Susan Huang received a B.S. in Physics from McGill University in 2003. She is currently in her first year of graduate studies at SUNY Albany's College of Nanoscale Science and Engineering, where she is researching organic solar cells. During her SULI internship at NREL, she developed a passion for renewable energy and hopes to establish a career developing and implementing renewable energy technologies.

David S. Ginley is currently a Group Manager in Process Technology and Advanced Concepts at the National Renewable Energy Laboratory, leading activities in the applications of nanotechnology, organic electronics, transition metal oxides (ferroelectric materials, rechargeable Li batteries, and transparent conductors) and ink jet printing. He leads a team in the development of nanoparticle-based precursors to electronic materials, particularly as they apply to photovoltaic and optoelectronic technologies. Recent new activities include a program on combinatorial approaches to electronic materials and a program on polymer based photovoltaic cells and OLEDs. Over the past 25 years, he has been active in developing a basic understanding of the relationships between structure and the optoelectronic properties in a variety of materials. Dr. Ginley graduated from the Colorado School of Mines with a B.S. degree in Mineral Engineering Chemistry. He subsequently received a Ph.D. from MIT in inorganic chemistry, where he worked in inorganic photochemistry and in the emerging area of photoelectrochemistry.

Alex Miedaner joined SERI in 1982 and is at present a Staff Chemist in the Center for Basic Sciences at NREL. His primary research involves the synthesis and characterization of nanostructured materials for energy conversion applications, the development and formulation of organometallic and nano particulate inks for direct write ink jet printing of various metals at mild temperatures, the preparation of precursor materials in spin coating and spray deposition of transparent conducting oxides, and chemical synthesis of organometallic transition metal compounds used for electrocatalysis and thermodynamic studies. He is interested in organometallic synthesis involving highly reactive and oxygen sensitive intermediates and heterogeneous reactions involving hydrothermal synthesis at elevated temperatures and pressures.

Tatiana Kaydanova graduated from Russian St. Petersburg Technical University with a M.S. in applied physics with emphasis on Solid State Physics and semiconductor devices in 1993. The topic of her thesis research was magnetic properties of high temperature superconducting YBCO ceramics. From 1995 to 1998 she worked as a scientist at Superconductor Core Technologies (Denver,CO) developing Pulsed Laser Deposition of superconducting and ferroelectric thin films and cleanroom processes for fabrication thin film microwave devices used in telecommunication applications. She has been employed at National Renewable Energy Laboratory (NREL) since 1998. At present Tatiana is a senior scientist and a member of Process Technology and Advanced Concepts group. Her research interests are in the areas of thin film optoelectronic oxide materials and direct write atmospheric approaches to fabrication of photovoltaic and other electronic devices. Currently Tatiana specializes in pulsed laser deposition, inkjet printing, structural material analysis and cleanroom semiconductor device fabrication processes.

CONDUCTING AND OPTICAL PROPERTIES OF TRANSPARENT CONDUCTING INDIUM-DOPED ZINC OXIDE THIN FILMS BY SOL-GEL PROCESSING

SUSAN HUANG, TATIANA KAYDANOVA, ALEX MIEDANER, DAVID S. GINLEY

ABSTRACT

Transparent conducting oxides were successfully prepared from mixed zinc nitrate hexahydrate and indium nitrate hydrate solutions in ethylene glycol using sol-gel technique. The In content in the film was varied (0, 2, 10, 20, 40, 75 and 100 atom %). Films were prepared by spin coating of the liquid precursors followed by thermal decomposition at 400° C after each layer. According to X-ray diffraction (XRD) measurements, the pure ZnO and pure InO films (0 and at 100 % In) were crystalline as-deposited. The crystallinity was suppressed in mixed compositions such that the films with compositions between 10 and 75 at % were amorphous. All the films were transparent with the transmission cut-off frequency near 400 nm, which is characteristic of TCO materials. All as-deposited films were conductive with 0 and 100 atom % In having the lowest resistivities. The resistivity of all compositions were improved by post-deposition reducing anneal in pure Ar at 300° C. The lowest resistivity of 0.2 Ωcm was obtained for the pure ZnO after Ar anneal. It was two-orders of magnitude higher than reported in the literature for the In-doped ZnO, which was attributed to the low processing temperature. The resistivities of as-deposited and annealed in Ar films were increased by consequent air anneal at 300° C.

INTRODUCTION

Transparent conducting oxides (TCO) have many applications based on their electro-optical properties. They are used in flat panel screens, laptop screens and solar cells, in electrochromic windows that respond to increasing sunlight by becoming darker, in oven windows and energy-efficient windows that keep buildings cool in the summer and trap heat inside during winter.

Achieving high electrical conductivity and good optical transmission in TCO materials is crucial for most applications. Other important parameters that determine the usefulness of TCOs are environmental stability, production cost, and processing compatibility with other device elements [1][2].

The TCOs that have already been largely investigated and used in the industry are zinc oxide (ZnO) and indium tin oxide (ITO). While ITO is easy to process and demonstrates excellent conducting and optical properties, there is a concern that scarce sources of In will not satisfy the industrial demands. In the recent years, this has stimulated the development of new TCO materials including doped ZnO.

Aluminum and indium doped ZnO [3][4] are of interest because doping improves conductivity of ZnO thin films. Most of the research to date has been focused on doping with < 5 atom %. ZnO and doped ZnO thin films have been prepared by sputtering [5], spray pyrolysis [6], and sol-gel [7] process. Developing sol-gel preparation is desirable because it is a low cost atmospheric process easily adaptable to industrial use. In sol-gel, thin films are formed from cross-linked liquid chemical precursors by spin-coating, drop-coating or dip-coating the substrate followed by thermal decomposition [8]. In this work, we investigated electrical and optical properties of indium-doped zinc oxide (IZO) thin films with a large range of In content variation (2-75%) prepared by low-temperature sol-gel method. The goal of the research was to find optimal compositions for best electrical and optical performance and to understand the effect of microstructure on conducting and optical properties of the material.

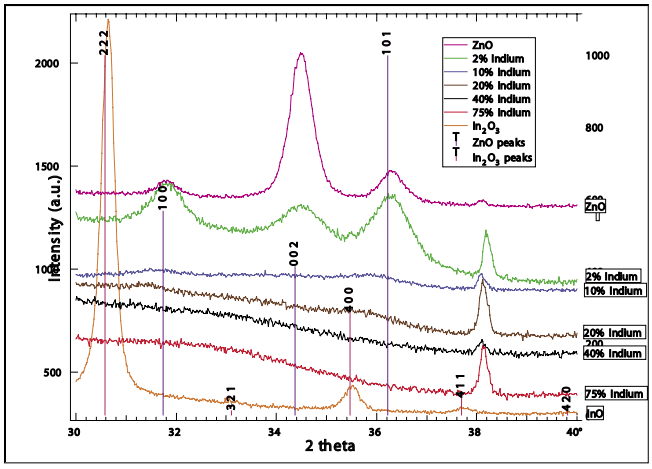

Figure 1. X-ray diffraction patterns of the ZnO films with various amounts of In doping.

METHODS AND MATERIALS

A variety of metal salts including zinc acetate dihydrate, zinc nitrate hexahydrate, indium acetate hydrate and indium nitrate hydrate in a variety of solvents including water, 2-propanol, acetic acid, ethylene glycol and ethanol were evaluated as precursors for spin-coated thin IZO films. The best film quality with respect to film uniformity and optical transparency were achieved using solutions of zinc nitrate hexahydrate and indium nitrate hydrate in ethylene glycol. These starting materials then were used in all consequent film preparations. Equimolar solutions of indium nitrate hydrate (1 g in 3 ml of ethylene glycol) and zinc nitrate hexahydrate (1 g in 3 ml of ethylene glycol) were prepared and mixed in the following ratios (by volume): 0, 2, 10, 20, 40, 55, 75 and

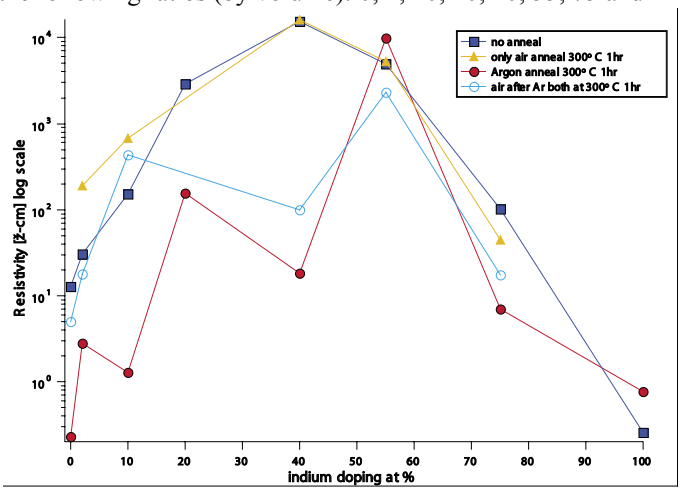

Figure 2. Resistivity measurements of the films under different annealing conditions.

100 atom %. The resulting clear solutions were aged at room temperature for a period of time ranging from one day to a week prior to use in order to allow for formation of the sol. As a result of the formation of the sol the viscosity of the aged solutions increased with time. Generally, solutions that had been aged for 2 days made the most uniform and transparent films. Solutions aged for shorter or longer periods of time were respectively not viscous enough or too viscous to produce even coatings by this approach.

The films were deposited on 1737 glass substrates using a spin coater. The substrates were spun at 3,000 rpm while a solution was dropped from a pipette onto a substrate. Each substrate was spun for a total of 30 s. The films were then heat-treated in a box oven in air at 400° C for 10 min in order to decompose the precursor components and form metaloxides. The decomposition temperature of both zinc nitrate and indium nitrate precursor was found from TGA (thermogravimetric analysis) of the precursor powders. The films were formed by consequent spin-coating and baking of 10 layers of the precursor solution resulting in overall thickness of 2500Å±500Å. Two sets of films of each composition (In content) were thus prepared.

As-deposited films were characterized by XRD in order to determine the phase content and the crystalline orientation of the films. Thickness of the films was measured by a DekTak profilometer. Electrical resistivity measurements were conducted using a Hall probe. Optical transmission measurements were made using a fiber-optic based spectrometer. AFM scans were performed on the films to evaluate the surface morphology.

After this initial characterization, one set of films was annealed in air at 300° C for 1 hour, while the second set was annealed in Argon at 300° C for 1 hr. The resistivity of the films after annealing was remeasured. Then the films annealed in Ar were annealed again in air at 300° C for 1 hour and their resistivities were characterized.

RESULTS

XRD results

The X-ray diffraction patterns of the as-deposited films are shown in Fig. 1. The film with 0% In content shows peaks that correlate to ZnO peaks indicating that the film is crystalline. The strongest peak corresponds to the (002) ZnO orientation indicating preferential orientation in (001) direction. The crystalline ZnO peaks can also been seen in the 2 at % In film although they are broader and weaker in intensity suggesting that crystallinity is being suppressed. For indium substitution of 10, 20, 40 and 75 at %, the films appear to be amorphous with no distinctive peaks except for the peak at ~ 39 º coming from the Aluminum sample holder while the film containing no zinc had an XRD signature corresponding to randomly oriented crystalline In_2O_3.

Electrical conductivity results

The dependence of resistivity on the amount of indium content of the films before and after post-deposition heat-treatments is presented in Fig. 2. In all cases, for as-deposited films, annealed in Ar and in air, the films with 0% and 100% In had the best conductivities of a set. The lowest resistivity

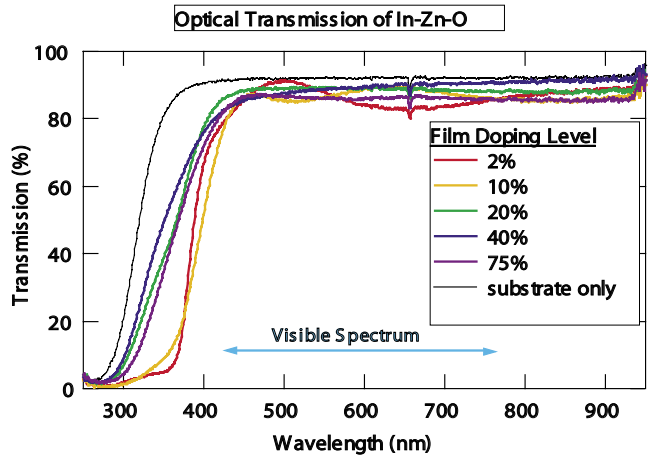

Figure 3. Optical transmission spectra for the thin films

of 0.2 Ωcm corresponded to pure ZnO film annealed in Ar. In as-deposited films the resistivity increases monotonically with the In content, reaches the maximum of 15300 Ωcm at 40 at % of In and then monotonically decreases with further increase of the In content.

The resistivity of the films annealed in air at 300° C for 1 hr increased for the 2-20 at % In films. The 20 at % is not represented on the graph because it acted as an insulator and the

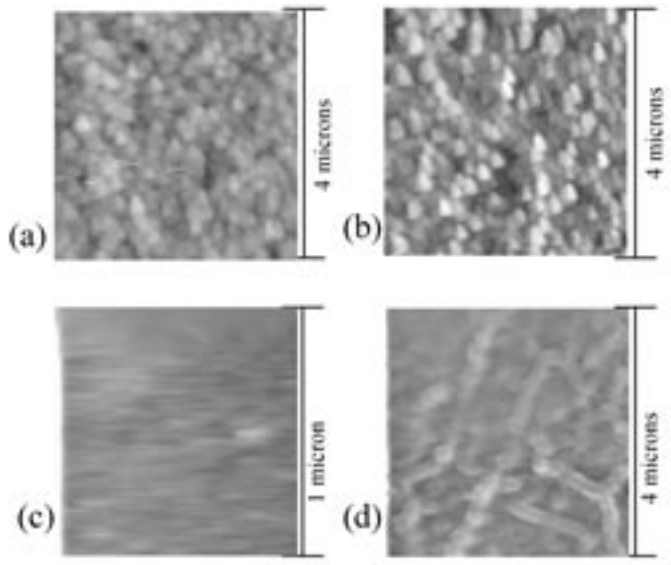

Figure 4. AFM images of (a) the 0 at %, (b) the 2 at %, (c) the 10-75 at % and (d) the 100 at % indium doping. Scans (a), (b) and (d) are 4 microns and (c) are 1 micron.

resistivity could not be measured. The resistivity of the 40 and 55 at % films were not affected by the air anneal and the resistivity of the 75% film slightly dropped. For the films annealed in argon at 300° C for 1 hr the resistivity decreased in all cases except for the 55 at % and pure In_2O_3 for which the resistivity slightly increased. The resistivities again increased by following anneal in air. In all cases for as-deposited and annealed films the pure ZnO and In_2O_3 had the lowest resistivity. Generally, the lowest resistivity found for the films was 100 times higher than those previously found in literature for In-doped ZnO by sol-gel [9]. The films reported in the literature however were fabricated using a higher annealing temperature.

Optical measurement Results

The optical transmission of the as-deposited films is shown in Fig. 3.

In the wavelength range between 425–900 nm, the films had high (more than 80%) transmission. The decrease in transmission at 400 nm is characteristic of TCO material.

AFM scans

The AFM images of the as-deposited films are shown in Fig. 4. The pure ZnO, 2 at % In and pure In_2O_3 films have granular structures. The films of 10-75 % compositions all had

smooth surfaces with no distinct features. This agrees with the XRD data that indicates the ZnO, In_2O_3 and 2 at % films are polycrystalline and the rest of the films are amorphous

DISCUSSION

We used mixed composition solutions of In and Zn precursors for film deposition to explore the tie line between In_2O_3 and ZnO. It was anticipated that good TCOs could be made across the compositional range [10]. This represents a new exploration of phase space and not simply a doping study. Very little is known of the range of compositions from 10 to 90% In. The structure across the composition variation was expected to be complex with representative crystalline, amorphous and superlattice ranges. In this study we found that for all mixed compositions of In and Zn including the 2% In-doped film generally higher resistivities than the best published results were obtained [9], [10]. Higher resistivities in our study could result from non-homogeneity of precursor decomposition or non-optimized annealing. At this early stage it is impossible to tell if phase separation is occurring even at the low 2% substitution level. The preliminary data collected in the experiments described above is not sufficient to explain the increased resistivity observed for the films with mixed compositions. In fact a recent combinatorial study using sputtered films shows a minumum in resistivity near 70% In [11]. The observed changes in resistivity may be a reflection of the need for additional annealing and may be a consequence of reduced crystallinity, which is supported by XRD and AFM. It has been previously demonstrated [12] that the mobility can be significantly lower in the amorphous materials than in the crystalline due to enhanced carrier scattering on structural defects resulting in higher resistivity for amorphous materials. The improvement in conductivity after a reducing Ar anneal for most compositions and the fact that it was reversed during air annealing suggests that the increase in conductivity for these films was caused by oxygen vacancies/cation interstitials rather than structural direct improvement.

The more dramatic drop of resistivity in mixed compositions (especially 40% film) may indicate that it was easier to create defects in the amorphous films of mixed compositions rather than in pure crystalline films resulting in a more dramatic increase of carrier concentration for the amorphous films. For future work, we plan to fabricate Van der Pauw patterns on our IZO samples in order to perform reliable Hall measurements so as to directly measure carrier concentration and the mobility of each compositions as-deposited and after anneals.

CONCLUSIONS

In-doped ZnO thin films were successfully made using the sol-gel method. The XRD data shows the pure films to have a crystalline structure while the mixed composition films were amorphous. It was found that generally the undoped pure ZnO and In_2O_3 had the lowest resistivities of the films made. The optical data demonstrates the high transmission properties of all of the films. The AFM scans supported the XRD data in that the 0 and 100 at % films were clearly crystalline in structure. It is possible that reduced mobility can result from crystalline – amorphous transition in thin films of mixed compositions producing higher resistivity materials, however at this point there is no clear experimental evidence in support of this speculation. It seems that although it is possible to produce IZO thin films using the sol-gel method, the low processing temperatures results in rather high resistivities. Future work will focus on different temperatures and times for post-heat-treatment to see the effects on the structural and electro-optical properties.

ACKNOWLEDGEMENTS

I would like to thank the Department of Energy Office of Science for allowing me to participate in the SULI program at NREL and the NREL Office of Education for putting together such an excellent program. Special thanks are due to Alex Miedaner for his endless encouragement and my mentor Tanya Kaydanova for her support and wisdom. I would also like to thank Banasri Roy, Maikel van Hest, Charles Teplin and rest of the NREL TCO team for generously offering their help.