2021 Spring Meeting Program
Hudson Mohawk AVS Chapter
Thursday May 6, 2021
4:00 – 6:00 PM

4.00 pm: Welcome / opening remarks: M. Hopstaken / V. Smentkowski

4.00 – 4.20 pm: Xiaolong Liu, Yi Xue Chong, Rahul Sharma, J. C. Séamus Davis**,** '*ATOMIC-SCALE VISUALIZATION OF ELECTRON-PAIR FLUIDS AND CRYSTALS*'

4.20- 4.40 pm: Iver J. Cleveland, Minh Tran, and Eray S. Aydil, '*PHYSICAL VAPOR DEPOSITION OF Yb-DOPED CESIUM LEAD HALIDE PEROVSKITES'*

4.40- 5.00: Minghua Zhang and Daniel Gall, '*EPITAXIAL GROWTH AND RESISTIVITY SIZE EFFECT OF MAX-PHASE Ti_4SiC_3(0001) LAYERS'*

5.00- 5.20: Benjamin Harrington, Alex Kaloyeros, and Spyros Gallis, *'Polarization-Dependent Visible Photoluminescence from Silicon Carbide Nanophotonic Structures'*

5.20- 5.40 pm: Minh N. Tran,[1] Iver J. Cleveland,[1] Gregory A. Pustorino,[1] and Eray S. Aydil[1], *'EFFICIENT NEAR-INFRARED EMISSION FROM LEAD-FREE YTTERBIUM-DOPED CESIUM BISMUTH HALIDE PEROVSKITE THIN FILMS*

5.40- 6.00: Ashley Maloney,' *Using Auger, EDS, and FIB to Detect, Identify, and Image Buried Metallic Particles'*

Zoom meeting details:
AVS Meetings Support is inviting you to a scheduled Zoom meeting.

Topic: AVS Hudson Mohawk Chapter Virtual Meeting
Time: May 6, 2021 04:00 PM EDT (US and Canada), check your timezone

Please contact Marco Hopstaken, marco_hopstaken@avs.org, for Zoom details.

ATOMIC-SCALE VISUALIZATION OF ELECTRON-PAIR FLUIDS AND CRYSTALS

Xiaolong Liu, Yi Xue Chong, Rahul Sharma, J. C. Séamus Davis

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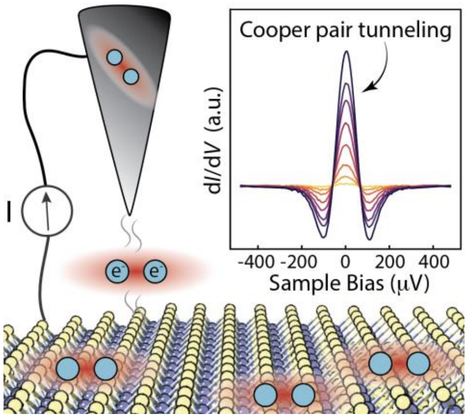
Pairing of electrons with opposite momenta takes place inside most conventional superconductors, leading to translationally invariant fluids of electron pairs. Meanwhile, electron pairs can form crystals known as pair density waves (PDWs) that break translational symmetry. Experimental evidence of PDWs, however, remains scarce due to the difficulty in imaging the superconducting condensate. In this talk, I will first introduce our recent discovery of a PDW state in a transition metal dichalcogenide, $NbSe_2$, using atomic-resolution scanned Josephson-tunneling microscopy (SJTM). Using the same SJTM technique, I will then discuss our capability in visualizing the velocity field and supercurrent density of electron-pair fluid flow around quantum vortices. Finally, I will share my perspective on applications of such novel techniques in other emerging quantum materials.



Schematic illustration of SJTM

PHYSICAL VAPOR DEPOSITION OF Yb-DOPED CESIUM LEAD HALIDE PEROVSKITES

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Inorganic halide perovskites have attracted attention with potential applications in high-efficiency solar cells. Recently, ytterbium-doped $CsPbCl_{3-x}Br_x$ (x<1) perovskite showed efficient quantum cutting, a process wherein photons absorbed at high energies (*e.g.*, > 2.5 eV) generate two photons with energies ~ 1.25 eV close to the silicon bandgap energy (1.1 eV). The mechanism for this quantum cutting process is not well understood, but the leading theories suggest that Pb vacancy defects in the perovskite efficiently trap excitons and transfer energy to two nearby Yb^{3+} ions, which subsequently emit from the Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition.[1] A thin layer of this material on a silicon solar cell can convert blue photons to two near-infrared (NIR) photons, decreasing energy losses due to the relaxation of the high-energy charge carriers to the band edges. In this way, silicon solar cell efficiencies can surpass the Quessier limit. The majority of reports on ytterbium-doped perovskites rely on nanocrystal or solution-based synthesis to make the materials.[2,3]

We are exploring physical vapor deposition, a solvent-free technique, to synthesize halide-perovskite thin films. Specifically, we deposited Yb-doped $CsPbCl_{3-x}Br_x$ films by co-evaporating CsCl, $PbCl_2$, $PbBr_2$, and $YbBr_3$ and controlling the flux of each using quartz crystal microbalances. Films were characterized with x-ray diffraction, scanning electron microscopy, optical absorbance, photoluminescence, and photoluminescence quantum yield measurements. Physical vapor deposition (PVD) by co-evaporation is a scalable approach to forming large-grained polycrystalline films. Specifically, we investigated the effects of Yb concentration, and post-deposition annealing at 350 ^oC in air and nitrogen environments on NIR PLQY of $CsPbCl_{3-x}Br_x$ films formed by PVD.

Yb-doped $CsPbCl_{3-x}Br_x$ films annealed at 350 ^oC for 2 hours emitted NIR PL at ~990 nm (Yb^{3+} $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition, 1.25 eV) with quantum yields (PLQY) exceeding 60%, when excited with photons with energies above the $CsPbCl_{3-x}Br_x$ bandgap. The PLQY depended strongly on the annealing environment. Surprisingly, films annealed in nitrogen-filled glove box had the lowest PLQY. Films annealed in the air had higher PLQY while films annealed in glove box first and then in the air had the highest. We hypothesize that grain growth in the glove box followed by oxygen passivation of remaining defects in the air is responsible for the high PLQYs in these films.

1. C. S. Erickson, M. J. Crane, T. J. Milstein, D. R. Gamelin, *J. Phys. Chem. C*, 2019, **123**, 12474-12484.
2. D. M. Kroupa, J. Y. Roh, T. J. Milstein, S. E. Creutz, D. R. Gamelin, *ACS Energy Lett.*, 2018, **3**, 2390-2395.
3. T. J. Milstein, D. M. Kroupa, D. R. Gamelin, *Nano Lett.*, 2018, **18**, 3792-3799.

EPITAXIAL GROWTH AND RESISTIVITY SIZE EFFECT OF MAX-PHASE $Ti_4SiC_3(0001)$ LAYERS

Minghua Zhang and Daniel Gall

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$Ti_4SiC_3(0001)$ layers with thickness 5.8 – 92.1 nm are deposited by magnetron co-sputtering from three elemental sources at 1000 °C onto 12-nm-thick TiC(111) nucleation layers on $Al_2O_3(0001)$ substrates. Their resistivities are measured *in situ* to experimentally verify the previously predicted low resistivity scaling for this MAX phase compound. The epitaxial growth exhibits an out-of-plane epitaxial relationship with Ti_4SiC_3 (0001) || TiC (111) || Al_2O_3 (0001), and an in-plane epitaxy with Ti_4SiC_3 $(10\bar{1}0)$ || TiC $(11\bar{2})$ || Al_2O_3 $(2\bar{1}\bar{1}0)$ and Ti_4SiC_3 $(10\bar{1}0)$ || TiC $(1\bar{2}1)$ || Al_2O_3 $(2\bar{1}\bar{1}0)$, as confirmed by X-ray diffraction θ-2θ scans, ω-rocking curves, and φ-scans. X-ray reflectivity analyses indicate a low surface roughness < 0.8 nm for all layers and X-ray photoelectron spectroscopy confirms a stoichiometric composition. The *in situ* measured resistivity increases from $\rho = 35.2\pm0.4$ to 37.5 ± 1.1 $\mu\Omega$cm with decreasing thickness $d = 92.1$ to 5.8 nm, and similarly from 9.5 ± 0.2 to 11.0 ± 0.4 $\mu\Omega$cm at 77 K. The measured resistivity scaling indicates only a minor effect of electron surface scattering with a room-temperature bulk resistivity $\rho_o = 35.1\pm0.4$ $\mu\Omega$cm in the basal plane and an effective mean free paths $\lambda = 1.1\pm0.6$ and 3.0 ± 2.0 nm at 293 and 77 K, respectively, assuming completely diffuse electron surface scattering. First-principles calculations predict a product $\rho_o\lambda = 19.3\times10^{-16}$ Ωm^2 which is 5 times larger than the measured temperature-independent effective $\rho_o\lambda = (3.8\pm2.1)\times10^{-16}$ Ωm^2. This is ascribed to a high surface scattering specularity $p = 0.8$. The overall results indicate that Ti_4SiC_3 is not directly applicable as interconnect material due to its relatively large ρ_o. However, the particularly small resistivity scaling with an effective λ that is over ten times smaller than that of Cu confirms the potential of MAX phase materials for high-conductivity narrow interconnects.

Polarization-Dependent Visible Photoluminescence from Silicon Carbide Nanophotonic Structures

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Semiconductor nanowires (NWs) have generated tremendous interest surrounding their use as a material platform in a multitude of important and exciting research fields. Nanowires exhibit anisotropic light absorption and emission properties, arising from the unique NW dimensionality and high dielectric contrast with its surrounding medium. Controlling light emission's directionality and polarization is essential for many photonic and optoelectronic-based applications, such as sensing, polarized light emission, and optical communication. Such optical characteristics can provide a significant advantage in the control and efficiency of emerging nanophotonic devices. For example, polarized emission can enable efficient coupling to optical cavities, an important technology for enhancing single-photon emission.

Herein, we investigate the anisotropic optical properties of ultrathin silicon carbide (SiC) NW-based array nanostructures using polarization-resolved photoluminescence (PL) spectroscopic techniques. To this end, we introduce a modular interface to our micro-PL spectroscopy setup to enable automated - highly repeatable measurements, where the same positions along the NW sample can be probed across multiple trials. This upgrade benefits current and future PL spectroscopic measurements for our samples. Furthermore, we demonstrate that the highly ordered and uniform nature of our ultrathin SiC NW arrays enables detection of NW-ensemble polarization effects, while allowing for flexibility in the fabricated NW geometry without compromising their polarization properties. The NWs exhibit high polarization anisotropy, with preferential absorption along their long axis. Accordingly, SiC NW-based arrays have the potential to be a tunable material platform towards the fabrication of polarization-sensitive nanodevices, such as polarized photodetectors and light sources.

EFFICIENT NEAR-INFRARED EMISSION FROM LEAD-FREE YTTERBIUM-DOPED CESIUM BISMUTH HALIDE PEROVSKITE THIN FILMS

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All-inorganic metal halide perovskites have attracted significant attention for applications as solar cells, light-emitting diodes, and photodetectors because they have strong and tunable absorptions and emissions. Lead-based perovskites have been the focus of many studies because they perform well in these applications, but lead is toxic. Bismuth-based halide perovskites are non-toxic alternatives to widely researched lead-containing halide perovskites for optoelectronics. Cesium bismuth bromide, in particular, may have suitable optical properties, but optical absorption and photoluminescence (PL) data reported to date are contradictory. We resolved these literature discrepancies and showed that $Cs_3Bi_2Br_9$ thin films deposited by physical vapor deposition (PVD) via coevaporation of CsBr and $BiBr_3$ show absorption and emission peaks at 433 and 472 nm, respectively. Peak location and lineshapes of blue-shifted absorption and emission previously reported and attributed to quantum confinement in $Cs_3Bi_2Br_9$ nanocrystals could be reproduced in $BiBr_3$ solutions in different solvents even without any $Cs_3Bi_2Br_9$. This suggests that high photoluminescence quantum yield (PLQY) and blue-shifted emissions reported below 472 nm may be originating from unreacted precursors and impurities in nanocrystal dispersions rather than from $Cs_3Bi_2Br_9$. We also doped $Cs_3Bi_2Br_9$ films with Yb to investigate the possibility of quantum cutting, generation of *two* near-infrared (NIR) photons (1.25 eV) from each ultraviolet or blue photon absorbed at energies >2.5 eV. Coating silicon solar cells with a material that can achieve quantum cutting with PLQY approaching 200% (2 photons for every high energy photon) has the potential to increase the silicon solar cell efficiencies above the Quessier limit, 33%. The addition of Yb that can substitute up to 50% of the Bi in $Cs_3Bi_2Br_9$ leaves the $Cs_3Bi_2Br_9$ structure unchanged and results in NIR Yb^{3+} $^2F_{5/2} \rightarrow$ $^2F_{7/2}$ emission (1.25 eV) with 14.5% quantum yield. A PLQY of 14.5% from Yb-doped $Cs_3Bi_2Br_9$ is promising because undoped $Cs_3Bi_2Br_9$ is otherwise not emissive due to rapid nonradiative recombination: the highest reliably measured visible PLQY in the literature is only 0.2%. Despite this, energy transfer from $Cs_3Bi_2Br_9$ to Yb appears to compete efficiently with nonradiative recombination and results in a 14.5% quantum yield. Moreover, NIR emission decreases sharply when the perovskite host's bandgap is reduced below 2.5 eV, twice the Yb^{3+} emission energy, by substituting bromine with iodine, raising the possibility that the emission mechanism may involve quantum cutting. This also raises the tantalizing possibility that $Cs_3Bi_2Br_9$ could be a potential lead-free quantum cutting material for solar spectrum shaping to increase solar cell efficiency.

Using Auger, EDS, and FIB to Detect, Identify, and Image Buried Metallic Particles

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Physical Electronics

Auger Electron Spectroscopy (AES) is a powerful analytical tool that provides quantitative elemental information from surfaces of solid materials. The average depth of analysis for an AES measurement is approximately 5 nm with lateral spatial resolution as small as 8 nm. The information AES provides about surface layers or thin film structures is important for many industrial and research applications where surface or thin film composition plays a critical role in performance including: nanomaterials, photovoltaics, catalysis, corrosion, adhesion, semiconductor devices and packaging, magnetic media, display technology, and thin film coatings used for numerous applications.

In this presentation, defect sites present on a Ti passivated Al sheet sample were identified and analyzed using a PHI 710 scanning Auger nanoprobe equipped with a 25kV Schottky field emission electron gun and a coaxial Cylindrical Mirror Analyzer (CMA). We demonstrate the use of AES in conjunction with a focused ion beam (FIB) to produce site specific imaging of microscale features beneath a sample surface. The combination of the two techniques allows for high spatial resolution analysis of buried particles and defects. This information can be very useful in helping to determine important parameters such as the origin of defects, corrosion mechanisms, coating problems, etc. We will highlight the advantages of FIB milling compared to traditional depth profiling. Energy dispersive x-ray spectroscopy (EDS) is also a powerful complementary technique to Auger analysis as it provides information from much deeper in the sample surface (few µm). With the combination of AES, FIB, and EDS, we show that buried metal particles can be first located and characterized with EDS, followed by the subsequent FIB milling and Auger spectroscopy of the particles. Auger's surface sensitivity and superior spatial resolution were then used to characterize the true composition and morphology of the freshly exposed particle.