

Wednesday Afternoon, November 12, 2014

Thin Film

Room: 307 - Session TF+EM+EN-WeA

Thin Film and Nanostructured Coatings for Light Trapping, Extraction, and Plasmonic Applications

Moderator: Tansel Karabacak, University of Arkansas at Little Rock

2:20pm **TF+EM+EN-WeA1 Enhanced Light Trapping by Glancing Angle Deposited Semiconducting and Metallic Nanostructure Arrays.** *Hilal Cansizoglu, R. Abdulrahman, M.F. Cansizoglu*, University of Arkansas at Little Rock, *M. Finckenor*, NASA Marshall Space Flight Center, *T. Karabacak*, University of Arkansas at Little Rock

Management of light trapping in nano materials has recently got attention owing to altering optical properties of materials commonly used in potential applications such as photovoltaics and photonics. Trapping the light inside the semiconducting nanostructure coating can increase optical absorption capacity of the material dramatically. Meanwhile, metallic nanostructures can serve as individual back reflectors if the light is achieved to be trapped among metallic nanostructures, which results in enhanced optical absorption of the possible surrounding absorber material around metallic structures. In this study, we examine light trapping in arrays of zig-zags, springs, screws, tilted rods, and tapered vertical rods of indium sulfide (In_2S_3) and aluminum (Al) as the model semiconducting and metallic materials, respectively. Nanostructures of different shapes were produced by glancing angle deposition (GLAD) technique. We investigated the effect of size and shape of the arrays on light trapping properties using ultraviolet-visible-near-infrared (UV-VIS-NIR) spectroscopy and finite difference time domain (FDTD) simulations. Optical characterization results show that light trapping by GLAD nanostructures can strongly depend on their shapes. Under normal incidence of light, 3D geometries of semiconducting nanostructures such as springs, screws, and tapered vertical rods can provide an enhanced optical absorption compared to zigzags, and tilted rods. In addition, total reflectance measurements reveal that reflectance is inversely proportional to metallic nanorod length in the wavelength range of 200-1800 nm. Meanwhile, FDTD optical modelling indicates an enhanced diffuse light scattering and light trapping through uniform distribution of diffracted light within the 3D In_2S_3 nanostructure geometries such as springs, screws and vertical rods. On the other hand, zigzags and tilted rods show light absorption at relatively low level similar to the experimental results. In addition, simulations reveal that average reflectance of Al nanorods can drop down to as low as ~50%, which is significantly lower than the ~90% reflectance of conventional flat Al film at similar wavelengths. Our results demonstrate that GLAD nanostructures can provide efficient light trapping through the control of their shapes and size.

2:40pm **TF+EM+EN-WeA2 Enhanced Photoresponsivity of Conformal TiO_2/Ag Nanorod Arrays Fabricated via (Successive) Glancing Angle and Atomic Layer Deposition.** *Ali Haider, N. Biyikli, A.K. Okyay*, Bilkent University, Turkey, *T. Karabacak, H. Cansizoglu*, University of Arkansas at Little Rock, *B. Teckcan*, Bilkent University, Turkey, *M.F. Cansizoglu*, University of Arkansas at Little Rock

Improved charge carrier collection and optical absorption are two main techniques to enhance the photocurrent of a nanostructured photodetector. In a nanostructured photodiode, longer carrier life time and shorter transit time of the photo-generated carriers provides efficient charge carrier collection while the nanostructured device architecture contributes towards trapping the light by diffuse light scattering and enhancing optical absorption. However, efficient charge carrier collection is limited by the random and non-uniform nano-network. For nanostructured Schottky photodetectors, uniform nanostructured geometries with larger aspect ratio can enhance the interface of the Schottky junction which in turn decreases the transit time of generated carriers. In addition, most of the nanofabrication methods that can produce uniform nanostructure geometries are limited to certain materials. Therefore, it is an overwhelming demand to develop innovative low-cost nanostructured photodetector fabrication methodologies which enables the use of a variety of semiconductor alloy families with uniform and optimized geometries for improving photoresponsivity performance. In this work, we demonstrate a proof-of-concept nanostructured Schottky photodiode fabrication method combining glancing angle deposition (GLAD) and atomic layer deposition (ALD) to fabricate metal-semiconductor radial junction nanorod arrays, which offers significantly enhanced photoresponse compared to conventional planar counterpart. Firstly, silver (Ag) nanorod (NR) arrays were deposited on Ag thin film/Si templates by utilizing glancing angle deposition (GLAD)

technique. A conformal and thin titanium dioxide (TiO_2) coating was deposited on silver nanorods via ALD. ALD emerge as highly attractive deposition technique for coating of nanorods due to its remarkable conformality and uniformity on the densely packed NR structures. Moreover, ALD also facilitates the ultra-precise control of deposited film thickness in the sub-nm scale. Following the growth of TiO_2 on Ag NRs, aluminum (Al) metallic top contacts were deposited by thermal evaporation to complete the fabrication of NR-based Schottky photodiodes. Due to the improved charge carrier collection and optical absorption, the resulting nanostructured detector exhibits a more-than two orders of magnitude photoresponsivity enhancement factor (3.8×10^2) under 3V reverse bias when compared to the corresponding thin film counterpart device with the same TiO_2 thickness. Our preliminary structural, optical, electrical, and photoresponse characterization results are presented.

3:00pm **TF+EM+EN-WeA3 Nanostructured Photonic Materials for Light-Trapping and Photon Management in Solar Energy Conversion.** *Koray Aydin*, Northwestern University **INVITED**

Nanophotonics, the emerging field of photon-material interactions at the nanoscale, poses many challenges and opportunities for researchers both in the basic and applied sciences. In this talk, I will describe our efforts in designing, realizing and characterizing nanostructured photonic materials including metals, transparent conductive oxides and inorganic semiconductors. By shaping materials at the nanoscale, one can drastically increase absorption in and/or scattering from nanostructures that could provide significant performance enhancements in solar energy conversion processes including photovoltaics and photocatalysis. First, I will discuss our research efforts on realizing broadband plasmonics absorbers enabled by nanophotonic light-trapping approaches in metal-insulator-metal resonators. By using reflective metals and transparent dielectrics, we have achieved significant absorption enhancement in the metallic parts opening routes for spectrally and spatially selective light-absorbing devices that could find use in thermophotovoltaics and hot-electron collection devices. Then, I will describe light-trapping in nanostructured inorganic silicon ultrathin films which results in drastic absorption enhancement over the entire solar spectrum and over the wide range of incident angles. This approach does not involve any plasmonic components and based solely on localized and delocalized resonances in semiconductor nanostructures. This novel resonant light absorption phenomenon in semiconductors could find use in photocatalytic and photovoltaic applications of inorganic semiconductors. Finally, I will talk about our results on nanostructured transparent conductive oxide contacts, which is capable of light trapping over broad range of wavelengths. Nanostructured TCO contacts could benefit both organic and inorganic photovoltaic materials, offering significant absorption and short circuit enhancements.

4:20pm **TF+EM+EN-WeA7 Porous Solid Phase Microextraction (SPME) Fibers by Oblique Angle Deposition.** *Anubhav Diwan, B. Singh*, Brigham Young University, *M. Kaykhani*, Sistan & Baluchestan University, Iran (Islamic Republic of), *B. Paul, P. Nesterenko*, University of Tasmania, Australia, *M.R. Linford*, Brigham Young University

Solid phase microextraction (SPME) is a solvent-free technique used for extracting organic compounds from matrices such as air or wastewater. It involves a fiber coated with a liquid or solid stationary phase that extracts target compounds directly from a solution or from the head space above a solution or material. Solid stationary phases provide faster extraction than liquid phases, but exhibit lower capacities. Porous solid phases have been able to overcome these issues by providing large surface areas for analyte adsorption. Commercial SPME fibers are rather expensive, swell in many solvents, and often extract limited numbers of compounds (show limited selectivity). Herein, we discuss the preparation of porous SPME fibers by oblique angle deposition (OAD) of sputtered silicon or other materials onto a fiber. OAD involves deposition of materials onto substrates placed at steep angles with respect to the direction of the incoming species, creating porous structures. The resulting nanoporous coatings can be modified with different functional groups to enhance selectivity of the phase towards target compounds. If normalized for thickness, our fibers show ca. three times the capacity of a commercial, 7 μm PDMS fiber. To confirm their morphologies, new OAD-based fibers have been characterized by scanning electron microscopy (SEM). Various silane coatings can be applied to our fibers, which will offer a range of selectivities. These coatings, e.g., a C18 silane, have been characterized on model planar substrates by X-ray photoelectron spectroscopy (XPS) and contact angle goniometry (wetting).

4:40pm **TF+EM+EN-WeA8 Chiral Patchy Particle Arrays: A Simple Fabrication Method to Achieve Plasmonic Circular Dichroism in the Visible Region**, *George Larsen, Y. He, W. Ingram, Y.P. Zhao*, University of Georgia, Athens

An object is said to be “chiral” if it cannot be made superimposable upon its mirror image solely by rotations and translations. That is, chiral objects do not exhibit reflective symmetry. By combining self-assembled colloid monolayers and glancing angle deposition (GLAD), we can create chiral patchy particle thin films that exhibit plasmonic activity in the visible region. Due to their chirality, these patchy particle films exhibit circular dichroism, i.e., they absorb right- and left-circular polarized light to different degrees. Interestingly, we find that the GLAD method relaxes requirements on the template quality, allowing for the production strongly chiral films from polycrystalline colloidal monolayers with randomly oriented domains. It is determined that the rotation direction during GLAD breaks the racemic symmetry of the templates by creating a chiral distribution of material which enhances the chirality of one set of enantiomers relative to the other. Microscopic analysis and geometric chirality calculations confirm that the optical chirality of the bulk film results from incomplete cancellations of even stronger local chiralities. By improving the quality of the colloidal monolayers and intentionally creating a chiral material distribution, we seek to use these chiral patchy particle arrays as plasmonic biosensors that are sensitive to the handedness of the target molecule.

5:00pm **TF+EM+EN-WeA9 Tunable Three-Dimensional Helically Stacked Plasmonic Layers on Nanosphere Monolayers**, *Yizhuo He*, G.K. Larsen, W. Ingram, Y.P. Zhao*, University of Georgia, Athens

Chiral metamaterials are artificial materials designed to interact with left- and right-handed circularly polarized light in different ways. Such a unique optical property enables applications such as negative refractive index, circular polarization, enantiomer sensing, etc. Practical applications usually require the fabrication of large-area chiral metamaterials on substrates with tunable chiroptical properties, especially in visible to near infrared wavelength region. We report a simple and scalable method to fabricate three-dimensional chiral metamaterial combining glancing angle deposition and self-assembled colloidal monolayers. Ag and SiO₂ are deposited alternately on colloidal monolayers. By controlling the azimuthal rotation of substrates between depositions, Ag and SiO₂ layers can be helically stacked in left-handed and right-handed fashions to form continuous helices. These helically stacked plasmonic layers (HSPLs) exhibit localized surface plasmon resonances (LSPR) and strong chiroptical responses in visible to infrared region, which is also confirmed by finite-difference time-domain simulations. The most important feature of HSPLs is the great tunability of chiroptical spectra. By increasing the nanosphere diameter from 200 nm to 500 nm, the HSPL structure can be scaled up and thus the LSPR peak redshifts from 520 nm to 1000 nm. Since the chiroptical response originates from the strong interaction of metal layers with light, i.e. LSPR, the chiroptical spectra also redshifts accordingly without a significant change in magnitude. With such flexibility in the design, HSPLs may act as tunable chiral metamaterials, as well as serve as different building blocks for chiral assemblies.

5:20pm **TF+EM+EN-WeA10 Co-deposition of Mixed-Valent Oxides of Molybdenum and Germanium (Mo_xGe_yO_z): A Route to Tailored Optical Absorption**, *Neil Murphy*, Air Force Research Laboratory, *L. Sun*, General Dynamics Information Technology, *J.G. Jones*, Air Force Research Laboratory, *J.T. Grant*, General Dynamics Information Technology

Mixed-valent oxides of molybdenum and germanium were deposited simultaneously using reactive magnetron co-deposition within an oxygen-argon environment. The films’ stoichiometry, optical and physical properties were varied through changes in oxygen partial pressure induced by systematic variation of the potential applied to the molybdenum cathode. The oxygen partial pressure was determined from the drop in pressure as measured by a capacitance manometer, assuming constant argon partial pressure. To facilitate deposition, a constant power of 100 W DC was applied to the germanium cathode, while power was applied to the molybdenum target using a modulated pulse power supply. Modulated pulse power magnetron sputtering was used due to its ability to generate high target power densities, allowing for rapid reduction of oxygen on the surface of the “oxygen poisoned” molybdenum cathode, as well as for its highly metallic plasma resulting in increased oxygen-gettering capability. Changes in the modulated pulse power supply’s capacitor bank charge, stepped from settings of 300 to 380 V, resulted in films ranging from mixtures of transparent GeO₂ (Ge⁴⁺) and MoO₃ (Mo⁶⁺) to the introduction of various absorptive ionic species including Mo⁵⁺, Mo⁴⁺, Ge²⁺ and Ge⁰, as determined from X-ray photoelectron spectroscopy. The presence of each of

the aforementioned ions results in characteristic changes in the films’ band energies and optical absorption, measured using UV-VIS-NIR optical spectroscopy. As deposited Mo_xGe_yO_z thin films grown using this method have been shown to have band gaps that are able to be tailored between 2.8 eV and 0.6 eV, spanning useful ranges for devices operating in the visible and near-infrared.

5:40pm **TF+EM+EN-WeA11 Permanent Optical Tape and Solid State Data Storage Devices**, *Hao Wang, R. Gates, N. Madaan, J. Bagley, A. Diwan, A. Pearson, S. Jamieson, K. Laughlin*, Brigham Young University, *Y. Liu*, Lehigh University, *B. Lunt, M. Asplund*, Brigham Young University, *V. Shutthanandan*, Pacific Northwest National Laboratory, *R.C. Davis, M.R. Linford*, Brigham Young University

Recently we have prepared novel write–once–read–many (WORM) optical stacks on Mylar for archival data storage in an optical tape format.¹ Here, a nanoscale, co-sputtered bismuth–tellurium–selenium (BTS) alloy was employed as the write layer with carbon protective layers on both the top and bottom of the BTS film. We have successfully written information (matrix of marks) on the C/BTS/C optical stack using a 532 nm laser. Both the optical stack structure (film thickness) and writing conditions (laser power and laser spot size) have been optimized. Films were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectrometry, scanning electron microscopy, spectroscopic ellipsometry, and atomic force microscopy.^{2,3}

We have also recently developed novel WORM solid-state memory elements. These consisted of nanoscale, bowtie-like sputtered carbon films to which a voltage (ca. 10 V) is applied. These fuses have been successfully blown, and the carbon fuse shape, thickness of the carbon layer, and writing voltage have been optimized. Other aspects of the device are currently being optimized.

References

- [1] Wang, H.; Lunt, B.M.; Gates, R.J.; Asplund, M.C.; Shutthanandan, V.; Davis, R.C.; Linford, M.R. Carbon/ternary alloy/carbon optical stack on Mylar as an optical data storage medium to potentially replace magnetic tape, *ACS Appl. Mater. Interfaces*, **2013**, *5*, 8407-8413.
- [2] Wang, H.; Diwan, A.; Lunt, B.M.; Davis, R.C.; Linford, M.R. XPS and SIMS characterization of a BiTeSe write layer for permanent optical tape storage, *Proceedings of ISOM 2013*, ISOM 2013 International Conference, Incheon, South Korea, 2013.
- [3] Wang, H.; Lunt, B.M.; Davis, R.C.; Linford, M.R. Simulation of laser writing on Bi-Te-Se alloy/carbon/Mylar permanent optical storage tape, *ISOM 2013 International Conference*, Incheon, South Korea, 2013.

Authors Index

Bold page numbers indicate the presenter

— A —

Abdulrahman, R.: TF+EM+EN-WeA1, 1
Asplund, M.: TF+EM+EN-WeA11, 2
Aydin, K.: TF+EM+EN-WeA3, **1**

— B —

Bagley, J.: TF+EM+EN-WeA11, 2
Biyikli, N.: TF+EM+EN-WeA2, 1

— C —

Cansizoglu, H.: TF+EM+EN-WeA1, **1**;
TF+EM+EN-WeA2, 1
Cansizoglu, M.F.: TF+EM+EN-WeA1, 1;
TF+EM+EN-WeA2, 1

— D —

Davis, R.C.: TF+EM+EN-WeA11, 2
Diwan, A.: TF+EM+EN-WeA11, 2; TF+EM+EN-
WeA7, **1**

— F —

Finckenor, M.: TF+EM+EN-WeA1, 1

— G —

Gates, R.: TF+EM+EN-WeA11, 2
Grant, J.T.: TF+EM+EN-WeA10, 2

— H —

Haider, A.: TF+EM+EN-WeA2, **1**
He, Y.: TF+EM+EN-WeA8, 2; TF+EM+EN-
WeA9, 2

— I —

Ingram, W.: TF+EM+EN-WeA8, 2; TF+EM+EN-
WeA9, 2

— J —

Jamieson, S.: TF+EM+EN-WeA11, 2
Jones, J.G.: TF+EM+EN-WeA10, 2

— K —

Karabacak, T.: TF+EM+EN-WeA1, 1;
TF+EM+EN-WeA2, 1
Kaykhaii, M.: TF+EM+EN-WeA7, 1

— L —

Larsen, G.K.: TF+EM+EN-WeA8, 2;
TF+EM+EN-WeA9, 2
Laughlin, K.: TF+EM+EN-WeA11, 2
Linford, M.R.: TF+EM+EN-WeA11, 2;
TF+EM+EN-WeA7, 1
Liu, Y.: TF+EM+EN-WeA11, 2
Lunt, B.: TF+EM+EN-WeA11, 2

— M —

Madaan, N.: TF+EM+EN-WeA11, 2
Murphy, N.R.: TF+EM+EN-WeA10, **2**

— N —

Nesterenko, P.: TF+EM+EN-WeA7, 1

— O —

Okyay, A.K.: TF+EM+EN-WeA2, 1

— P —

Paul, B.: TF+EM+EN-WeA7, 1
Pearson, A.: TF+EM+EN-WeA11, 2

— S —

Shutthanandan, V.: TF+EM+EN-WeA11, 2
Singh, B.: TF+EM+EN-WeA7, 1
Sun, L.: TF+EM+EN-WeA10, 2

— T —

Teckcan, B.: TF+EM+EN-WeA2, 1

— W —

Wang, H.: TF+EM+EN-WeA11, **2**

— Z —

Zhao, Y.P.: TF+EM+EN-WeA8, 2; TF+EM+EN-
WeA9, 2