Electronic Materials and Photonics Division
Room 101A - Session EM+2D+AN+MI+MP+NS-TuA

Solar/Energy Harvesting and Quantum Materials and Applications

Moderators: Yohannes Abate, Georgia State University, Nicholas Strandwitz, Lehigh University

2:20pm EM+2D+AN+MI+MP+NS-TuA-1 Plasmonic Metasurface Electrodes for Excitonic Solar Cells., *Deirdre O'Carroll,* Rutgers, the State University of New Jersey **INVITED**

Excitonic organic solar cell technologies, while not currently competitive with inorganic-semiconductor analogues, can exhibit very small device embodied energies (due to comparatively low temperature and low energy-use fabrication processes), which is of interest for minimizing overall device cost and energy-payback time. To improve energy conversion efficiency in thin-film excitonic organic solar cells, light management using nanophotonic structures is necessary. Here, our recent work on improving light trapping in deeply-subwavelength excitonic organic semiconductor films using plasmonic metasurfaces will be presented. Numerous exciton-metasurface interaction phenomena, such as absorption-induced scattering, exciton-plasmon coupling and morphology-dependent surface plasmon light-trapping are observed to give rise to improved light trapping at different regions of the solar spectrum. Additionally, an approach to achieve the theoretical limits to the efficiency of excitonic organic photovoltaics (~22%) will be proposed that involves control of radiative recombination rate, and optimization of both photoluminescence quantum efficiency and photon recycling in organic semiconductor thin-films.

3:00pm EM+2D+AN+MI+MP+NS-TuA-3 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of an Inhomogeneous Semiconductor for Photovoltaics, *M Berg,* Sandia National Laboratories; *J Kephart, A Munshi, W Sampath,* Colorado State University; *Taisuke Ohta, C Chan,* Sandia National Laboratories

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals line up with respect to each other. Such electronic structures of materials can be determined using photoemission spectroscopy (PES). PES measurements, however, remain challenging for inhomogeneous materials with nano- to micrometer lateral dimensions due to its mesoscopic probing area, typically no less than several microns. Photoemission electron microscopy (PEEM) is a cathode lens electron microscopy technique that combines photoemission imaging with spectroscopic modes of operation to provide PES spectra from areas less than one micron in size. Here, we present PEEM studies of the electronic structure of polycrystalline cadmium telluride (CdTe) thin films, a test case to examine the applicability of this new microscopic approach to photovoltaic materials. Post-deposition $CdCl_2$ treatment of CdTe is known to increase photovoltaic efficiency. However, the precise chemical, structural, and electronic changes that underpin this improvement are still debated. In this study, PEEM was used to spatially map the vacuum level and ionization energy of CdTe films, enabling the identification of electronic structure variations between grains and grain boundaries. *In vacuo* preparation and inert environment transfer of oxide-free CdTe surfaces isolated the separate effects of $CdCl_2$ treatment and ambient oxygen exposure. Qualitatively, grain boundaries displayed lower work function and downward band bending relative to grain interiors, but only after air exposure of $CdCl_2$-treated CdTe. This study highlights the importance of probing the spatially varying electronic structure, elucidating the concurrent impacts of processing steps ($CdCl_2$ treatment and oxygen exposure) to develop a comprehensive picture of local electronic structure in an inhomogeneous semiconductor.

3:20pm EM+2D+AN+MI+MP+NS-TuA-4 Modification of Bandgap for Lead-Free Double Perovskite $Cs_2AgInCl_6$ with Bi Doping, *Hassan Siddique,* University of Science and Technology of China; *H Da, X Wang,* University of Science and Technology of China, China; *R Dai, Z Wang,* University of Science and Technology of China; *Z Ding, Z Zhang,* University of Science and Technology of China, China

Lead halide perovskites have the excellent luminescent properties but exist some vital disadvantages such as instability and Pb toxicity. Lead-free double perovskites draw attention due to a possible candidate for environment-friendly materials. Direct bandgap lead-free halide of $Cs_2AgInCl_6$ is one of them. [1] In this work Bi doping $Cs_2AgInCl_6$ (CAIC) was successfully prepared. Bi dopant above 15% CAIC can restrict the parity forbidden transition responding to sub absorption peak around 600 nm.[2] On the other hand, the intensity of photoluminescence enhances with the increasing Bi dopant and touches the maximum around 30% doping, then gradually loses its intensity with further doping due to the mechanism of the concentration quenching at room temperature. Bi doping in CAIC can also modify the band gap. The absorption spectra indicate that the band gap reduces from 3.10eV without Bi doping to 2.68eV for $Cs_2AgIn_{0.30}Bi_{0.70}Cl_6$. PL decay life time reveals the good intrinsic excitonic feature with less defect trappers [3]. Average life time for $Cs_2AgIn_{0.70}Bi_{0.30}Cl_6$ is 490 ns which is least among all other $Cs_2AgIn_{(1-x)}Bi_xCl_6$ doping. Thermogravimetric analysis (TGA) result reveals thermal stability of $Cs_2AgIn_{0.30}Bi_{0.70}Cl_6$ for the high-temperature 506ºC. The Bi doping can decrease the band gap, restrict defect states, enhance PL and improve stability; these good performances make $Cs_2AgIn_{(1-x)}Bi_xCl_6$ more suitable for optoelectronic properties.

4:20pm EM+2D+AN+MI+MP+NS-TuA-7 Optimized (Quantum) Photonics, *Jelena Vuckovic,* Stanford University **INVITED**

Photonics has numerous applications ranging from optical interconnects, classical and quantum computing, to sensing (such as LIDAR and AR), and imaging. However, the state of the art photonics is bulky, inefficient, sensitive to environment, lossy, and its performance is severely degraded in real-world environment as opposed to ideal laboratory conditions, which has prevented from using it in many practical applications. Therefore, it is clear that new approaches for implementing photonics are crucial.

We have recently developed a computational approach to inverse-design photonics based on desired performance, with fabrication constraints and structure robustness incorporated in design process [1,2]. Our approach performs physics guided search through the full parameter space until the optimal solution is reached. Resulting device designs are non-intuitive (see Figure), but are fabricable using standard techniques, resistant to temperature variations of hundreds of degrees, typical fabrication errors, and they outperform state of the art counterparts by many orders of magnitude in footprint, efficiency and stability. This is completely different from conventional approach to design photonics, which is almost always performed by brute-force or intuition-guided tuning of a few parameters of known structures, until satisfactory performance is achieved, and which almost always leads to sub-optimal designs.

Apart from integrated photonics, our approach is also applicable to any other optical and quantum optical devices and systems. In recent years, color centers in diamond and silicon carbide (SiC) have emerged as a possible platform for implementation of quantum circuits [3,4]. We demonstrate how such quantum hardware can also be optimized to be robust, efficient, and scalable.

References
[1] A. Piggott et al, *Nature Photonics* 9, 374–377 (2015)]

[2] L. Su et al, *ACS Photonics* ASAP (2018)

[3] J.L. Zhang et al, Nano Letters 18 (2), 1360-1365 (2018)

[4] M. Radulaski et al, Nano Letters 17 (3), 1782-1786 (2017)

5:00pm EM+2D+AN+MI+MP+NS-TuA-9 Optical Properties of Single Silicon Vacancies in 4H-SiC, *H Banks,* National Research Council Postdoc residing at the Naval Research Laboratory; *O Soykal,* Sotera Defense Solutions, Inc, residing at the Naval Research Laboratory; *S Pavunny, R Myers-Ward, D Gaskill, Samuel Carter,* U.S. Naval Research Laboratory

Defects in wide bandgap materials have generated substantial interest as promising systems for quantum information and quantum sensing due to bright, stable optical emission that is often coupled to long-lived spin states. One promising defect system is the silicon monovacancy in SiC (V_{Si}), which has a spin-3/2 ground state that can be optically polarized and

maintain long spin coherence times even at room temperature. SiC is an attractive material in terms of mature growth and fabrication technology and also has a low natural abundance of nuclear spins, which reduces spin dephasing. While significant work has been performed to study the spin properties of V_{Si} for ensembles and even single defects, the optical properties and their connection to the spin system are less developed. Here we report on high resolution optical spectroscopy of single V_{Si} defects, specifically V2 defects, at low temperatures. Using laser excitation spectroscopy, the zero phonon line (ZPL) transitions corresponding to the $m_s=\pm1/2$ and $m_s=\pm3/2$ spin states are resolved, with a linewidth down to 70 MHz and a splitting of 1 GHz. While there is significant variation in the transition energies from one defect to another, the splitting of these lines is very uniform. We also find that emission from the V2 defect under resonant excitation of these lines rapidly decays on two very different timescales. Slow decay on a 10 ms timescale is attributed to photoionization of V_{Si} and can be prevented by periodically exciting the defect with a second laser at 745 nm. Fast decay on a µs or shorter time scale occurs due to a combination of intersystem crossing and spin polarization of the ground state. A significant difference in the decay rates of the two transitions is observed, which gives rise to spin-dependent photoluminescence intensity and non-resonant optical spin polarization. These results further our understanding of the connection between the optical and spin properties of this defect system that are necessary to optically control and readout the spin system as well as to develop a spin-photon quantum interface.

5:20pm **EM+2D+AN+MI+MP+NS-TuA-10 Photoluminescence Studies on Patterned Silicon Vacancy Defects in Li Ion Implanted 4H-SiC for Scalable Quantum Device Applications**, *Shojan Pavunny*, U. S. Naval Research Laboratory; *S Carter, H Banks, R Myers-Ward, P Klein,* U.S. Naval Research Laboratory; *E Bielejec,* Sandia National Laboratories; *M DeJarld, A Bracker, E Glaser, D Gaskill,* U.S. Naval Research Laboratory

Recently, silicon vacancy defect centers (V_{Si}) in the CMOS compatible wide bandgap semiconductor SiC hexagonal polytypes have drawn great research interest for future applications in scalable quantum information and quantum sensing mainly due to their high electronic spin (S = 3/2) with a long coherence time at room temperature. Realization of future densely integrated quantum devices will greatly benefit from the ability to deterministically induce the desired V_{Si} density at the optimal location in the three-dimensional solid-state matrix with nanometer accuracy and excellent optical properties. With this motivation, we demonstrate targeted formation of arrays of V_{Si} ensembles as well as single defects in high-quality 4H-SiC epilayers by a direct, maskless focused ion beam implantation technique with a designed lateral separation of ~5 µm and a ~25 nm spot size. We have carried out high-resolution optical spectroscopy studies (E⊥c and E∥c) on these arrays, in which lithium ions are implanted at doses varying from $10^{12} - 10^{15}$ Li/cm² at a fixed energy of 100 keV to a depth of ~400 nm from the surface. Photoluminescence intensity and defect conversion yield with dose, photostability, fluorescence saturation, and V_1:V_1' intensity evolutions with temperature and excitation power were investigated. Results obtained from temperature dependent photoluminescence studies can provide key insights in the design and fabrication of scalable and reproducible three dimensional SiC quantum hybrid devices including photonic crystal cavities.

5:40pm **EM+2D+AN+MI+MP+NS-TuA-11 Processing of Cavities in SiC Material for Quantum Technologies**, *Rachael Myers-Ward*, *K Hobart, K Daniels, A Giles, M Tadjer, L Luna, F Kub, S Pavunny, S Carter, H Banks, E Glaser,* U.S. Naval Research Laboratory; *P Klein,* Sotera Defense Solutions; *K Qiao, Y Kim, J Kim,* Massachusetts Institute of Technology; *K Gaskill,* U.S. Naval Research Laboratory

Silicon carbide is a material of interest for quantum computing and sensing applications owing to deep point defect centers with long spin coherence times (which characterizes the lifetime of the qubit), specifically the V_{Si} [1], divacancies [2] and nitrogen-vacancy centers [3]. These spin qubits have been isolated and coherently controlled, where V_{Si} have T_2 coherence times up to 100 µs [4] and divacancies to 1 ms [2], making these two defects of most interest to date. While the current spin coherence times have been shown to be as long as 1 ms, further improvements are needed to fully realize the potential of SiC for quantum applications. In this work, we create V_{Si} in epitaxial SiC and investigate fabricating the layers into microstructures suitable for using the V_{Si} photoluminescence (PL) emission. We have found 4H-SiC epitaxial layers grown under standard growth conditions and with varying doping densities from 10^{14} to 10^{18} cm^{-3} have no measureable V_{Si} present, as determined by confocal PL. To introduce V_{Si}, we used 2 MeV electron irradiation in doses ranging from 0.75 to 75 kGy.

This results in V_{Si} PL ranging from single to ensemble emission within the confocal volume. Hence, we are able to tune the vacancy concentration.

In order to improve the indistinguishable photons from the V_{Si} and/or divacancies for real applications, photonic crystal cavities (PCC) are used to tune the emission energy [4]. Our PCC design consists of a planar array of cylindrical holes approximately 220 nm wide in a slab of SiC, ~300-500 nm thin having an area 50 x 50 µm², similar to [4]. To maximize the PCC quality factor, the slab should have a large index of refraction difference on the top and bottom; i.e., an air gap is desired under the slab. To achieve this goal, we have identified four fabrication methods to create the PCC. One of these techniques is to use remote epitaxy as an innovative approach which entails growing epitaxial graphene on a SiC substrate by means of Si sublimation. Silicon carbide is then grown on a monolayer of graphene to the desired film thickness [5]. This thin SiC layer is then transferred, facilitated by the weak van der Waal forces at the graphene/SiC substrate interface, to a substrate more amenable to cavity fabrication. All four fabrication methods will be presented in detail.

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6:00pm **EM+2D+AN+MI+MP+NS-TuA-12 Investigation of Localized Electronic structures of PbSe Quantum Dot Superlattice on a Highly Oriented Pyrolytic Graphite (HOPG)**, *Il Jo Kwak*, *S Ueda,* University of California at San Diego; *A Abelson, C Qian, M Law,* University of California, Irvine; *A Kummel,* University of California at San Diego

Lead-Chalcogenide quantum dots are of interest due to the facility of adjustment of their electrical and optical properties. Using a colloidal self-assembly technique, extended arrays of nanocrystal QDs superlattices can be generated. The quantum confinement within individual QDs in the superlattice is relaxed and delocalization of wave functions occurs due to coupling of the QDs. In the QD solids, bulk-like electronic bands with a bandwidth of 100~200 meV are expected to form which yield much higher carrier mobility and diffusion length compared to weakly-coupled QDs; however, the electronic properties of such highly ordered QD arrays are not fully understood. The local density of state of a highly ordered monolayer PdSe superlattice was investigated by low temperature scanning tunneling microscopy.

A monolayer of PbSe QDs was prepared using the Langmuir Schaefer deposition technique. First, oleate-capped PbSe QDs dispersed in hexane were drop casted onto diethylene glycol surface. After the hexane was evaporated, a (111) in-plane oriented polycrystalline FCC superlattice was formed on the diethylene glycol surface. NH$_4$SCN solution was applied onto the oleate-capped PbSe superlattice film. The injection of NH$_4$SCN initiates the ligand exchange and phase transformation from an FCC to a simple cubic structure superlattice. A monolayer QD superlattice was prepared on a HOPG substrate. Afterward, the HOPG sample was loaded into a commercial UHV scanning tunneling microscopy chamber with a base pressure of 1x10^{-10}torr. The sample was annealed to remove hydrocarbons and ligands from the surface. The topography of the QDs was observed with a tungsten tip. The STM images were acquired in constant current mode.

STM imaging showed the PbSe QD monolayer had 4-fold symmetry with an average inter QD spacing of 7nm. It is also found the height fluctuation of the QDs was 1nm indicating size variation of the QDs and imperfect crystal structure of the superlattice. Scanning tunneling spectroscopy was performed to investigate the electronic structure of the PdSe QDs using a variable z-mode with an external lock-in amplifier in the bias range of -2 to 2V. Single site STS showed resonant peaks from molecular orbitals of QDs before the ligand exchange process; however, the peaks were not observed after the ligand exchange due to necking between the QDs in the superlattice. In addition, the size of band gap was decreased as increasing the number of nearest neighboring QDs due to necking between QDs. Layer 2 QDs showed more p-type behavior than layer 1 QDs possibly due to the band bending effect at the interface of HOPG and QD superlattice.

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