as the deposition potential for Y-doped ZnO. With Zn^{2+}, Y^{3+} and OH^- ions in the solution, the following two precipitation reactions lead to Y-doped ZnO:

$$Zn^{2+} + 2OH^- \rightarrow ZnO + H_2O \quad \text{(R6)}$$

$$2Y^{3+} + 6OH^- \rightarrow Y_2O_3 + 3H_2O \quad \text{(R7)}$$

By adjusting the Y^{3+}/Zn^{2+} ratio in the solution, the Y/Zn ratio, thus the doping level, is adjusted to achieve minimum resistivity in as-deposited ZnO. The thickness of the ZnO films is ~400 nm.

We also investigated deposition conditions for finer crystal grains. The two deposition conditions we examined are solution pH and temperature. We have investigated the effect of solution temperature on grain size. The temperature range investigated is from the original 70°C to 65°C, 60°C, 55°C and 50°C. We have found that below 55°C, there is little deposition of ZnO. At 60 and 65°C, ZnO does deposit but the deposition rate is very small, on the order of ~4 nm/min. This means that for a 500 nm film, the deposition time will be almost 2 hours, which is too long for a reasonable throughput. We have played with solution pH from 4.5 to 6.0, but the pH has little impact on the deposition rate. From these two sets of experiments, we concluded that, although lower solution temperatures reduce film roughness, the deposition rate becomes too low.

2) Task 3: Post-Deposition Annealing

The optimum post-deposition annealing conditions for Y-doped ZnO have been identified. Figure 1 shows the sheet resistance of Y-doped ZnO as a function of Y^{3+}/Zn^{2+} ratio in the deposition solution, where the as-deposited sample is annealed in 1 atm N_2 at 300°C for 3 hours in a tube furnace. With the Y^{3+}/Zn^{2+} ratio of 0.1 in the solution ($Y(NO_3)_3$ concentration 10 mM), the ZnO film achieves the minimum sheet resistance of 1.5 Ω/□. This corresponds to a resistivity of 6.3×10^{-5} Ω-cm for ZnO. Even with possible measurement errors considered, i.e. the ITO sheet resistance is 50% lower and the ZnO film is 50% thicker, the corresponding resistivity is only 1×10^{-4} Ω-cm. These are the lowest resistivities reported for any solution-prepared ZnO doped with an abundant element. They compare favorably to vacuum-prepared Al-doped ZnO.

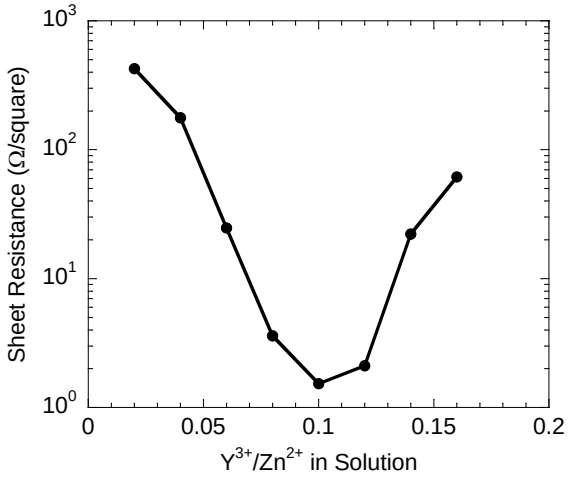

Figure 1. Measured sheet resistance of Y-doped ZnO films as a function of Y^{3+}/Zn^{2+} ratio in the deposition solution. The Y-doped ZnO samples were post-annealed in N_2 at 300°C for 3 hours.

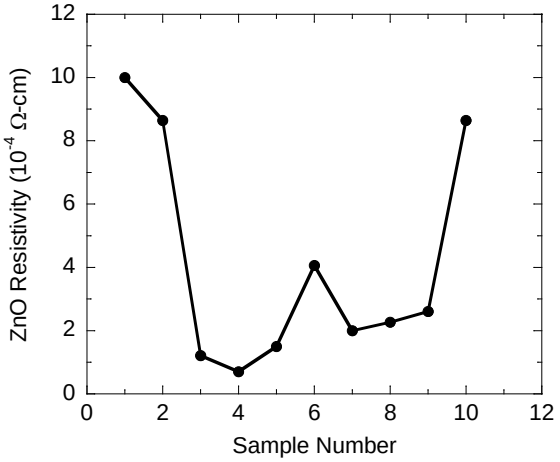

Figure 2. Statistics of the resistivity results for ten Y-doped ZnO samples prepared and annealed under the same conditions: Y^{3+}/Zn^{2+} ratio 0.1, solution temperature 70ºC, annealing temperature 300ºC, annealing time 3 hours, and annealing ambient N_2.

Figure 2 shows the resistivities from ten Y-doped ZnO samples deposited and annealed under the same conditions: Y^{3+}/Zn^{2+} ratio 0.1, solution temperature 70ºC, annealing temperature 300ºC, annealing time 3 hours, and annealing ambient N_2. Six out of the ten samples have

resistivity at or below 2×10^{-4} Ω-cm, while three samples are above 8×10^{-4} Ω-cm. The lowest resistivity for this set of samples is 7×10^{-5} Ω-cm. The fluctuation in resistivity is likely due to the nonuniform ZnO films and fluctuations in Y concentration in the ZnO films due to growth kinetics.

We investigated the effect of post-deposition annealing on film roughness. We prepared ZnO samples to measure their roughness by AFM (as-deposited). The samples were then annealed under the same conditions and measured again by AFM for their roughness. We found that the mean-square roughness of the as-deposited samples is ~100 nm by AFM. After post-annealing at 300°C for 3 hours in N_2, the roughness is reduced to ~30 nm, a factor of 3 reduction. It indicates that post-annealing is a more effective method to reduced film roughness.

3) Task 4: Investigation of Film Properties

Characterization of Y-doped ZnO has been finished. X-ray diffraction is performed to confirm that the samples are actually ZnO, as shown in Figure 3. The sample is deposited at the Y^{3+}/Zn^{2+} ratio of 0.08 and solution temperature of 70°C. The sample is post-annealed in N_2 at 300°C for 2.5 hours. The only peaks observed are either ZnO peaks or In_2O_3 peaks, where In_2O_3 is the substrate, and no metallic Zn or $Zn(OH)_2$ peak appears. The 34.4°, 36.2°, 47.6°, and 62.9° peaks marked with solid dots correspond to ZnO(002), (101), (102) and (103), respectively. The remaining peaks are In_2O_3(222), (400) and (622), which are marked with open dots.

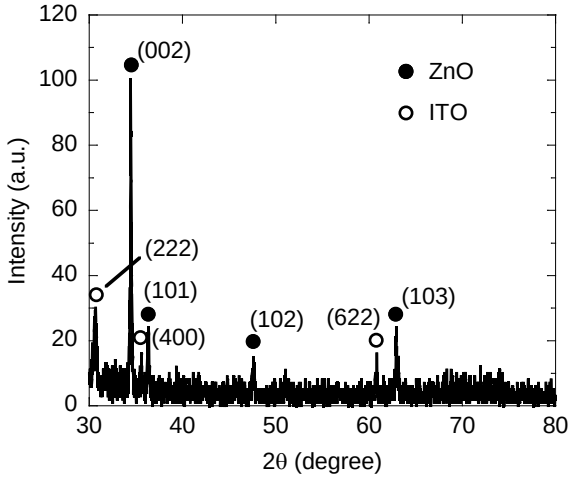

Figure 3. X-ray diffraction pattern of a Y-doped ZnO sample post-annealed in N_2 at 300°C for 2.5 hours. The sample was deposited with the Y^{3+}/Zn^{2+} ratio of 0.08 and at solution temperature of 70°C.

Figure 4 shows the total transmittance and absorbance of a Y-doped ZnO sample deposited at the Y^{3+}/Zn^{2+} ratio of 0.08 and solution temperature of 70ºC. The sample was post-annealed at 300ºC for 2.5 hours in N_2. The absorbance was calculated from the following equation: A = 1 – T – R. The Y-doped ZnO sample shows high transmittance of ~80 % and low absorbance of 5–10 % for a thickness of 400 nm. Figure 5 shows a scanning electron micrograph of the morphology of as-deposited Y-doped ZnO. The sample was deposited at the Y^{3+}/Zn^{2+} ratio of 0.08 and solution temperature of 70ºC. The micrograph shows a continuous but textured polycrystalline ZnO film. The grain size varies between 100 and 800 nm. Many grains have a

hexagonal shape, suggesting preferential growth along the c-axis of ZnO.

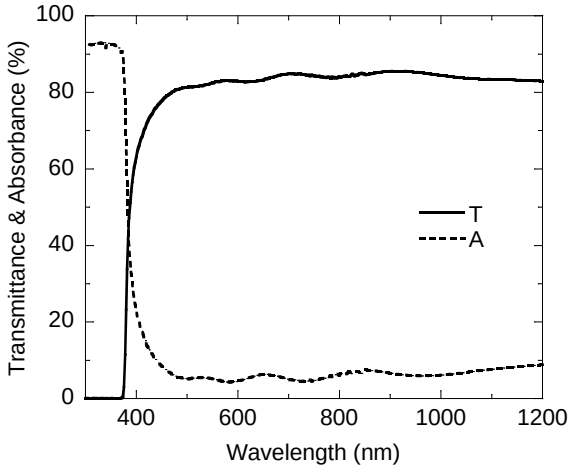

Figure 4. Total transmittance and absorbance of a Y-doped ZnO sample post-annealed in N_2 at 300ºC for 2.5 hours. The sample was deposited with the Y^{3+}/Zn^{2+} ratio of 0.08 and at solution temperature of 70ºC.

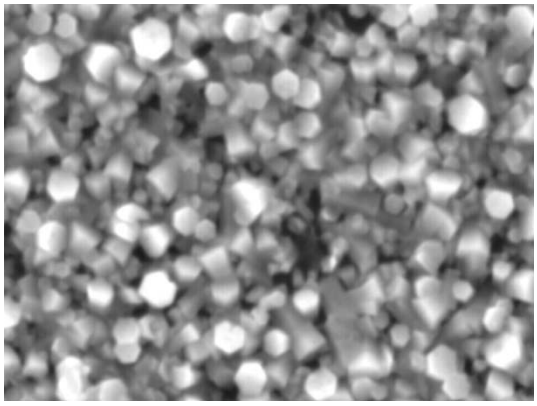

Figure 5. SEM micrographs of an as-deposited Y-doped ZnO sample. The ZnO sample was deposited at the Y^{3+}/Zn^{2+} ratio of 0.08 and at solution temperature of 70ºC.

Figure 6 shows energy dispersive spectroscopy measurements of the Y concentration (in the form of Y/Zn ratio) in as-deposited samples as a function of Y^{3+}/Zn^{2+} ratio in the deposition solution. The Y concentration in the ZnO film increases with increasing Y concentration in the solution, but in a nonlinear fashion. It also reveals that the Y/Zn ratio in the film corresponding to the Y^{3+}/Zn^{2+} ratio of 0.1 in the solution is 0.08, or the Y concentration in the record-resistivity ZnO film is 3.7 atomic %.

3.4 Industrial Collaborations on Y-Doped ZnO

We started to look for industrial collaborations to verify and apply this new TCO in commercial solar cells. We asked for commercial CIGS solar cells from HelioVolt to test Y-doped ZnO. Since our electrochemical tools can handle only small samples, we have asked and HelioVolt has agreed to cut their commercial-size cells into small sizes for before shipping them to us. However, we found that CIGS dissolves in during the deposition of Y-doped ZnO by electrodeposition.

We also started to look for an equipment vendor to design an electrochemical tool for large-area uniform deposition. Commercial solar cells are tens of square inches to a few square feet in size. Deposition of a uniform TCO film on solar cells of that size presents a challenge for electrochemical deposition. We have contacted Precision Process Equipment Inc., a company with expertise in electrochemical equipment for large-area uniform deposition.

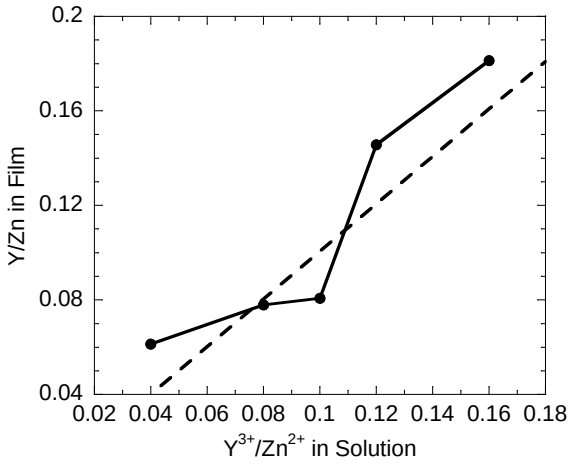

Figure 6. Measured Y/Zn ratio in Y-doped ZnO films by EDS as a function of Y^{3+}/Zn^{2+} ratio in the deposition solution. The dashed line indicates where Y/Zn ratio in film is equal to Y^{3+}/Zn^{2+} ratio in solution.

4. Publications/Presentations

1) M. Tao, X. Han, and K. Han, Solution-Based N-Type Doping in Metal Oxides for Next-Generation Solar Cells, in Photovoltaics for the 21st Century 5, edited by M. Tao, P. Chang, C. Claeys, K. Kakimoto, K. Rajeshwar, M. Sunkara, and D. Yang, ECS Transactions, vol. 25, no. 15, pp. 67-78 (2009).
2) X. Han, K. Han, and M. Tao, Electrodeposition of Group-IIIA Doped ZnO as a Transparent Conductive Oxide, in Photovoltaics for the 21st Century 5, edited by M. Tao, P. Chang, C. Claeys, K. Kakimoto, K. Rajeshwar, M. Sunkara, and D. Yang, ECS Transactions, vol. 25, no. 15, pp. 103-9 (2009).
3) X. Han, K. Han, and M. Tao, Low Resistivity Yttrium-Doped Zinc Oxide by Electrochemical Deposition, Journal of the Electrochemical Society, vol. 157, pp. H593-7 (2010).
4) M. Tao, Next-Generation Inorganic Solar Cells beyond Silicon, 2nd World Materials Summit for Advanced Energy Materials and Sustainable Society Development (Suzhou, China, 2009).
5) X. Han and M. Tao, Electrodeposition of Low-Resistivity Y-Doped ZnO and Its Thermal Stability, 35th IEEE Photovoltaic Specialist Conference (Honolulu, Hawaii, 2010).

8. Incremental Accomplishments

1) The main technical objective of the project, i.e. electrodeposited ZnO with a resistivity at low 10^{-4} Ω-cm, was accomplished with gallium as the dopant. In this case, the

lowest resistivity was 3.8×10^{-4} Ω-cm. The sample went through post-deposition annealing at 300°C for 2 hours in vacuum. This demonstrates that the performance of electrodeposited ZnO is comparable to that of sputter-deposited ZnO for solar cell applications (October 2009).

2) A postdoc fellow was recruited and joined UTA to work on this project (November 2009).
3) An ideal dopant for ZnO has been identified, i.e. Y. The known reserve of Y on the planet is 610,000 tons, according to U.S. Geological Survey, which is tens of times more abundant than Ga, In, Tl, or Sc. Initial experiments suggest that the resistivity of Y-doped ZnO by electrodeposition can go below 1×10^{-4} Ω-cm. Additional experiments are being carried out to confirm the resistivity. If true, this could make Y-doped ZnO the standard "on-top" TCO in solar cells (January 2010).
4) With Y as the dopant for ZnO, we have confirmed with an extensive study that resistivity below 1×10^{-4} Ω-cm can be reproducibly achieved in electrodeposited Y-doped ZnO. All the experimental conditions for 1×10^{-4} Ω-cm Y-doped ZnO are within the typical process windows for thin-film solar cells.
5) We are now focusing on manufacturability issues such as large-area uniformity. We have high hope that Y-doped ZnO will become an industrial standard "on-top" TCO in thin-film solar cells.