

Thursday Afternoon, October 21, 2010

Energy Frontiers Topical Conference

Room: Mesilla - Session EN+SS+TF-ThA

Transparent Conductors

Moderator: S. Gupta, University of Alabama

2:00pm EN+SS+TF-ThA1 **Synthesis of ZnO:F by DC Reactive Magnetron Sputtering**, X. Noirfalise, University of Mons, Belgium, T. Godfroid, Materia Nova, Belgium, G. Guisbiers, IEMN Lille, France, R. Snyders, University of Mons, Belgium

Nowadays, numerous applications in the electronics and/or optoelectronics field need transparent thin films presenting a good electrical conductivity. The transparent conductive oxides (TCO) which reveal a large band gap and a good electrical conductivity fulfil these requirements. Recently, due to the significant increase of the demand, the prize of the most employed TCO, namely indium tin oxide (ITO) has strongly increased. Therefore, an alternative to this material becomes necessary. Among all the candidates, ZnO:F and Cd₂SnO₄ present the best performance in term of transparency and electrical conductivity. For obvious environmental reasons the latter cannot be considered. Therefore, ZnO:F is identified as the best candidate to replace ITO in TCO applications.

The most employed techniques for the synthesis of ZnO:F are Chemical Vapor Deposition and Spray Pyrolysis which both require organometallic precursor and high temperature processing. Another drawback of these technologies is the low chemical purity of the synthesized films because of the presence of the precursor decomposition products. At the contrary, reactive magnetron sputtering is an environmentally friendly technology allowing the synthesis of thin films with very fine control of the chemistry. Therefore, the aim of this works is to study the reactive magnetron sputtering of ZnO:F.

Thin films were prepared by DC reactive sputtering using a zinc target in an Ar/O₂/F₂ mixture. In a first attempts, ZnO films have been synthesized in order to optimize the matrix properties in terms of crystallinity and transparency. The studied parameters were the DC power (P_{DC}), the total pressure (P_{Tot}) and the O₂ flow (f_{O2}). Our data reveal that the ZnO films presenting the best features are prepared for P_{DC} = 70 W, P_{Tot} = 30 mTorr and f_{O2} = 3 sccm.

The second step was to introduce fluorine in this matrix. Therefore, we have studied the crystallographic, chemical, electrical and optical properties of the deposited films as a function of the fluorine content. In our deposition window, all films present a high transmission in the visible (> 80%). Our XRD data reveal decrease of the crystallite size with the increase of the fluorine content. Above a fluorine concentration of 2-3%, the ZnO:F crystallinity decreases. Our XPS and XRD data suggest that F atoms substitute O atoms in the ZnO structure. Finally, the electrical properties have been investigated by Hall effect measurements. For the optimal synthesis conditions (~ 2% of fluorine in the film), a charge carrier density of ~ 10²⁰ cm⁻³, an electrical resistivity of 10⁻² Ω.cm and charge mobility of about 4 cm²/V.sec have been measured.

2:20pm EN+SS+TF-ThA2 **Relationship Between Resistivity Stability and Structure of Transparent Conducting Impurity-doped ZnO Thin Films**, J.-I. Nomoto, T. Hirano, T. Miyata, O. Ueda, T. Minami, Kanazawa Institute of Technology, Japan

Recently reported results show that the resistivity stability for moisture-resistance and heat-resistance tests in transparent conducting impurity-doped ZnO thin films prepared on low temperature glass substrates is considerably affected by the film thickness as well as the kind and content of doped impurity. In this paper, we discuss the relationship between the obtainable resistivity stability and the structure in Al-, Ga- and B-doped ZnO (AZO, GZO and BZO) thin films prepared with a thickness in the range from 30 to 3000 nm by various deposition methods. Transparent conducting AZO, GZO and BZO thin films were prepared on glass substrates at 200°C by dc or rf magnetron sputtering, vacuum arc plasma evaporation and pulsed laser depositions. The resulting film structures were evaluated using a scanning electron microscope (SEM), an atomic force microscope (AFM) and a transmission electron microscope (TEM). The surface morphology of the impurity-doped ZnO films was found to change significantly after exposure to a highly moist environment (air at 85% relative humidity and 85°C) for 1000 h, as evidenced from AFM and SEM images; although the resistivity stability in these tests tended to improve with increasing impurity-doped ZnO thin film thickness, the effect was considerably dependent on the kind of doped impurity. In contrast, the surface morphology changed only slightly even after exposure to an oxidizing atmosphere (air at a temperature of 200°C) for 1000 h. The

resistivity stability in the heat-resistance tests was found to depend significantly on whether the testing temperature was lower or higher than approximately 300°C. The amount of resistivity increase in the moisture-resistance and heat-resistance tests was found to correlate with the structure of the impurity-doped ZnO thin films, as evidenced from TEM images. The variation exhibited in the resistivity stability in these resistance tests is mainly attributed to micro-structural differences associated with the crystallinity of the deposited impurity-doped ZnO thin films.

2:40pm EN+SS+TF-ThA3 **Bulk and Surface Physics of Indium Oxide Thin Films Grown on Cubic Zirconia by O-plasma Assisted Molecular Beam Epitaxy**, R.G. Egdell, University of Oxford, UK **INVITED**

Tin doped indium oxide (In₂O₃) aka ITO is one of the most important transparent conducting oxides, yet it is only recently that many fundamental aspects the bulk and surface physics of indium oxide itself and of ITO have been addressed [1-3]. We have an ongoing programme concerned with growth of In₂O₃ on Y-stabilised ZrO₂ by oxygen plasma assisted molecular beam epitaxy and will review our most recent work in this area. Issues that will be addressed include the following:

The influence of surface energies and strain on the growth of In₂O₃ on low index zirconia surfaces. Mechanisms for relief of strain, including crystallographic tilting and development of nanostructures during high temperature MBE growth.

The influence of strain on the optical properties of ultrathin In₂O₃ films.

Surface structure and surface physics of In₂O₃ and ITO surfaces, including development of electron accumulation layers for material with low bulk doping levels.

References

- 1 P D C King *et al.*, Physical Review Letters 2008 **101** 116808
- 2 A Walsh *et al.*, Physical Review Letters 2008 **100** 167402/1-4
- 3 K H L Zhang *et al.*, Chemistry of Materials 2009 **21** 4353-4355

3:40pm EN+SS+TF-ThA6 **Recent Developments in Transparent Conducting Oxides for Thin-Film Solar Cells**, J. Burst, M. Scott, T. Gessert, National Renewable Energy Laboratory, S. Weiss, B. Rogers, Vanderbilt University, T. Coutts, Timothy J. Coutts Consulting, Inc

Transparent conducting oxides (TCOs) are utilized in all thin-film solar cells. Their function is to reduce electrical losses associated with collection of photogenerated current. However, they exhibit optical and electrical losses of their own and many researchers have tried to reduce these losses either by adjusting deposition conditions, post-deposition annealing, or by using completely novel materials. In our own work, we have shown that it is important to develop TCOs with high free-carrier mobility rather than high concentrations, which causes increased optical losses. Our latest results suggest significant gains in the performance of thin-film solar cells may be made via relatively minimal changes to the TCOs.

We have shown that the properties of transparent conducting oxides (TCOs) can be improved by doping them with approximately 1 atomic % cations whose oxides exhibit high dielectric permittivity. Our experiments have shown that TCOs doped with "high permittivity" cations have increased permittivity compared to the undoped TCO. Also, for similar carrier concentrations and mobilities, the doped TCOs have free-carrier absorption bands shifted to longer wavelengths (1500 nm doped v. 1300 nm undoped), thereby reducing optical losses compared to the undoped TCO. These observations are consistent with predictions based on the Drude free-electron model. In addition, there is evidence that the increased permittivity helps screen scattering centers, thereby leading to enhanced mobility. We will demonstrate that increasing film permittivity reduces optical losses in several standard TCO materials (ZnO, SnO₂, and In₂O₃). Film resistivity as low as 6x10⁻⁵ Ω.cm (corresponding to a sheet resistance of about 1 Ω/ sq for a film 500 nm thick) has been achieved without compromising the high optical transmittance. The study has also indicated that TCO films with additions that alter permittivity appear to be less sensitive to variation in deposition ambient and temperature. Although this insight will clearly assist development of future TCO materials, we believe the results are even more relevant to present TCOs that may embody industrial advantages but remain limited by low mobility. *This abstract is subject to government rights.*

4:00pm EN+SS+TF-ThA7 **The Study of AZO/Au/AZO as a Transparent Electrode for Organic Light Emitting Diodes**, J.H. Park, Hanyang University, Republic of Korea

Transparent conducting oxide (TCO) thin films and coatings are an important and integral part of a number of electro optical devices because TCOs play an important role as transparent electrodes for flexible

optoelectronic devices such as liquid crystal displays, solar cell panels, and organic light emitting devices (OLEDs). Typical TCOs are impurity-doped indium oxides, tin oxides and zinc oxides that offer commercially acceptable performance in terms of conductivity transmittance, environmental stability, reproducibility and surface morphology. The Al-doped ZnO (AZO) films show low resistance and high transmittance in the visible range of the spectrum. However, their resistivity is rather high in some cases to adapt as a transparent electrode for advanced applications. Recently, in order to improve properties of TCO, thin metal or metal alloy film was embedded between TCO layers. In this study, we will discuss the effect of Au middle layer thickness on the electrical and optical properties of the multilayer TCOs and OLED applications. The AZO films were deposited on Corning Eagle 2000 glass substrates by atomic layer deposition (ALD). The optimization conditions of AZO films were 1/19 ratio of TMA/DEZ and 180°C. And Au middle layer was deposited by e-beam evaporator. The AZO/Au/AZO films exhibit better electrical properties compared to the AZO films. The carrier concentration was increased from 1.9×10^{20} to $5.8 \times 10^{20} \text{ Cm}^{-3}$. The mobility was decreased from 12.6 to 12.4 Cm^2/Vs . The resistivity was decreased from 2.6×10^{-3} to $8.5 \times 10^{-4} \Omega \text{ Cm}$. However transmittance was decreased from 91 to 76 %, on average. The AZO/Au/AZO films were used as anode electrodes for red emission OLED application. The device showed that a maximum luminance of $2.4 \times 10^3 \text{ cd/m}^2$ at 11 voltage. More detailed electrical and physical results will be discussed and presented.

4:20pm **EN+SS+TF-ThA8 Origin of the Distribution of Electrical Properties of ITO Sputtered Films on Substrate, Y. Hoshi, Y. Yasuda, Tokyo Polytechnic University, Japan, H. Shimizu, Niigata University, Japan**
The ITO films deposited by magnetron sputtering and facing target sputtering at low substrate temperature have quite different distributions of film properties. However, their origin was still not clear. In this paper, we clarify the origin of the different distributions between the sputtering methods, and will propose a sputtering method to deposit the ITO films with good uniformity.

In the deposition of ITO films by a conventional planar magnetron sputtering, the films deposited at the center of the substrate have higher oxygen content than the films deposited at the end of the substrate. It should be noted that the film deposited by a facing target sputtering has much lower oxygen content than the films deposited by conventional planar magnetron sputtering. As a result, the ITO films with poor transparency were always obtained by the sputtering in pure Ar gas, when a Facing Target Sputtering system was used.

These phenomena can be explained by the following model; When sputter-deposition of ITO films was performed at a low temperature, only oxygen atoms produced by the sputter-emission from the target surface promote the oxidation of indium atoms on the film surface. In other words, oxygen molecules cannot oxidize the indium atoms at a low temperature.

In addition, oxygen atoms sputter-emitted from the target have different angular distributions than indium atoms have. That is, the emission ratio of oxygen atoms to indium atoms sputter-emitted from the target surface changes depending on the emission angle and gradually decreases with an increase of the emission angle. This phenomenon mainly causes the distribution of the properties of ITO films on the substrate, although bombardment of high energy negative oxygen ions also affects the distribution of film properties in planar magnetron sputtering.

In order to deposit uniform film on the substrate, compensation of the angular distribution in the emission ratio of oxygen atoms to indium atoms is necessary. Use of two sputtering sources arranged like a facing target sputtering system is one of the solutions to compensate the distribution and obtain the films with more excellent uniformity.

4:40pm **EN+SS+TF-ThA9 Deposition of Al-doped ZnO by Atomic Layer Deposition Using Ozone as the Oxygen Source, W.L. Gladfelter, H. Yuan, B. Luo, S.A. Campbell, University of Minnesota**

Transparent conducting oxide (TCO) films are used in many photovoltaic and optoelectronic devices. The need to deposit conformal films at relatively low temperature has raised interest in atomic layer deposition (ALD). Literature reports establish that n-doped zinc oxide has been deposited by ALD using water as the source of oxygen and aluminum or gallium as the dopant. The interest in replacing water with ozone has led to many new ALD routes to metal oxide films, including ZnO. In this presentation we will describe an effective ALD route to Al-doped ZnO. Aluminum-doped ZnO (AZO) films were grown on Si and SiO₂/Si substrates in the temperature range from 150 - 300°C using diethylzinc as the zinc precursor and ozone as the oxygen source. Trimethylaluminum was used as the aluminum precursor. Two approaches to doping were studied. In one a nanolaminate was formed by interspersing a trimethylaluminum/ozone cycle in between the diethylzinc/ozone cycles. The overall aluminum concentration depended on the number of

diethylzinc/ozone cycles. The second approach involved co-injection of both metal precursors in which their relative concentrations were controlled by adjusting the precursor vessel temperature. The influence of the deposition method on the composition, structural, electrical, and optical properties of the AZO films as a function of doping metal concentration will be reported. X-ray diffraction patterns showed all the samples were polycrystalline and exhibited preferential (0001) orientation. The (0002) reflection for AZO films shifted in opposite directions depending on the deposition method. The carbon content of the films was below the detection limit of Auger electron spectrometry. The lowest resistivity ($6 \times 10^{-4} \Omega \cdot \text{cm}$) of the AZO films was obtained using the co-injection process. The average optical transmission was over 85 % in the range of 400-800 nm and the optical band gap increased with increasing doping in accordance with Burstein-Moss effect. The resistivity of AZO films grown by the co-injection method decreased to $3 \times 10^{-4} \Omega \cdot \text{cm}$ after rapid thermal annealing (RTA) in an Ar atmosphere.

5:00pm **EN+SS+TF-ThA10 Atomic Layer Deposited (ALD) Al-doped ZnO Films for Transparent Conductor Applications, P. Banerjee, University of Maryland, W.-J. Lee, G.-Y. Bae, Dong-Eui University, Republic of Korea, S.-B. Lee, G.W. Rubloff, University of Maryland**

Among various materials for thin film transparent conductor applications, Al-doped ZnO (AZO) is a particularly attractive material because of its excellent properties, such as higher thermal stability, good resistance against damage by hydrogen plasma and potentially, low cost compared to indium tin oxide (ITO). Of the various available deposition techniques, Atomic layer deposition (ALD) provides superb control at the nanoscale for thickness, uniformity, conformality and Al doping of AZO films. This is particularly attractive for use in nanostructures, as well as in more conventional applications such as liquid crystal displays.

We report here results for structural, optical and electrical properties of ultrathin ALD AZO films as a function of at% Al. AZO films of ~ 100nm thickness were deposited on quartz substrates at 150C using a commercial BENEQ TFS 500 reactor using diethyl zinc (DEZ) and H₂O as precursors for ZnO, and trimethyl aluminum (TMA) and H₂O as precursors for Al₂O₃. Al-doping was incorporated in a film by introducing a single cycle of TMA-H₂O after fixed cycles of DEZ-H₂O pulses. This 'super' cycle was repeated until the desired thickness was achieved. Al-doping was varied from 0.0at% to 24.5at%, on various samples, as determined by EDX. In addition, XRD, AFM, UV-Vis spectroscopy and temperature-dependent (80K-340K) Hall measurements were carried out to understand the structural, optical and electrical properties in these films.

Strong texture effects were observed in the AZO films on the quartz substrates as the films preferentially crystallized along the [100] direction. This texturing effect is different from the [002] normally reported for AZO films deposited using established methods other than ALD. Crystallinity and electrical conductivity peaked at 3at% Al, consistent with previous published work. AFM results show a dramatic drop in surface roughness with Al doping. Optical transmittances of over 80% were obtained for all films in the visible region.

Calculation of lattice parameter constants from XRD data and analysis within the framework of the Burstein-Moss effect, reveal that AZO films act as substitutionally doped films for Al doping less than ~7.3at%. Beyond this value of doping, phase segregation and possible formation of a low conductivity phase cause a reduction in the concentration and mobility of free carriers and hence a degradation of the electrical properties.

5:20pm **EN+SS+TF-ThA11 Silicon-Titanium Oxides as Transparent Conductors for Photovoltaic Applications, J. Chivers, T. Vandervelde, Tufts University**

We report on the use of Earth-abundant silicon-dioxide and titanium-dioxide as a transparent conducting oxide (TCO) and antireflective (AR) coating. TCOs are a critical component in modern photovoltaic devices, used as a front-side contact that won't block incident light. At present, many TCOs require rare-Earth materials (e.g. Indium), which is problematic for large-scale manufacturing. The abundant, well characterized materials used here can be integrated into an existing product line quickly and cheaply. The varied band gap and index of refraction conditions inherent in the SiTiO₂ system allow controlled variation of material properties during monolithic growth. Some TCOs may also act as an AR coating, further increasing light absorption. The ideal AR coating would gradually change from the index of refraction of air to that of the underlying semiconductor. Most AR coatings used today make this transition in a small number of steps, which limits their efficacy. In this work, we investigate deposition processes that slowly grade the index of refraction while maintaining conductivity and transparency.

Authors Index

Bold page numbers indicate the presenter

— B —

Bae, G.-Y.: EN+SS+TF-ThA10, 2
Banerjee, P.: EN+SS+TF-ThA10, **2**
Burst, J.: EN+SS+TF-ThA6, **1**

— C —

Campbell, S.A.: EN+SS+TF-ThA9, 2
Chivers, J.: EN+SS+TF-ThA11, **2**
Coutts, T.: EN+SS+TF-ThA6, 1

— E —

Egdell, R.G.: EN+SS+TF-ThA3, **1**

— G —

Gessert, T.: EN+SS+TF-ThA6, 1
Gladfelter, W.L.: EN+SS+TF-ThA9, **2**
Godfroid, T.: EN+SS+TF-ThA1, 1
Guisbiers, G.: EN+SS+TF-ThA1, 1

— H —

Hirano, T.: EN+SS+TF-ThA2, 1

Hoshi, Y.: EN+SS+TF-ThA8, 2

— L —

Lee, S.-B.: EN+SS+TF-ThA10, 2
Lee, W.-J.: EN+SS+TF-ThA10, 2
Luo, B.: EN+SS+TF-ThA9, 2

— M —

Minami, T.: EN+SS+TF-ThA2, 1
Miyata, T.: EN+SS+TF-ThA2, 1

— N —

Noirfalise, X.: EN+SS+TF-ThA1, 1
Nomoto, J.-I.: EN+SS+TF-ThA2, **1**

— P —

Park, J.H.: EN+SS+TF-ThA7, **1**

— R —

Rogers, B.: EN+SS+TF-ThA6, 1
Rubloff, G.W.: EN+SS+TF-ThA10, 2

— S —

Scott, M.: EN+SS+TF-ThA6, 1
Shimizu, H.: EN+SS+TF-ThA8, 2
Snyders, R.: EN+SS+TF-ThA1, **1**

— U —

Ueda, O.: EN+SS+TF-ThA2, 1

— V —

Vandervelde, T.: EN+SS+TF-ThA11, 2

— W —

Weiss, S.: EN+SS+TF-ThA6, 1

— Y —

Yasuda, Y.: EN+SS+TF-ThA8, 2
Yuan, H.: EN+SS+TF-ThA9, 2