Thin Film
Room 2022 - Session TF-WeM

Thin Films for Photovoltaics and Energy Applications

Moderator: J. Lewis, RTI

8:00am **TF-WeM1 Preparation of Transparent Conducting B-doped ZnO Films by Vacuum Arc Plasma Evaporation**, ***T. Miyata***, *Y. Honma, T. Minami,* Kanazawa Institute of Technology, Japan

Recently, a newly developed vacuum arc plasma evaporation (VAPE) method providing high-rate film depositions on large area substrates has attracted much attention for transparent conducting oxide film depositions. In this paper, we describe highly transparent and conductive B-doped ZnO (BZO) thin films prepared by the VAPE method using sintered BZO fragments. It was found that the obtained electrical and optical properties of deposited BZO thin films were considerably affected by the B content doped into films as well as the preparation condition of the BZO fragments used. Fragments suitable for preparing low resistivity BZO films were obtained by breaking previously sintered disks into small pieces; a mixture of ZnO and B@sub 2@O@sub 3@ powders was pressed and then sintered at a temperature above about 900@super o@C in a pure Ar gas atmosphere to produce the disks. In particular, the B content doped into deposited BZO thin films could be controlled by varying the B content of the BZO fragments used. The lowest resistivity was obtained with a B content (B/(B+Zn) atomic ratio) of approximately 1 at.%. To obtain high transmittance, it was necessary to introduce O@sub 2@ gas during film preparation on low temperature substrates that were below approximately 150@super o@C. Low resistivities of 7.9X10@super â?"4@ and 5.1X10@super â?"4@@ohm@cm and a high average transmittance above 85% in the visible region were obtained in BZO thin films prepared with a high deposition rate at glass substrate temperatures of 100 and 200@super o@C, respectively.

8:20am **TF-WeM2 Photonic Band Edge Engineering through Nano Coating of Cu Thin Film on 3D Photonic Crystals**, ***D.-X. Ye***, *Z.-P. Yang, J. Bur, S.Y. Lin, T.-M. Lu,* Rensselaer Polytechnic Institute

Photonic crystals have extraordinary applications in illuminations, solar cells, and photovoltaic devices by redistributing the energy. At the edge of a photonic band gap, the photon group velocity approaches zero giving the coherent photon localization. Therefore, spontaneous emission near the photonic band edge can be totally suppressed. For energy applications, interesting photonic crystals are those with a band edge close to visible wavelengths. However, the band edge on this side is limited both by the fabrication methods and by the nature of the dielectric materials used. Here we present our strategy of breaking these limitations by conformal coating of Cu films using chemical vapor deposition (CVD). First, on pre-fabricated Si and W woodpile structures, 70 nm thick Cu was coated by CVD. Optical measurements showed that the photonic band edge is pushed from ~1500 nm to ~700 nm in these structures. Another class of photonic crystals is constructed using arrays of square nanosprings by oblique angle deposition technique. This technique was first used to fabricate the Si spring photonic crystals by M. J. Brett et al. However, the dimensions of the nanosprings cannot be maintained due to the fan-out growth. We designed a substrate rotation method to overcome this difficulty which is referred as swinging technique. In swinging technique, the substrate is rotated azimuthally back-and-forth within an angular range with a constant rotation speed. Uniform Si photonic structure can be fabricated without fan-out problem now. On the other hand, the other limitation of this technique prevents the geometry of the nanosprings to be optimized to achieve a large band gap. We solved this problem again by further Cu coating on Si nanosprings. The overall photonic crystal shows a complete band gap in the near infrared region. In summary, Cu coating on photonic crystals provides an easy path to modify the properties of photonic crystals.

8:40am **TF-WeM3 Thin-Film Superlattice Thermoelectric Energy Conversion Materials and Devices**, ***R. Venkatasubramanian***, RTI International **INVITED**

The increasing cost of energy produced from fossil fuels has further renewed the emphasis on issues such as energy efficiency, alternative fuels and so-called sustainable technologies. Nearly 60% of the world' energy, today, is wasted as heat. A prime example is the internal combustion engine - where almost 70% of the fuel's calorific value is lost as heat through the exhaust and radiator. Thermoelectric devices can convert this waste heat to much-needed electric power. Thermoelectrics is also relevant for solid-state, noise-free, CFC-free, refrigeration and air-conditioning. These applications have been limited in the past, mainly due to the efficiency of materials, low power density, as well as scalability. Using thin-film nanoscale materials, which allow unique physics such as thermal conductivity reduction without deterioration of electronic conduction, we have been able to achieve a significant improvement in materials performance (Nature 2001). The thin-film nature has enabled devices with high specific power (in Watts/cc) and cooling densities (in Watts/square cm); the former is attractive for portable power while the latter is highly relevant for high-perforamance electronics cooling. In addition to these applications, our long-term vision is to contribute to energy eficiency, by harnessing untapped heat sources. We will describe our early efforts in the applcation of this technology for automotive waste-heat recovery. We will also compare the advantges offered by thin-film thermoelectrics for solar-thermal-to-electric power versus convenional photovoltaics.

9:20am **TF-WeM5 Synthesis of CuO and Cu2O by a Process Combining Sputtering and Rapid Thermal Annealing**, ***J.H. Hsieh***, Mingchi University of Tech., Taiwan

Cu2O and CuO thin films were first deposited using magnetron sputtering, then, annealed by a rapid thermal annealing system at various temperatures and oxygen partial pressure. After processing, the films were characterized using UV-VIS photometer, four point probe, and Hall measurement system. The electro-optical properties of these films were compared with those prepared by direct sputtering.

9:40am **TF-WeM6 Microcrystalline Silicon Deposition Efficiency Optimization**, ***B. Strahm***, *A.A. Howling, L. Sansonnens, Ch. Hollenstein,* Ecole Polytechnique Fédérale de Lausanne, Switzerland

Microcrystalline silicon is widely used in solar cells, because of its better performances and stability compared to the standard amorphous silicon. However, the low light absorption of microcrystalline silicon implies that thick layers have to be deposited. Therefore high deposition rates (> 1 nm/s) have to be achieved in order to allow a cost-effective mass production of solar cells. An analytical plasma chemistry model has been used to determine the amorphous/microcrystalline silicon microstructure transition and the gas utilization efficiency as a function of plasma parameters. Modeling results show that high gas utilization efficiency is not incompatible with microcrystalline silicon deposition. In situ deposition rate and infra-red absorption measurements in a large area RF-PECVD capacitive reactor have been used to determine the gas utilization efficiency and the silane depletion. Ex situ Raman spectroscopy was used to measure the crystallinity of the deposited layers. Experimental data have validated the analytical plasma chemistry model and the results were used to build up a new experimental approach to optimize microcrystalline silicon deposition efficiency. Starting with appropriate plasma parameters (RF input power, excitation frequency and silane flow rate and concentration) and by varying only hydrogen flow rate and pressure, the gas utilization efficiency can be increased to values higher than 80 %. This high efficiency has not only the advantage of high deposition rate, but also reduces raw material consumption and powder formation.

10:40am **TF-WeM9 Chemical-Kinetics Analysis of In-Vacuum Cu@sub 2@Te Thermal Decomposition and Comparison to Equilibrium Vapor-Pressure Measurements**, ***G. Teeter***, National Renewable Energy Laboratory

Auger electron spectroscopy measurements of polycrystalline Cu-foil substrates exposed to elemental Te vapor at substrate temperatures below 373 K indicate that copper-telluride films are formed at the substrate surface that have a 2:1 Cu-to-Te ratio, as predicted by the Cu-Te phase diagram for a system in equilibrium. When these films are annealed above about 700 K in vacuum, Te desorbs from the substrate with zero-order kinetics. An analysis of Te desorption traces that assumes the reaction Cu@sub 2@Te(s) --> 2Cu(s) + @alpha@Te(v) + 1/2(1-@alpha@)Te@sub 2@(v) finds a thermal-decomposition activation energy of 217 ± 3 kJ/mol. These Te-desorption data are compared to the Te impingement rate calculated from Cu@sub 2@Te equilibrium vapor-pressure data@footnote 1@ from the literature and found to be in excellent agreement. This abstract is subject to government rights. This work was performed with the support of U.S. Department of Energy Contract DE-AC36-99-GO10337. @FootnoteText@ @footnote 1@B. Brunetti, V. Piacente, P. Vassallo, and A. R. Villani, Mater. Chem. Phys. 70, 263-267 (2001).

11:00am **TF-WeM10 B doped Be Coatings for NIF Target Development**, ***H. Xu***, *K. Moreno, K. Youngblood, A. Nikroo,* General Atomics*; J. Cooley,* Los Alamos National Laboratory*; C. Alford, S. Letts, A.V. Hamza, T. van Buuren,* Lawrence Livermore National Laboratory

Sputtered beryllium and copper-doped beryllium coatings as thick as 170 µm have been deposited on spherical substrates to produce hollow shells that are required as targets for inertial fusion experiments.@footnote 1@ Be coatings by magnetron sputtering have achieved ~93-95 percent bulk density consistently up to 170 µm in thickness. Coatings on the spherical substrates exhibit columnar structure through the entire thickness. Transmission Electron Microscopy (TEM) indicates the presence of sub-micron voids mainly aggregated along the columnar structure and grain boundaries as well as some intra-granular voids. Ultra Small Angle X-ray Scattering (USAXS) was used to determine the size and distribution of pores within the coatings, which correlated well with the TEM data. Holes drilled in beryllium shells produced in this manner allow filling with the fusion fuel. Gas retention of these shells has been examined using mass spectrometry. It appears that a fraction of the pores in the coatings are interconnected, which leads to leakage in the hollow shells. Boron-doped Be layers at concentrations of ~5-20 atomic percent near the eutectic phase have been added to the Be shells. The addition of these layers has led to a significant improvement in D@sub 2@ gas retention of shells. However there remains a considerable scatter in the measured leakage. @FootnoteText@ @footnote 1@S. Haan et al., Phys. Plasma 2 (1995) 2480.

11:20am **TF-WeM11 Morphological Changes in CIGS2 Upon Thickness Reduction of Absorber Layer and its Correlation with Device Performance**, ***P. Vasekar,*** *N.G. Dhere,* Florida Solar Energy Center

Chalcopyrites are important contenders among thin film solar cells due to direct band gap and higher absorption coefficient. Copper-Indium-Gallium Sulfide (CIGS2) is a chalcopyrite material with a near-optimum band gap of 1.5 eV. At FSEC PV Materials Laboratory, record efficiency of 11.99 % has been achieved on a 2.7 µm CIGS2 film prepared by sulfurization. Copper indium sulfide modules are being commercialized by Sulfurcell in Germany. The availability and cost of Indium can be a limiting factor. The required amounts of metals can be lowered by using thinner films. Efforts are being made to reduce the thickness while maintaining the comparable performance. At NREL, 17.16 % efficiency has been obtained with 1 µm copper-indium-gallium selenide absorber layer. Thickness reduction up to 0.75 µm seems plausible. It has been estimated that thickness can be reduced even to 0.5 microns without light trapping. We have already obtained about 6.4 % efficiency for CIGS2 with thickness of 1 µm. Initially small size grains are formed during the film growth. With continuing growth to large thicknesses, more favorably oriented grains grow faster and coalesce to form compactly packed large-grain morphology. Solar cell performance in smaller grain chalcopyrite absorber deteriorates due to larger fraction of grain boundaries. It is essential to hasten the grain growth through coalescence to retain quality even in thinner films. This work presents a study of morphology of CIGS2 absorber layers of decreasing thicknesses and the assessment of the efficacy of various techniques in improving morphology and thus the device performance and yield even at thicknesses below 1 µm.

11:40am **TF-WeM12 Thermoelectric Properties of Compositionally Graded Co-Doped TiO@sub 2@ Thin Films**, ***N. Nguyen,*** University of Washington*; D. Kukuruznyak,* National Institute for Materials Science, Japan*; A. Yamamoto,* Advanced Industrial Science and Technology Institute, Japan*; T. Chikyow,* National Institute for Materials Science, Japan*; F.S. Ohuchi,* University of Washington

There has been a recent interest in improving thermoelectric performance using segmented thermoelectric elements. Concentration gradient of dopants in the material can be regarded as a continuously segmented component composed of a single parent material. In terms of material processing, concentration gradient is more advantageous, and may result in better compatibility for device applications, especially for thin film structures. The compositionally graded Co-doped TiO@sub 2@ thin films were grown on (001) LaAlO@sub 3@ substrates by a pulsed laser deposition. Spatial distribution of the electrical resistance and thermopower mapping of the samples were mapped using a custom-designed scanning conducting probe. The Seebeck coefficients were varied from -10 µV/K to -30 µV/K, whereas the resistivity changed from 1 @Ohm@cm to 150 @Ohm@cm. The I-V characteristics under the presence of the temperature gradient were then measured by applying a current source in such a way that the thermopower current was suppressed by applying the current in the opposite direction. Power factors (S@super 2@@sigma@) were then evaluated as a function of temperature, where those for Co-doped TiO@sub 2@ were increased as compared to non-doped TiO@sub 2@ by a factor of multiple times. A part of the reason for enhancement of the power factor may relate to a spin entropy effect induced by Co doping to TiO@sub 2@. Since the maximum power factor occurs at certain temperature and/or range for given concentration of the Co-doping, the concentration graded films have an advantage to broaden the temperature range for operation with the peak performance occurring continuously over the wide temperatures of interest.

12:00pm **TF-WeM13 Procedure for Performance Monitoring of Thin-Film Photovoltaic Modules**, ***N.G. Dhere,*** *A. Kaul, B. Kumar, S. Khatri,* Florida Solar Energy Center

Thin film PV modules from all five leading US PV manufacturers are being tested at Florida solar energy center. Grid-connected photovoltaic systems are usually subjected to harsh environmental conditions and high voltage bias. Hence a study is undertaken for understanding key reliability issues and exploring avenues for improving manufacturing technology. Array output voltage, current, and back-of-module temperatures along with meteorological parameters namely; solar irradiance, UV, relative humidity, ambient temperature, wind speed, etc, are being monitored continuously. Error analysis of statistical data and PV system performance monitoring to Performance Test Conditions (PTC) is carried out using regression. Current-Voltage Characteristics (I-V) of the module arrays taken on quarterly basis, serve as a supplement to the continuous data monitoring. I-V measurements provide characteristic data of PV arrays, such as open circuit voltage, short circuit current, peak power, fill factor etc. The PTC power calculated for each month supported by quarterly I-V measurements are used to assess the degradation rate, if any, for each module array over a period of several months. This paper presents procedure of data acquisition and analysis for verification of possible degradation of thin-film PV modules.

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