Thin Films Division
Room 316 - Session TF2-WeA

Solution Based and Graphene or Polymer Deposition Techniques

Moderators: Parag Banerjee, University of Central Florida, **Mark Losego**, Georgia Institute of Technology

4:20pm **TF2-WeA-7 The Truth About Graphene - Where Is It and Why It Is Taking This Long to Get Here**, *M. Baraket,* ***Michael Stanford,*** General Graphene Corporation

Graphene is a monolayer of sp^2-bonded carbon atoms assembled in a honeycomb lattice structure that has attracted incredible attention for its many promising properties. It has been said that Graphene can do anything you need - except get out of the laboratory. The CVD-grown large area graphene has yet to become useful outside the laboratory due to its cost which is usually well over $10,000 dollars per square meter. Consequently, graphene's accessibility has been severely restrained with virtually no chance to integrate into industrial applications requiring high product volumes. To address this, General Graphene has scaled-up the graphene growth using an atmospheric pressure CVD process to produce cost effectively truly large-scale mono and multilayers graphene. This led us to produce different graphene types from polycrystalline graphene grown on polycrystalline copper to single oriented grown on single oriented copper to various forms of multilayer. All this can be produced with a single machine with production rates exceeding >30,000 m^2/year. Now that costs and production are in line with industrial applications – the final step is to integrate graphene into targeted applications where its unique properties and abilities provide significant competitive advantages. On the other hand, there is not a single transfer method that works for all applications. This leads to a variety of transfer methods, each with their strengths and weaknesses.

In this talk a brief history of graphene will be presented with emphasis on the challenges faced in growth and transfer along with current state-of-the-art applications with real-world performance and cost data.

4:40pm **TF2-WeA-8 Initiated Chemical Vapor Deposition (iCVD) for Shape-Programmed Polymer Nanoparticles**, ***Rong Yang,*** Cornell University

Shape-programmed polymer nanoparticles (PNPs) represent a critical opportunity to advance research in small molecule drug delivery, self-assembly for soft robotics, and metamaterials with emergent properties. Extant techniques like emulsion polymerization commonly used to synthesize PNPs primarily produce particles that are spherically shaped. To achieve non-spherical PNPs, time-consuming solution-based protocols are commonly required, along with additional fabrication and purification steps. The limited selection of monomers, restricted by their solubility, leads to a narrow range of PNP shapes and chemistries, whose deployment is further hindered by the laborious and costly synthesis. Here we present the rapid synthesis of shape-programmed PNPs without the need for nano/microfabrication, enabled by two fresh strategies revolving around initiated chemical vapor deposition (iCVD) polymerization.

The first strategy is a novel template- and solvent-free technique we recently developed, namely condensed droplet polymerization (CDP), which delivers unprecedented flexibility in PNP synthesis. With CDP, particle sizes and dimensions could be varied continuously, from sub-10 nm to above 1 µm. As a proof-of-principle, we demonstrated the synthesis of polymer nanodomes (hydrophilic, hydrophobic, cross-linked, fluorinated, biocompatible) within minutes (seconds for polymerization).

The second strategy is to leverage structured liquids, such as liquid crystals, as templates for the polymerization with reactants, i.e., monomers and initiators, delivered with picomole precision in the vapor phase. The precise delivery of reactants allows polymerization to proceed without disturbing the dynamic structures of liquid templates. A variety of shapes, including nanospheres, domes, disks, and porous networks could thus be obtained using a single technique.

These novel strategies build upon an existing manufacturing instrument, i.e., iCVD, and hence can be scaled down for decentralized manufacturing, or scaled up for industrial production in semi-continuous roll-to-roll fashion. The ability to manufacture shape-programmed soft materials is critical for advancing a wide cross-section of applications ranging from soft robotics to tough yet injectable implants.

5:00pm **TF2-WeA-9 Synthesis, Properties and Applications of Donor-Acceptor Conductive Polymers by Oxidative Chemical Vapor Deposition**, ***Marek Charyton,*** *N. Boscher,* Luxembourg Institute of Science and Technology (LIST), Luxembourg

Conjugated polymers (CPs) have recently gained great scientific attention as promising materials for next generation of photo(electro)catalysts due to their unique physical (thermal and chemical stability, light resistance), optical (broad and intensive absorption) and electronic properties (redox potential, excellent conductivity). Many strategies to tailor the photocatalytic performance of CPs was studied, focusing on tuning band gap or enlarge the separation of electron-hole pairs. Alternatively, the photocatalytic properties of CPs can be also modified by their molecular design. Alternating electron-rich (donor, D) and electron-poor (acceptor, A) units along the polymer's backbone highly impact conductivity and reactivity of the designed polymers. However, to enable large-scale fabrication of optoelectronic, organic materials conductive polymers such as CPs have to be synthetised in straight-froward and low-cost processes. Herein, we propose Oxidative Chemical Vapor Deposition (oCVD) as a method that fulfils these requirements. This solvent-free technique allows to form polymers *via* vapor phase deposition directly on the desired surface thus, reducing significantly use of chemical reagents during the process. Moreover, in contrast to conventional liquid methods such aspalladium catalyzed polymerization solubilizing groups are not needed therefore, the method is not limited to only sufficiently soluble monomers. Despites the many merits of oCVD the method have not been widely studied yet. Up to date, the monomers studied in the polymerization *via* oCVD were limited to single electron rich systems like thiophene, EDOT, pyrrole, porphyrins etc.. This presentation describes the development of conductive donor-acceptor conjugated polymer obtained using oCVD method. The conductivity of the obtained thin films was tuned up to 9.75 S cm^{-1} by modification of reaction conditions. Further optical, electrochemical properties and photo(electro)catalytical performance of obtained materials were studied showing the fabricated layers can be used as efficient catalysts for water splitting reaction.

5:20pm **TF2-WeA-10 Effect of doping and annealing on the Optical and Magnetic properties of Sol-Gel deposited NiZn Ferrite films**, ***Roni Paul,*** *S. Kothapally, J. Abu Qahouq , S. Kotru,* The University of Alabama

Ferrite films are of interest in high-frequency applications because of their high resistivity, lower eddy current losses, and better magnetic properties compared to metal alloy films. In this work we investigated the effect of doping (Cu and Co) and annealing on the optical and magnetic properties of NiZn Ferrite films. Films with three different compostions $Ni_{0.5}Zn_{0.5}Fe_2O_4$,$Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$and $Ni_{0.35}Co_{0.2}Zn_{0.45}Fe_2O_4$ were deposited on quartz substrate using the sol-gel technique. The grown films were annealed at 500 and 800°C in a Rapid Thermal Annealing (RTA) furnace. The structural, optical, and magnetic properties of undoped and doped films were studied as a function of annealing temperature using X-ray Diffractometer (XRD), UV-VIS spectrophotometer, and Vibrating Sample Magnetometer (VSM), respectively. Bandgap of the materials was calculated using absorbance data collected from the UV-VIS spectrophotometer. Permeability values were extracted from the hysteresis loop. The $Ni_{0.35}Cu_{0.2}Zn_{0.45}Fe_2O_4$film annealed at 800°C exhibited maximum permeability (33.94) with minimum bandgap (2.5eV). The results will be presented.

5:40pm **TF2-WeA-11 A Scalable Method for Rare Earth Oxide Thin Films by Chemical Solution Deposition**, ***Daniel Rodriguez,*** *A. Edgar, D. Vodnik, I. Usov,* Los Alamos National Laboratory

Rare-earth metals are a diverse group of elements with properties found nowhere else on the periodic table, and when in their oxidized forms, they exhibit unique traits, such as corrosion resistance to molten metals. In this study, we have applied a chemical solution deposition (CSD) process for coating stainless steel (SS) with thin films of both erbia (Er_2O_3) and yttria (Y_2O_3).

The focus of this talk will discuss different approaches for depositing rare-earth oxides onto SS304/SS316 geometries by both dipping and spraying. For dipping techniques, the formation of Er_2O_3 and Y_2O_3 coatings takes advantage of metal-nitrate solution chemistry, and its transformation into metal-oxide by both thermal annealing and ultra-violet photo-curing. For spray coating (Fig.1), deposition of Y_2O_3 involves deployment of aerosols with inclusion of binding agents such that the oxide is physically stable on the substrate, but also by incorporating substrate treatments to improve its

chemical bonding. The results will reflect how fine adjustments to CSD methods leads to improved adhesion strength, composition, uniformity, and reproducibility of both coating thickness and micro-structure. Last, the scalability of CSD will be explained and compared to chemical and physical vapor deposition methods.

The outcome of this work is expected to reduce cost of the metal casting process and provide direct economic and environmental impact. In addition, there are interesting fundamental questions about the properties of rare-earth materials. Therefore, by identifying materials with practical applications, more experiments can be done to further understand the underlying physics and chemistry.

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