A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

National Renewable Energy Laboratory
Innovation for Our Energy Future

Transparent Conducting Contacts Based on Zinc Oxide Substitutionally Doped with Gallium

Preprint

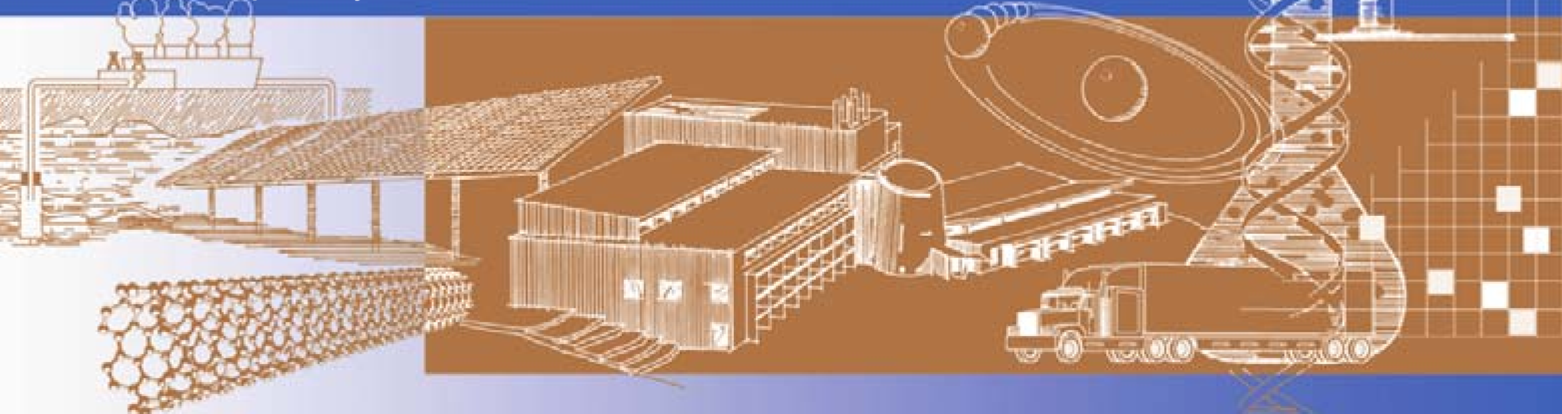
C.W. Gorrie
University of Florida

M. Reese, J.D. Perkins, J.L. Alleman,
M.S. Dabney, B. To, D.S. Ginley, and J.J. Berry
National Renewable Energy Laboratory

Presented at the 33rd IEEE Photovoltaic Specialists Conference
San Diego, California
May 11–16, 2008

Conference Paper
NREL/CP-520-42570
May 2008

NREL is operated by Midwest Research Institute ● Battelle   Contract No. DE-AC36-99-GO10337



Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: mailto:reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

Transparent Conducting Contacts Based on Zinc Oxide Substitutionally Doped with Gallium

Christopher W. Gorrie[1]. Matthew Reese, John D. Perkins, Jeff L. Alleman, Matthew S. Dabney, Bobby To, David S. Ginley, Joseph J. Berry*
[1]*Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611*
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401

ABSTRACT

We have employed a high-throughput combinatorial approach to explore a range of Ga doping levels from ≈2-7.5 at% gallium in materials sputtered from ceramic oxide targets on glass substrates. Using our combinatorial approach this compositional spread is examined over a range of substrate temperatures and sputtering atmospheres. Structural, optical, and electrical analysis is then performed using our suite of combinatorial characterization tools. In parallel we have used pulsed laser deposition (PLD) from ceramic targets to produce state of the art Ga:ZnO films on glass at a variety of substrate temperatures for comparison to our combinatorial studies. Our best PLD materials were deposited at a nominal substrate temperature of 300 ^{o}C and resulted in a film with a resistivity of 7.7×10^{-5} Ω·cm and transparency in excess of 85% in the visible.

INTRODUCTION

Transparent conducting oxides (TCOs) are a critical element in photovoltaic devices. While many of the main industrial TCOs include a significant fraction of indium, the increasing cost of indium has driven development of low cost, high performance TCOs. In the context of organic photovoltaic devices, concerns about the effects of mobile indium ions and their impact on device stability has also motivated the search for indium-free TCOs. One particular class of indium-free TCOs is based on substitutionally-doped zinc oxide which is of considerable interest due to its excellent transparency and conductivity. Isoelectronic substitution of Zn with Mg or other group II materials permits the bandgap and work function of these materials to be engineered. In addition, while considerable research efforts have been made to examine aluminum-doped zinc oxide, gallium has only more recently become the subject of considerable research efforts. Gallium doping promises similar transparency and conductivity with potentially superior stability.[1-3]

We report our initial examinations of Ga:ZnO using a high throughput combinatorial approach. In our current experiments, compositionally-graded sample libraries are deposited by co-sputtering from two ceramic oxide targets. The depositions are made on 50×50 mm glass substrates, creating a single-sample combinatorial library spanning a range of compositions. The compositional range can then be tuned via the sputtering parameters to span a sub-range between the two target compositions. In addition to our combinatorial studies, we report our results for Ga:ZnO material deposited by pulsed laser deposition (PLD). This deposition technique permits the exploration of the ultimate materials performance. Unlike the combinatorial studies in which a range of composition can be examined, our current PLD capability permits only single-composition Ga:ZnO to be deposited. In addition, PLD is not as readily scalable as sputtering.

EXPERIMENTS AND DISCUSSION

Room Temperature Combinatorial Studies

The combinatorial studies of gallium-doped zinc oxide (Ga:ZnO) are carried out in a vacuum system with a base pressure of under $1X10^{-6}$ Torr. Sputtering was performed using two Angstrom Instruments Mag 2 guns, each positioned in an off-axis configuration approximately 8 cm from the substrate surface, measured center to center. Depositions were performed in an atmosphere of $4.5X10^{-3}$ torr Ar. Ceramic targets of ZnO and Ga:ZnO (8 at% Ga) were employed to span a range of gallium doping levels from ≈4-8 at% across our initial libraries based on calibration depositions. In addition, electron probe micro analysis (EPMA) and inductively coupled plasma spectroscopy (ICP) measurements were used to examine selected samples to make a more precise determination of the change in composition across selected libraries. This additional EPMA and ICP data was consitent with the calibration depositions used for the libraries reported here.

The first combinatorial studies for room temperature depositions display relatively uniform crystallographic texturing and peak location across the combinatorial library as can be seen in the x-ray diffraction (XRD) in Figure 1. The XRD texturing is characteristic of ZnO films and of the peak intensity is maximal at the location corresponding to the ZnO (200) peak, Close examination of the XRD frames taken from the high Ga region of the library also reveals some indications of phase segregation and peaks corresponding to Ga_2O_3. Electrically these room temperature RF sputtered libraries have a range of resistivity/conductivity. Raw sheet resistance data for the same library seen in Figure 1 is presented in Figure 2. The sheet resistance along with thickness data

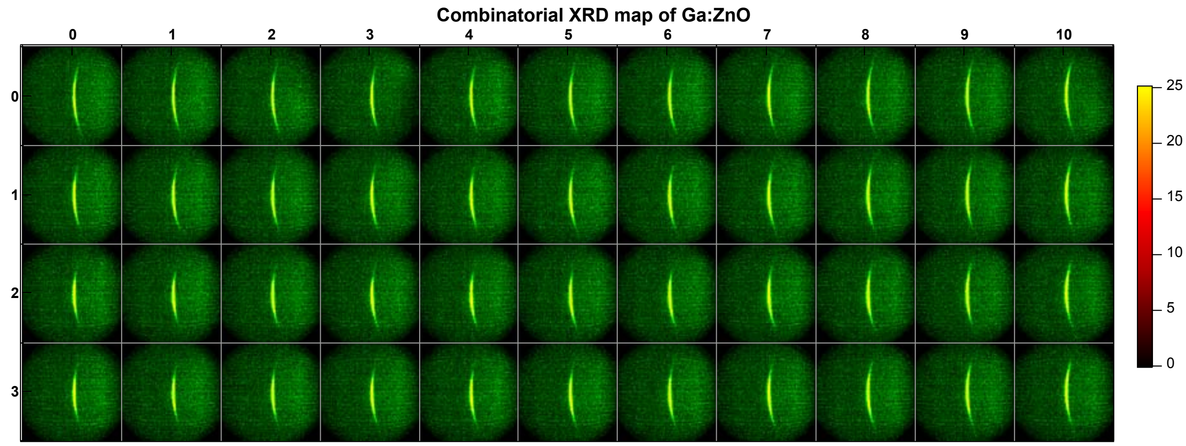


Figure 1: Combinatorial x-ray diffraction map of Ga:ZnO deposited at room temperature. Each frame on the figure displays a two-dimensional x-ray pattern with the horizontal axis spanning 2θ (20 to 50 degrees) and the vertical axis corresponding to χ (-15 to 15 degrees) axis. The color scale indicates the x-ray intensity in arbitrary units. Frames are taken across 2”x2” library at 11 spots (columns) sampled along the Ga gradient and 4 spots (rows) examined perpendicular to the Ga compositional gradient.

determined from calibration depositions and *ex-situ* optical measurements permit the determination of the resistivity/conductivity of the libraries at various locations across the compositional gradient.

In addition to room temperature depositions we have also done preliminary depositions of Ga:ZnO libraries at elevated substrate temperatures. The XRD from these samples is similar to the room temperature depositions in that all display the ZnO (200) peak and texturing characteristic of ZnO, Conductivity data from the center row of several libraries deposited at a range of elevated substrate temperature are shown in Figure 3. In addition to the electrical properties the libraries have optical transparency T>80% in the visible spectral range (data not shown). This data indicates that conductivity is a function of not only the composition but also closely related to the deposition temperature. A more complete analysis of the complex relationship between XRD, conductivity, transparency, Ga content and sputtering atmosphere is ongoing.

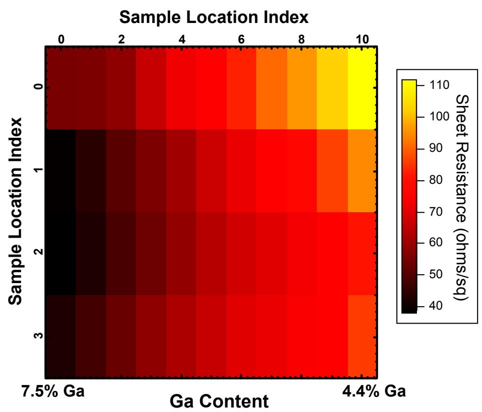


Figure 2: Map of sheet resistance verses sample position for a Ga:ZnO combinatorial library (same sample as Figure 1). Data for 11 sample locations (columns) along the compositional gradient and 4 sample locations perpendicular to the gradient were taken, and are correlated with the frames shown in Figure 1.

Ga:ZnO by Pulsed Laser Deposition

In parallel to the combinatorial studies we have also examined single composition GZO samples deposited by pulsed laser deposition (PLD). The single composition PLD films are deposited on glass substrates using a KrF

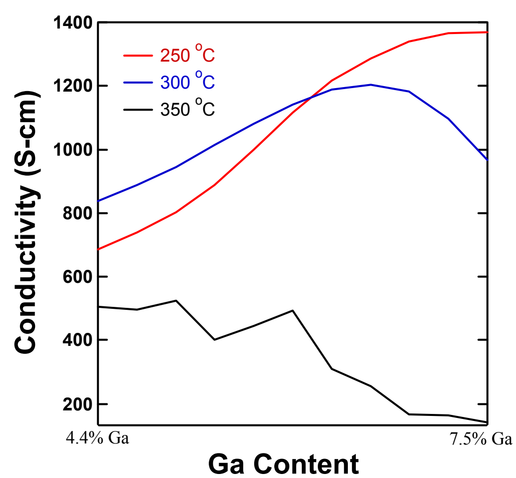


Figure 3: Conductivity across several Ga:ZnO compositional libraries at substrate temperatures ranging from 250 to 350 °C.

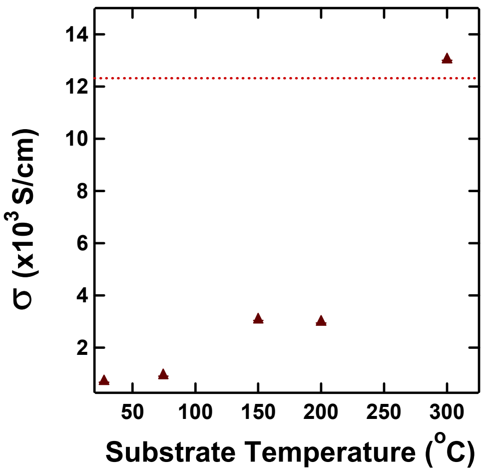


Figure 4: Conductivity for Ga:ZnO (2 at.% Ga) deposited on glass using pulsed laser deposition as a function of substrate temperature. Dashed red line indicates values reported in the literature by Park *et al [4].*

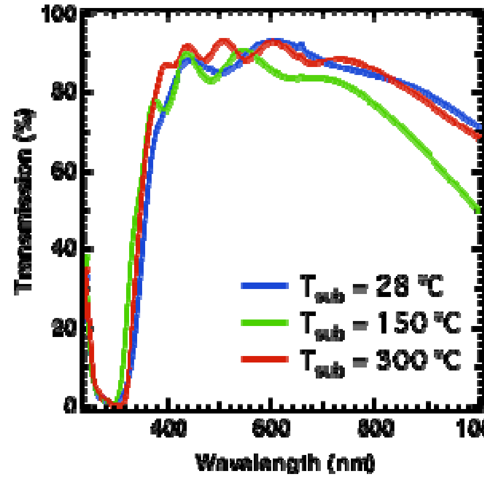


Figure 5: Optical transmission data for Ga:ZnO (2 at.% Ga) films and glass substrates. Inset shows image of Ga:ZnO deposited at 300 °C.

laser with an operational wavelength of 242 nm and single composition ceramic targets. A base pressure of <1.0×10^{-7} was obtained prior to deposition in a 1.1×10^{-3} O_2 atmosphere. The experiments employed a 280 mJ pulse energy to deliver an energy density to the target of approximately 0.76 J/cm^2 after optical losses. At a composition of ≈2 a.t.% Ga we examined a set of films deposited over a range of substrate temperatures. The results from this study are summarized in Figure 4. A substrate temperature of 300 °C resulted in a state of the art Ga:ZnO film with transport properties equivalent to the best results reported, with a conductivity in excess of 12000 S/cm and transparency of greater than 85% in the visible.[4] The transmission data for the combination of the glass substrate with GZO films is shown in Figure 5 along with an inset picture of the film deposited at 300 °C. In addition to the 2 a.t.% Ga target films were also deposited using targets of nominally 5 and 8 a.t. % Ga. The depositions from these targest where prefomed in a 1.1×10^{-3} torr O_2 atmosphere at a subsubstrate temperature of 300 °C. The resulting films had resonable transport (σ > 3000 S/cm) and optical properties (T>80% in the visible). The carrier concentration of these films was lower than that of the 2 a.t% Ga films and indicates that careful O_2 tuning may be required to optimize the TCO properties.

CONCLUSIONS AND FUTURE DIRECTIONS

The PLD based Ga:ZnO material clearly demonstrates the promises of this material as a high performance transparent contact. The effectiveness of PLD based Ga:ZnO materials as an indium tin oxide replacement in organic light emitting diodes has already been demonstrated.[5] In addition we are preparing experiments to examine the performance of Ga:ZnO in organic photovoltatic devices. Despite the success of the PLD material, the combinatorial libraries have, to date, not produced material with performance characteristics to rival traditional indium based TCOs although there are promising reports in the literature.[6] However, the studies reported here span only a modest range of temperatures and compositions. We are currently continuing with our combinatorial investigations to examine the correlation between the Ga at.% and the basic properties of sputtered Ga:ZnO. Device studies based on these combinatorial studies are also ongoing.

REFERENCES

[1] Yoon et al. Solid solubility limits of Ga and Al in ZnO. Journal of Materials Science Letters (2002) vol. 21 pp. 1703-1704

[2] Gu et al. Highly transparent and conductive Zn0. 85Mg0. 15O: Al thin films prepared by pulsed laser deposition. Solar Energy Materials and Solar Cells (2007)

[3] Ogawa et al. Blue Luminescence of MgZnO and CdZnO Films Deposited at Low Temperatures. Journal of The Electrochemical Society (2007) vol. 154 (9) pp. J283-J288

[4] Park et al. Effects of substrate temperature on the properties of Ga-doped ZnO by pulsed laser deposition. Thin Solid Films (2006) vol. 513 pp. 90-94

[5] Berry et al. Organic light emitting diodes using a Ga:ZnO anode. Accepted for publication in Applied Physics Letters

[6] Kim et al. Heat generation properties of Ga doped ZnO thin films prepared by rf-magnetron sputtering for transparent heaters. Thin Solid Films (2008) vol. 516 (7) pp. 1330-1333

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
May 2008

2. REPORT TYPE
Conference Paper

3. DATES COVERED *(From - To)*
11-16 May 2008

4. TITLE AND SUBTITLE
Transparent Conducting Contacts Based on Zinc Oxide Substitutionally Doped with Gallium: Preprint

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
C.W. Gorrie, M. Reese, J.D. Perkins, J.L. Alleman, M.S. Dabney, B. To, D.S. Ginley, and J.J. Berry

5d. PROJECT NUMBER
NREL/CP-520-42570

5e. TASK NUMBER
PVA74201

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401-3393
University of Florida, Gainesville, Florida 32611

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-42570

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES

14. ABSTRACT *(Maximum 200 Words)*
We have employed a high-throughput combinatorial approach to explore a range of Ga doping levels from ≈2-7.5 at% gallium in materials sputtered from ceramic oxide targets on glass substrates. Using our combinatorial approach this compositional spread is examined over a range of substrate temperatures and sputtering atmospheres. Structural, optical, and electrical analysis is then performed using our suite of combinatorial characterization tools. In parallel we have used pulsed laser deposition (PLD) from ceramic targets to produce state of the art Ga:ZnO films on glass at a variety of substrate temperatures for comparison to our combinatorial studies. Our best PLD materials were deposited at a nominal substrate temperature of 300 ^{o}C and resulted in a film with a resistivity of 7.7×10^{-5} Ω·cm and transparency in excess of 85% in the visible.

15. SUBJECT TERMS
PV; transparent conducting oxides; gallium; pulsed laser deposition; substrate; organic photovoltaics; combinatorial approach;

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES
Unclassified	Unclassified	Unclassified	UL	

19a. NAME OF RESPONSIBLE PERSON

19b. TELEPHONE NUMBER (*Include area code*)

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

F1147-E(09/2007)