Plasma Science and Technology Division
Room B131 - Session PS+EM-WeM

Plasma Processing of Materials for Energy

Moderators: Ankur Agarwal, KLA-Tencor, Saravanapriyan Sriraman, Lam Research Corp

8:00am **PS+EM-WeM-1 Plasma Processes for High Efficiency Multi-Junction Solar Cells Fabrication***, **Maxime Darnon**, M Volatier, P Albert, M de Lafontaine, P St-Pierre, G Hamon,* LN2, CNRS / Université de Sherbrooke, 3IT, Canada*; C Petit-Etienne, G Gay, E Pargon,* LTM, CNRS / Université Grenoble Alpes, France*; V Aimez, S Fafard, A Jaouad,* LN2, CNRS / Université de Sherbrooke, 3IT, Canada **INVITED**

Multijunction solar cells provide the highest efficiency for solar energy conversion into electricity. With record efficiency above 45%, they are used in concentrated photovoltaic systems where their cost is mitigated by the sunlight concentration. Conventional technics for such solar cells' fabrication include III-V materials epitaxy on germanium, electrodes lift off, antireflective coating deposition by physical vapor deposition and isolation by saw dicing. In this presentation, we will show how plasma processes can advantageously be used to replace some of these steps and how it could enable the fabrication of new architectures of solar cells.

A low-damage III-V plasma etching step can isolate the solar cells one to the other before the mechanical saw dicing. This reduces the density of recombination centers at the edge of the solar cells and provides therefore a higher open circuit voltage. Deep germanium plasma etching can also be used for solar cells dicing with trenches as small as 10 µm. As an alternative to physical vapor deposition, plasma enhanced chemical vapor deposition can coat high transparency silicon nitride and silicon oxide that form an excellent anti-reflective coating and passivate surface recombination centers.

In addition to their benefit for conventional solar cells fabrication, these plasma-based processes also provide opportunity for the fabrication of new kinds of multijunction solar cells, such as ultra small solar cells (<0.07 mm^2), front-side contacted solar cells, back-side contacted solar cells, and through cell via contacted solar cells.

8:40am **PS+EM-WeM-3 Combinatorial Synthesis of Ternary Oxides by Reactive Sputtering for CdTe Solar Cells***, **Yegor Samoilenko**, G Yeung, C Wolden,* Colorado School of Mines

Polycrystalline CdTe-based solar cells have reached efficiencies of over 22% in the recent years. The road towards high V_{oc} and 25% devices requires a combination of low interface recombination velocity, higher lifetime, and higher carrier concentration in the CdTe absorber. It was recently demonstrated that the impact of the interface recombination on the performance of the device is more pronounced as carrier concentration and lifetime increase. Magnesium zinc oxide (MZO) has been identified as a transparent emitter that enables high efficiency in CdTe based solar cells. By controlling the alloy composition one may tune the conduction band alignment with CdTe absorber at the front interface to reduce recombination. Most previous work has employed MZO targets sputtered in Ar. However there are open questions as to what the optimal composition, its stability, and sensitivity to subsequent processing.In this work we perform a combinatorial study of MZO buffer layer prepared by co-sputtering of Zn and Mg in oxygen-containing atmosphere. Combinatorial libraries are formed with a band gap variation of more than 0.4 eV across a 2 inch substrate. These are integrated into standard CdTe to determine the optimal composition based on using J-V characteristics. In addition, the stability of these films is assessed by surface spectroscopy, and routes to stabilize performance are introduced.

9:00am **PS+EM-WeM-4 Potential Applications of TiN-based Plasmonic Nanoparticles: From Plasmon-induced Chemistry to Photothermal Absorption***, A Alvarez Barragan, C Berrospe Rodriguez, **Lorenzo Mangolini**,* University of California, Riverside

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of plasmon-driven photocatalysts. Gold and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into molecules adsorbed to their surface. However, the chemical instability of silver and the low thermal stability of both metals, in addition to their high cost, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the visible-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry make it a strong alternative to mainstream plasmonic metals. The present work encompasses a comprehensive study of the synthesis of TiN nanoparticles via a non-thermal plasma method. It also highlights the potential of this material as an alternative in plasmonic catalysis and as a high-temperature-resistant photothermal absorber. TiN particles are synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. Platinum nanoparticles were subsequently deposited on the TiN by photo-induced reduction of an aqueous solution of chlorplatinic acid (H_2PtCl_6). The reduction of the precursor metal was driven by electron hole pair generation via plasmon decay. The addition of methanol as a hole scavenger increased the electron lifetime, leading to the obtention of metallic platinum. This reaction occurred at temperatures below 40°C under visible light illumination. In addition, a novel TiN@SiO_xN_y core-shell structure is facilitated by the modular capabilities of the non-thermal plasma synthesis method. The plasmon peak of the extinction spectrum of the core-shell particles is enhanced by 60% compared to the uncoated TiN particles. The high temperature resistance of these heterostructures is also demonstrated, as their optical properties remain stable at 700 °C under vacuum and at 400 °C in air. This work strengthens the case for alternative plasmonic materials in fields dominated by precious metals, and heavily driven by materials cost.

9:20am **PS+EM-WeM-5 Plasma-induced Strain in MoS_2 Films for the Electrochemical Hydrogen Evolution Reaction***, T Liu, X Liu, **Souvik Bhattacharya**,* Case Western Reserve University*; Z Ye, R He,* Texas Tech University*; X Gao, R Akolkar, R Sankaran,* Case Western Reserve University

There has been recent interest in growing layered materials such as molybdenum disulfide (MoS_2) over large areas for electronic and energy applications. One such approach is chemical vapor deposition (CVD) in which vapor precursors are thermally decomposed to nucleate a thin film at the surface of a substrate. A plasma may also be employed to assist in decomposition of the precursor molecule through gas-phase excitation, for example in plasma-enhanced CVD (PECVD) or plasma-enhanced atomic layer deposition (PEALD). Here, we report a plasma-assisted approach which is fundamentally different than these deposition techniques which we term plasma-enhanced chemical film conversion (PECFC). Precursor films are first prepared as a thin film on a substrate from liquids and subsequently converted by a combination of heating and plasma treatment. The process is additive, in that the precursor is only present where it is desired and there is little materials wastage, and substrate-independent, by circumventing the need for adsorption, allowing direct growth on application-specific substrates.

In this talk, we will present results for the synthesis of MoS_2 films and their application as electrocatalysts for the hydrogen evolution reaction (HER). A single-molecule precursor, ammonium tetrathiomolybdate (ATM), was first dispersed in solution with linear polyethylenimine (L-PEI) and spin-coated to produce a well-defined thin film less than 50 nm thick. The precursor film was then treated by an atmospheric-pressure dielectric barrier discharge (DBD) in a background of argon and hydrogen gas (80:20) at 500 ^{o}C. Conversion to crystalline MoS_2 was confirmed by X-ray diffraction and micro Raman spectroscopy. Atomic force microscopy was performed to study possible nucleation and growth mechanisms by varying the growth temperature and treatment time. The chemical composition was analyzed by X-ray photoelectron spectroscopy which showed an ideal stoichiometric ratio of 1:2 Mo:S.

A potential application of MoS_2 films is HER because it is composed of earth abundant elements and has been shown to be highly active through its edge sites. We carried out a systematic study of the origin of HER activity in our films, both after initial conversion and after several other post-synthesis treatments . The investigation showed that our initially-converted films have tensile strain leading to intrinsic activity that is comparable to previously reported sulfur vacancy generation by post-synthesis plasma treatment steps. In our case, the strain is induced in the initial fabrication step, providing a simpler and more scalable process to produce efficient HER electrocatalysts.

9:40am **PS+EM-WeM-6 Comparison of Pulsed and Continuous Wave Argon Plasmas for the Synthesis of Vertical Graphene Nanosheets***, **Zoe Mann**, E Fisher,* Colorado State University

Vertical graphene nanosheets (VGNs) have unique structural and electronic properties that make them applicable in fields such as energy storage, electronics, and sensing. VGNs are often grown using high-power, high-temperature processes and hazardous or unsustainable precursors such as methane. For this reason, we sought to develop a simple, efficient, and more environmentally-friendly way to synthesize VGNs. In this work, VGNs are synthesized from butter or coconut oil (sustainable, non-toxic precursors) spread on a Ni foam or Cu substrate and then treated with a high peak power pulsed plasma process. The materials formed through this process are compared to those produced with a continuous wave treatment of equivalent power and a low peak power pulsed plasma treatment, as well as to the untreated material. We used a range of characterization techniques to assess the materials, including scanning election microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cyclic voltammetry, providing data on the morphology, surface chemistry, bulk characteristics, and electrochemical performance, respectively. SEM imaging shows that VGNs grown by the high power pulsed PECVD technique have high surface area and abundant ultra-thin edges. XPS analysis of untreated butter and the low-power pulsed plasma treated samples reveals binding environments consistent with the chemical composition of triglycerides (the primary chemical component in butter/oil), whereas the XPS and Raman spectra of VGNs indicate the presence of sp^2-hybridized carbon. Notably, cyclic voltammograms of VGNs formed on Ni foam are characteristic of a capacitor, and these materials do not exhibit the deleterious side reactions found with VGNs formed on the Cu substrate. To better understand the underlying chemistry occurring during plasma treatment, optical emission spectroscopy data were collected, revealing key information on species important for VGN synthesis, such as atomic and molecular carbon.

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