Tuesday Afternoon, October 20, 2015

Nanometer-scale Science and Technology
Room: 212B - Session NS+EN+SS-TuA

Nanophotonics, Plasmonics, and Energy
Moderator: David Wei, University of Florida

2:20pm **NS+EN+SS-TuA1 Subnanoscale Exciton Dynamics of C_{60}-based Single Photon Emitters Explored by Hanbury Brown Twiss Scanning Tunneling Microscope**, ***Pablo Merino Mateo***, *C. Grosse, A. Rosławska, K. Kuhnke, K. Kern*, Max-Planck-Institut für Festkörperforschung, Germany

Electron-hole pair (exciton) creation and annihilation by charges are crucial processes for technologies relying on efficient charge-exciton-photon conversion. Photoluminescence has been instrumental for this purpose with near-field techniques approaching 20 nm spatial resolution. However, molecular resolution is still out of reach and individual charge carriers cannot be addressed with these methods. In the present contribution we show how to overcome these limitations by using scanning tunneling microscopy (STM) to inject current at the atomic scale and Hanbury Brown-Twiss (HBT) interferometry to measure photon correlations in far-field electroluminescence.

Quantum systems like molecules or quantum dots cannot emit two photons at the same time which results in an antibunching of the emitted photon train and a dip in the photon-photon correlation function. Such single photon emitters are key elements for quantum cryptography and their miniaturization to the nanoscale would be desirable. This requires reproducible emitter separations typically below the optical diffraction limit and has imposed strong limitations on suitable structures and materials.

Using our HBT-STM setup on localized trap states in C_{60} multilayers we were able to study single photon emission at the ultimate molecular scale. Controlled injection allows us to generate excitons in C_{60} and probe them with charges one by one. We demonstrate electrically driven single photon emission and determine exciton lifetimes in the picosecond range. Monitoring lifetime shortening and luminescence saturation for increasing carrier injection rates provides access to charge-exciton annihilation dynamics with Ångstrom spatial resolution. Comparison with theory reveals exciton quenching efficiencies close to unity. Our approach introduces a unique way to study single quasi-particle dynamics on the ultimate molecular scale.

2:40pm **NS+EN+SS-TuA2 Low-Damage Etching Process for the Fabrication of GaAs based Light-Emitting Devices**, ***Cedric Thomas***, *A. Higo,* Tohoku University, Japan, *T. Kiba,* Hokkaido University, Japan, *Y. Tamura,* Tohoku University, Japan, *N. Okamoto, I. Yamashita,* Nara Institute of Science and Technology, Japan, *A. Murayama,* Hokkaido University, Japan, *S. Samukawa*, Tohoku University, Japan

Fabrication of quantum dots (QD) and their use for optical devices are still facing big challenges, for instance a high-density and three-dimensional array of QDs is hardly achieved. We report here the fabrication of stacked layers of GaAs QDs (called nanodisks, NDs) of less than 20 nm in diameter by a top-down approach and their optical characteristics when embedding in light emitting device.

The fabrication process consists of a bio-template [1] used to create a high density etching mask coupled to a low-damage etching process using neutral beam (NB) [2]. The bio-template is realized by a self-assembled monolayer (SAM) of proteins called ferritins (cage like proteins) of 12 nm outside diameter with a 7 nm iron oxide core. The proteins are functionalized with poly-ethylene glycol (PEG) to control the ferritin-to-ferritin distance and avoid any ND coupling after fabrication. After removing the protein shell by oxygen based treatment, a high-density (ca. $1x10^{11}$ cm^{-2}) nano-pattern of cores is used as etching mask. The NB etching consists of an inductively couple plasma chamber separated from the process chamber by a carbon electrode with a high aspect-ratio aperture array. Therefore, the charged particles are efficiently neutralized and the UV photons from the plasma almost completely screened

Stacks of GaAs and AlGaAs layers were grown by metalorganic vapor phase epitaxy (MOVPE), with a GaAs cap layer of a few nanometer thick. SAM of ferritins was done by spin-coating. After removing protein shell by oxygen annealing in vacuum, a hydrogen radical treatment was performed to remove to remove the oxide layer. Etching was then realized by pure chlorine NB. Regrowth of AlGaAs barrier was done by MOVPE. Finally, temperature dependence of photoluminescence emission and ND light emitting diode were measured and results discussed [3].

[1] I. Yamashita et al., Biochim. Biophys. Acta 1800 (2010) 845

[2] S. Samukawa et al., Jpn. J. Appl. Phys. 40 (2001) L997

[3] A. Higo et al., Sci. Reports 5 (2015) 9371

3:00pm **NS+EN+SS-TuA3 Surface Plasmon-Mediated Selective Deposition of Au Nanoparticles on Ag Bowtie Nano-Antennas**, ***Jingjing Qiu***, *D. Wei*, University of Florida

Utilizing intrinsic surface properties to selectively direct and control nanostructure growth on a nanostructure is fundamentally interesting and holds great technological promise. We observed a surface plasmon resonance (SPR)-induced selective deposition of gold nanoparticles (Au NPs) at the tip of a silver (Ag) bowtie nanostructure using 532 nm laser excitation. Nanoscale secondary ion mass spectrometry (NanoSIMS) was applied to chemically image the distribution of elements after deposition, reaching a spatial resolution of ~50 nm and an elemental analysis sensitivity of 50 ppm. Possible mechanisms underlying this selective deposition were proposed based on the experimental evidence and theoretical discrete dipole approximation (DDA).

3:20pm **NS+EN+SS-TuA4 Broadband Light Trapping in Nanopatterned Substrates for Photovoltaic and Photonic Applications**, ***Carlo Mennucci***, Department of Physics, University of Genova, Genova, Italy, *C. Martella, M.C. Giordano, D. Repetto, F. Buatier de Mongeot*, University of Genova, Italy

Here we report on self-organised nanofabrication method applied to substrates of relevance in the field of optoelectronic and photonics in view of light trapping applications. We demonstrate the optical functionalization of glass [1], crystalline semiconductor (GaAS and Si [2]) and TCO substrates recurring to a self-organised pattern formation based on low-energy Ion Beam Sputtering (IBS). High aspect ratio nanoscale features are formed recurring to defocused IBS through a self-organised sacrificial Au nanowire stencil mask. Ion-beam irradiation at grazing angle leads to the formation of quasi-periodic one-dimensional nanostructures with a characteristic lateral size in the range of 200nm and a root-mean-square roughness (σ) of the surface, measured by Atomic Force Microscope, ranging from 80 to 150nm.

These nanostructures confer broadband anti-reflective bio-mimetic functionality to crystalline semiconductor substrates (GaAs and Si [2]) as well as to glass and TCO substrates in the Visible and Near Infra-Red part of the spectrum. In fact, suppression of the reflected light intensity is due to high aspect ratio sub-wavelength features which leads to a progressive transition of the refractive index from the value of air to that of the substrate (index grading) analogous to that observed in the corneas of nocturnal moths. At the same time the patterned substrates have shown enhanced broadband light scattering due to the extended vertical dynamic of the surface corrugations with lateral size comparable or bigger than light wavelength. Moreover, Angular Resolved Scattering measurements has recently proved that nanostructured glasses can scatter light in the Visible and Near Infra-Red range of spectrum more efficiently and at wider angles with respect to standard Ashai-U substrates commonly used in optoelectronic device applications.

In order to asses the light trapping effect, identical amorphous thin film silicon solar cells (p–i–n single junctions) are grown on nano-patterned and on reference flat glass superstrates.Their performance is assessed by measuring their I–V characteristic and EQE under standard AM1.5g test conditions. The first encouraging results demonstrated that solar cells grown on patterned substrates with RMS roughness σ around 80 nm exhibit a 15% relative enhancement in photocurrent.

References:

[1] C. Martella, D. Chiappe, P. Delli Veneri, L.V. Mercaldo, I. Usatii, F.Buatier de Mongeot, Nanotechnology 24 (22), 225201 (2013).

[2] C. Martella, D. Chiappe, C. Mennucci, F. Buatier de Mongeot ,J.Appl.Phys. 115,194308 (2014).

4:20pm **NS+EN+SS-TuA7 *In Situ* Visualization of Intercalation-Driven Nanoparticle Phase Transitions using Plasmon-EELS**, ***Jennifer Dionne***, Stanford University **INVITED**

A number of energy-relevant processes rely on nanomaterial phase transitions induced by solute intercalation. However, many of these phase transitions are poorly understood, since observing them in nanomaterials – and in particular in individual nanoparticles – can be extremely challenging. This presentation will describe a novel technique to investigate intercalation-driven phase transitions in individual nanoparticles, based on *in-situ* environmental transmission electron microscopy (TEM) and plasmon electron energy loss spectroscopy (EELS). As a model system, this presentation will focus on the hydrogenation of palladium nanoparticles.

We use the plasmon-EEL signal at varying hydrogen pressures as a proxy for hydrogen concentration in the particle. First, we investigate the hydriding properties of single-crystalline particles, free from defects and grain boundaries, and free from elastic interactions with the substrate. We obtain single particle loading and unloading isotherms for particles ranging from approximately 10 nm to 100 nm, allowing us to address outstanding questions about the nature of phase transitions and surface energy effects in zero-dimensional nanomaterials. We find that hydrogen loading and unloading isotherms of single crystals are characterized by abrupt phase transitions and macroscopic hysteresis gaps. These results suggest that thermodynamic phases do not coexist in single-crystalline nanoparticles, in striking contrast with ensemble measurements of Pd nanoparticles. Then, we extend our single-particle techniques to explore the hydriding properties of polycrystalline and multiply-twinned nanoparticles, including Pd nanorods and icosahedra. In contrast to single crystalline nanoparticles, these particles exhibit sloped isotherms and narrowed hysteretic gaps. Based on these results, we develop a model to deconvolve the effects of disorder and strain on the phase transitions in nanoscale systems. Lastly, we describe techniques to generate high-resolution plasmon-EELS (and hence phase) maps of nanoparticles. These mapping studies promise unprecedented insight into the internal phase of nanomaterials, and can be complemented with diffraction and dark-field imaging studies. We will discuss how these results could be used to interpret the thermodynamics of Li-ion insertion in battery electrodes, hydrogen absorption in state-of the-art metal hydride catalysts, or ion exchange reactions in quantum dot syntheses.

5:00pm **NS+EN+SS-TuA9 Pulsed Laser-Induced Self-Assembly of Noble Metal Nanoparticles and an EELS Characterization**, ***Yueying Wu***, University of Tennessee, *G. Li,* University of Notre Dame, *C. Cherqui, N. Bigelow,* University of Washington, *J.P. Camden,* University of Notre Dame, *D. Masiello,* University of Washington, *J.D. Fowlkes,* Oak Ridge National Laboratory, *P.D. Rack*, University of Tennessee

Controlled nanoscale synthesis of plasmonic nanostructures based on noble metals is critical for realizing many important applications such as surface-enhanced Raman spectroscopy (SERS), subwavelength waveguides, plasmonically enhanced photovoltaics, and photocatalysis. Recently pulsed laser induced dewetting (PLiD) has been shown to be an intriguing self and directed assembly technique for elemental and alloyed metallic nanoparticles. The liquid-phase assembly takes place in single to tens of nanoseconds and is governed by liquid phase instabilities and hydrodynamics of liquid thin films which produce arrays of random or highly ordered nanoparticles. In our recent studies, the PLiD of un-patterned, as well as nanolithographically pre-patterned thin films of various shapes and sizes was investigated for the purpose of understanding how initial boundary conditions facilitate precise assembly. The resultant ultra-smooth and metastable nanoparticles (~20nm to 1μm) are expected to be ideal building blocks for plasmonic applications. Based on this, we present a study on the self-assembly of gold and silver alloy thin films and also provide a comprehensive characterization of the resultant nanoparticles using electron energy loss spectroscopy (EELS) and through simulation using full-wave electron-driven discrete-dipole approximation (e-DDA). The study provides for the first time a thorough mapping of the plasmonic modes of synthesized Au-Ag alloy nanoparticles over a large size range.

5:20pm **NS+EN+SS-TuA10 Flexible, Adaptive Optoelectronic Camouflage Skins Using Concepts Inspired by Cephalopods**, ***Cunjiang Yu***, University of Houston

Octopus, squid, cuttlefish and other cephalopods exhibit exceptional capabilities for visually adapting to or differentiating from the coloration and texture of their surroundings, for the purpose of concealment, communication, predation and reproduction. Long-standing interest in and emerging understanding of the underlying ultrastructure, physiological control and photonic interactions has recently led to efforts in the construction of artificial systems that have key attributes found in the skins of these organisms. In spite of several promising options in active materials for mimicking biological color tuning, such as cholesteric liquid crystals, electrokinetic and electrofluidic structures, colloidal crystals and plasmonics, existing routes to integrated systems do not include critical capabilities in distributed sensing and actuation.

The results reported here show that advances in heterogeneous integration and high performance flexible/stretchable electronics provide a solution to these critical sub-systems when exploited in thin multilayer, multifunctional assemblies. The findings encompass a complete set of materials, components, and integration schemes that enable adaptive optoelectronic camouflage sheets with designs that capture key features and functional capabilities of the skins of cephalopods. These systems combine semiconductor actuators, switching components and light sensors with inorganic reflectors and organic color-changing materials in a way that allows autonomous matching to background coloration, through the well-known working principle of each device.

Demonstration devices capable of producing black-and-white patterns that spontaneously match those of the surroundings, without user input or external measurement, involve multilayer architectures of ultrathin sheets of monocrystalline silicon in arrays of components for controlled, local Joule heating, photodetection and two levels of matrix addressing, combined with metallic diffuse reflectors and simple thermochromic materials, all on soft, flexible substrates. Systematic experimental, computational and analytical studies of the optical, electrical, thermal, and mechanical properties reveal the fundamental aspects of operation, and also provide quantitative design guidelines that are applicable to future, scaled embodiments.

5:40pm **NS+EN+SS-TuA11 Controlled Deposition of High Quality Nanocrystal Multilayer Structures for Optoelectronic Applications**, ***Sara Rupich***, *A.V. Malko, Y.N. Gartstein, Y.J. Chabal*, University of Texas at Dallas

In order to meet the world's growing energy demand, harvesting energy from the sun is necessary. While silicon-based solar cells remain the industry standard, hybrid Si/nanocrystal (NC) structures exhibit significant promise for the development of the next generation of photovoltaic devices. In most current NC-based photovoltaics, photons are absorbed, separated and extracted in the NC layer; however, conversion efficiencies are limited by interface quality and carrier mobility. Hybrid Si/NC structures offer an alternative approach. In these structures, light is absorbed in the NC layer and transferred via efficient excitonic radiative (RET) and non-radiative (NRET) energy transfer into the underlying Si substrate where charge extraction and collection occurs. In order to utilize such structures, the controllable deposition of tens of layers of NCs needs to be realized where the composition of each layer can be varied. While many techniques exist to deposit NCs on substrates (i.e. spin coating, dropcasting), these methods result in thick films with limited control over the composition. Composition controlled structures need to be built up one layer at a time.

Here, we present the controllable deposition of dense, NC multilayer structures on Si and SiO_2 substrates via evaporation-driven self-assembly at the air-liquid interface. Using a layer-by-layer approach, CdSe/ZnS NC multilayers were assembled, up to 15 layers in thickness. Extensive spectroscopic (UV-vis absorbance, photoluminescence (PL), ellipsometry) and microscopic (scanning electron microscopy and atomic force microscopy) characterization provided evidence for the successful deposition of high quality NC multilayers in each cycle. Additionally, the NCs were found to retain their quantum yields in the multilayers structures indicating that the deposition process does not introduce additional interface trapping centers and showing their promise for integration into optoelectronic devices. Using time-resolved PL measurements, a gradual increase in the average measured NC PL lifetime was observed as a function of layers for NC multilayers on Si surfaces. This behavior was confirmed by theoretical modeling and is indicative of the gradual reduction in ET efficiency as a function of distance and.

As this process is applicable to NCs of different size, shape and composition, the fabrication of band gap graded multilayers structures is possible, which would enable energy harvesting schemes based on directed energy flows.

6:00pm **NS+EN+SS-TuA12 Efficient Coupling of Visible Light to Thin Film Waveguides; FDTD Field Model Results for Nanometer Scale Graded Index/Waveguide Structures.**, ***Adam Lambert***, *E. Demaray*, AVS

Previous work utilizing Finite Difference Time Domain (FDTD) models with 20 nm resolution demonstrated normal incident plane wave AM 1.5 solar light could be coupled and concentrated into modes of a lateral duct with ~ 91% efficiency for tapered concentrator with spatially uniform refractive index. However, for efficient coupling and mode compression into high index waveguides in advanced devices, continuously graded index films on the order of 150-200nm with nonlinear profiles have been shown to be near ideal anti-reflective coatings which Antropy Technology can now produce at high volume using modern sputter coating processes. Such devices could be revolutionary not only in the field of photonics, but could also open the path for an wide variety of green energy and advanced lighting applications. This presentation focuses on current advances in the parametric investigation of nonlinear refractive index profiles and related sputter coating production processes. The FDTD problem solving framework provides the fully resolved time dependent propagation of the electromagnetic field, accounting for the nonlinear influence of subwavelength structures and allowing for detailed design of the thin film product. We are reporting resolution capabilities are in the 1-5nm range depending on the relevant length scales for the process. Quantification of power, absorption/heat, and other variables relevant to R&D can easily be extracted during post processing. Parallel Monte Carlo simulations predict the refractive index profile resulting from dual source, inline, biased pulse

DC sputter coating. The combination allows for highly accurate feasibility studies and front end process design. Both quantified numerical results as well as qualitative animations of the influence of the subwavelength devices are presented for both processes, as well as a detailed overview of the potential applications.

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