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Title: Imaging Non-equilibrium Hot Carrier Dynamics in 2D Materials and Their Heterostructures with Scanning Ultrafast Electron Microscopy - Novel Functional Materials
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Submitted By: Bolin Liao Email: bliao@ucsb.edu
Phone: (617) 852-5995

STEM Degrees: 0 **STEM Participants:** 6

Major Goals: Background: Photocarrier dynamics in emerging low-dimensional and quantum materials are not only crucial for the development of next-generation photovoltaic cells, photo-sensors and other optoelectronics devices, but also of fundamental interest for understanding the non-equilibrium coupling of unusual electron and phonon states. Immediately after electron-hole pairs are photo-excited in semiconductors, they are transiently in a highly non-equilibrium state and possess excessive kinetic energy (effectively described by a high electronic temperature of thousands of degrees). In this short-lived state (femtosecond to picosecond level), the hot photocarriers can exhibit unusual properties, including superdiffusion with a diffusivity several orders of magnitude higher than the equilibrium value. This hot carrier transport effect is further amplified in two-dimensional materials due to the limited phase space for electron-phonon interaction that cools down the hot photocarriers. If this hot carrier transport regime can be effectively probed, modeled, and harnessed, devices with significantly enhanced efficiency and performance can be designed. For example, it has been proposed that if the initial kinetic energy of the hot photocarriers can be collected by a photovoltaic cell, a much higher power conversion efficiency can be achieved than the standard Shockley-Queisser limit. Effective capture of the hot photocarrier's excessive kinetic energy has also been predicted to greatly boost the sensitivity of photosensors. Furthermore, more efficient transport of the photocarriers in the "hot" regime can, in general, improve the efficiency of optoelectronic devices. All of these applications are highly relevant to DoD's interest. However, a major obstacle is that conventional spectroscopic methods to probe photoresponse of materials are intrinsically limited in their temporal and/or spatial resolution to directly map photoexcited carrier dynamics in emerging materials. Currently hot photocarrier dynamics are almost exclusively studied by ultrafast optical pump-probe spectroscopic methods. Although these methods can provide high temporal resolution (femtosecond and beyond), they are intrinsically limited in their spatial resolution by the optical diffraction. The best spatial resolution that can be attained is on the order of the optical wavelength used, typically hundreds of nanometers. This is insufficient to capture the initial diffusion process of the photoexcited hot carriers. In particular, a combination of sub-picosecond time resolution and nanometer spatial resolution is highly desirable to match the intrinsic time and length scales of the microscopic energy carrier transport and interaction. This combined high spatial and temporal resolution is also necessary to characterize emerging materials, such as two-dimensional materials, that can only be fabricated with high quality in relatively small forms (thin films or flakes). Furthermore, device applications would eventually require fabrication and characterization of heterostructures (junctions and interfaces) formed by 2D materials with a much smaller length scale on the nanometer level. To overcome these limits, a fundamentally different probe mechanism and the corresponding instrumentation need to be developed.

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Goals of this Project: The overarching goal of this project is the develop the scanning ultrafast electron microscope (SUEM) facility at UCSB and apply SUEM to study photocarrier dynamics in emerging materials including two-dimensional materials and their heterostructures. SUEM is an emerging technique that combines the temporal resolution of femtosecond lasers and the spatial resolution of a scanning electron microscope (Figure 1). The key concept is to generate short electron pulses (with sub-picosecond durations) by illuminating a photocathode using femtosecond laser pulses via the photoelectric effect. The short electron pulses are subsequently accelerated to high energies (up to 30 keV in our system) and focused onto the sample surface. These short high-energy electron pulses have a wavelength below a nanometer and thus can in principle achieve much higher spatial resolution than optical methods, while maintaining a high temporal resolution. Due to the requirement of a dedicated femtosecond laser and an SEM, this is a high-risk-high-payoff major instrumentation development project. We plan to build a fully operational SUEM setup at UCSB within the first two years of the project and apply SUEM to directly image hot photocarrier dynamics in emerging materials and their heterostructures. We believe the combined high spatial-temporal resolution can help elucidate the physical nature of the hot carrier superdiffusion immediately after photoexcitation. To achieve this goal, however, instrumentation development alone is not sufficient. As a nascent technique, SUEM still lacks a solid theoretical foundation on the physical mechanisms that contribute to the image contrast. Simulation tools are also lacking that can accurately describe the spatial-temporal dynamics of photoexcited hot carriers. To facilitate the interpretation of the SUEM observations, we also aim to develop accompanying theory and simulation tools, particularly on understanding electron-phonon interactions in two-dimensional materials and the impact of photoexcitation on the secondary electron emission processes.

Detailed goals include:

1. Develop and benchmark a fully functional SUEM setup at UCSB, including mechanistic studies of the SUEM contrast mechanisms. In particular, we will elucidate the relative contributions to the SUEM contrast from bulk photoexcitation effects and the surface photovoltage effect.

2. Develop first-principles simulation tools to understand electron-phonon interaction in two-dimensional materials, particularly their impact on thermal transport and hot photocarrier cooling processes.

3. Apply SUEM to directly visualize photocarrier dynamics in two-dimensional materials and their heterostructures, and potentially other emerging materials of interest. In particular, we aim to elucidate the physical mechanisms underlying the superdiffusion behavior of photocarriers in these materials and the photocarrier dynamics around heterojunctions formed by 2D materials.

Accomplishments: The most significant accomplishment of this project is the development of a state-of-the-art and fully operational SUEM at UCSB. This is the only operational SUEM in a U.S. university right now. We have also assisted the development of SUEMs in Sandia National Laboratory (A. Talin group) and Oak Ridge National Laboratory (B. Lawrie group). We have systematically benchmarked our SUEM setup and demonstrated 1 picosecond time resolution and 10 nm spatial resolution, a significant improvement over the optical diffraction limit. We have further applied SUEM to study photocarrier dynamics in 2D materials and their heterostructures, and many emerging materials beyond 2D materials. Our pioneering SUEM studies have generated detailed insights into the transport process of hot photocarriers in distinct material systems (2D vs 3D, inorganic vs organic). In the development process, we have produced 9 journal papers (3 under review), including our leading efforts to apply SUEM to image photo-induced dynamics in a wide range of materials: 2D MoS2 heterostructure (Nano Letters, 2021), semiconducting polymer (Nano Letters, 2021), boron arsenide single crystals (under review in Matter) and hybrid halide perovskites (under review in Science). In addition to these proof-of-technique demonstrations of SUEM, we also focused on developing fundamental understanding of the SUEM contrast, including the role of the surface photovoltage effect (JPCA, 2020) and a Monte Carlo code that can directly simulate the effect of photo-excitation on secondary electron emission processes (under review in JAP). Accompanying the experimental development, we also developed first-principles simulations of electron-phonon interactions in 2D materials (PRB, 2019). In addition to publications, during this award period, PI Liao has given 19 invited talks and seminars to disseminate our results. More detailed descriptions of the accomplishments are listed below:

1. With SUEM, we directly visualized the charge separation behavior at a junction formed by 2D materials with

different thicknesses for the first time (Figure 2). The goal of this work is to understand how heterostructures formed by 2D materials interact with photoexcited electron-hole pairs and how this interaction can be potentially utilized in future optoelectronic devices based on 2D materials. Unlike their 3D counterparts with ubiquitous surface defects and dangling bonds, 2D materials have naturally passivated surfaces so the surface potential of 2D materials can be sensitively engineered for device applications. One concept is the so-called "band-bending junctions" , where 2D materials with different surface potentials are joined together. We fabricated such a device by forming junctions between MoS2 regions with different thicknesses. We took advantage of the unique spatial-temporal resolution of SUEM to directly image how this band-bending junction interacts with photoexcited hot carriers. Surprisingly, we observed that this junction, lacking a built-in potential as in conventional p-n junctions, can efficiently separate photoexcited electrons and holes, indicating potential use of this structure for solar cells and photodetectors. With complementary ARPES and Kelvin probe characterizations, we attributed this charge-separation behavior to the different surface potentials at the two regions that drives lateral transport of electrons and holes. This is the first experimental demonstration of an operational band-bending junction. This band-bending junction may find applications in future electronic devices based on 2D materials.

2. We applied SUEM to image the photo-induced elastic response in a semiconducting polymer (P3HT) and we correlated this photo-response to the strong modulation of its electronic structure due to photo-induced strain (Figure 3). The goal of this work is to image the photoexcited charged species in organic conductors that can differ from those in inorganic materials. We also aim to demonstrate the capability of SUEM to characterize a wide range of materials including organic ones. Two main physical mechanisms in semiconducting polymers are investigated in this work: the strong photon-lattice coupling that leads to a large photo-induced strain and the impact of the strain on the electronic properties of the semiconducting polymer. Using SUEM, we observed characteristic ring-shaped contrast in P3HT that we attributed to strain-induced modulation of its electronic structure. This study demonstrates the capability of SUEM to characterize organic materials and also provides new insight into the interaction between elastic strain and electronic properties of semiconducting polymers.

3. We used SUEM to characterize other emerging materials with unusual photocarrier dynamics. For example, we measured the photo-induced hot carrier diffusion in single crystals of boron arsenide (Figure 4), a III-V semiconductor that has attracted a lot of attention recently due to its ultrahigh thermal conductivity, which has been attributed to a large frequency gap between acoustic and optical phonon branches that limits the phonon scattering channels. We hypothesized that the same feature would to a significant phonon bottleneck effect that restricts the cooling of photoexcited hot carriers: when the hot photocarriers transfer their energy to optical phonons, these optical phonons cannot efficiently cool down due to their isolation from the acoustic branches. Due to the small size of available boron arsenide single crystals, it is challenging to characterize charge transport using conventional methods. With SUEM, we are able to directly visualize the initial fast diffusion process of the photo-excited hot carriers and extract the hot carrier transport time. The unusually long hot carrier lifetime (greater than 200ps) signals that cubic boron arsenide can be a promising candidate material for hot-carrier based photovoltaic, photosensing and photocatalytic applications. We also applied SUEM to probe in situ photo-induced ion migration in organic-inorganic hybrid halide perovskites (Figure 5). These perovskites are highly promising photovoltaic materials due to their high power conversion efficiency but suffer from material instability, partly due to its low ion migration barrier. SUEM is uniquely suitable to quantify photo-induced ion migration effect in these hybrid perovskites. We observed long-range and significant migration of the halide ions under illumination, as well as short-range migration of other ions. We correlated the ion migration to the local change of cathodoluminescence from the perovskites that can have profound influence on the performance of solar cells based on these materials.

4. We made several fundamental contributions to understanding the contrast mechanisms of SUEM: we designed a benchmarking experiment to prove that the surface photovoltage effect, where the band bending on the surface of a semiconductor can be altered by light, can lead to additional contrast in the SUEM images (JPCA, 2020). Although this effect complicates the image interpretation, it also indicates that SUEM can be applied to probe the surface band dynamics; we developed a Monte Carlo simulation code that can predict the change of secondary electron yield as a result of photo-excitation (JAP, under review). This code will play a fundamental role in further developing and understanding SUEM.

5. Accompanying the experimental development, we also developed first-principles simulation tools to understand the impact of electron-phonon interaction on phonon transport and hot-carrier cooling in 2D materials. In particular, our calculation has shown that the thermal conductivity of 2D materials can be controlled by electron-phonon

interactions induced by an external electrostatic gate, a phenomenon that can potentially lead to solid-state thermal switching devices (PRB 2019).

Training Opportunities: The award was used to directly support one graduate student (Usama Choudhry) who has led the SUEM development project at UCSB. This project provided the opportunity for him to be trained systematically in ultrafast optics, electron microscopy and condensed matter physics. The student is now in his fifth year and will finish his Ph.D. degree next year. He will pursue a postdoctoral position in related fields and eventually plans to become a professor or a researcher in a National Laboratory. In addition, this award made the SUEM development possible, which further enabled training opportunities for other students and postdocs whose research project involved the utilization of SUEM. For example, Dr. Taeyong Kim, who led the SUEM characterization of semiconducting polymers, has recently accepted a faculty position in Seoul National University, a top institute in South Korea. Another two graduate students have received systematic training in ultrafast optics supported by this award (Melanie Adams, Alex Ackerman). We have also provided research opportunities to undergraduate interns from underrepresented minority communities each summer.

Results Dissemination: This project has produced 9 journal papers (3 under review), 19 invited seminar/talks and 3 contributed conference presentations. Supported by this award, PI Liao also served as the sole editor of a multi-contributed book on Nanoscale Energy Transport, published by Institute of Physics (IOP) Publishing.

Honors and Awards: 1. Hellman Family Faculty Fellowship Award, 2020

2. NASA Early Career Faculty Award, 2021

3. AFOSR Young Investigator Award, 2022

4. ONR Young Investigator Award, 2022

5. Phase 1 Finalist, DoD xTech HBCU & MSI Challenge, 2021

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PARTICIPANTS:

Participant Type: PD/PI
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Article Title: Controlling thermal conductivity of two-dimensional materials via externally induced phonon-electron scattering
Authors: Shengying Yue, Runqing Yang, Bolin Liao
Keywords: two-dimensional materials, thermal conductivity, thermal switch
Abstract: While the properties of surfaces and interfaces are crucial to modern devices, they are commonly difficult to explore since the signal from the bulk often masks the surface contribution. Here we introduce a methodology based on scanning electron microscopy (SEM) coupled with a pulsed laser source, which offers the capability to sense the topmost layer of materials, to study the surface photovoltage (SPV) related effects. This method relies on a pulsed optical laser to transiently induce an SPV and a continuous primary electron beam to produce secondary electron (SE) emission and monitor the change of the SE yield under laser illumination. We observe contrasting behaviors of the SPV-induced SE yield change on n-type and p-type semiconductors. We further study the dependence of the SPV-induced SE yield on the primary electron beam energy, the optical fluence, and the modulation frequency of the optical excitation, which reveal the details of the dynamics of the photocarriers in the pres
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Article Title: Probing Surface Photovoltage Effect Using Photoassisted Secondary Electron Emission
Authors: Yu Li, Usama Choudhry, Jeewan Ranasinghe, Alex Ackerman, Bolin Liao
Keywords: ultrafast electron microscopy, surface photovoltage effect, photocarrier dynamics
Abstract: While the properties of surfaces and interfaces are crucial to modern devices, they are commonly difficult to explore since the signal from the bulk often masks the surface contribution. Here we introduce a methodology based on scanning electron microscopy (SEM) coupled with a pulsed laser source, which offers the capability to sense the topmost layer of materials, to study the surface photovoltage (SPV) related effects. This method relies on a pulsed optical laser to transiently induce an SPV and a continuous primary electron beam to produce secondary electron (SE) emission and monitor the change of the SE yield under laser illumination. We observe contrasting behaviors of the SPV-induced SE yield change on n-type and p-type semiconductors. We further study the dependence of the SPV-induced SE yield on the primary electron beam energy, the optical fluence, and the modulation frequency of the optical excitation, which reveal the details of the dynamics of the photocarriers in the pres
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Article Title: Spatiotemporal imaging of thickness-induced band bending junctions
Authors: Joeson Wong, Artur Davoyan, Bolin Liao, Andrey Krayev, Kiyoung Jo, Eli Rotenberg, Aaron Bostwick, C
Keywords: band bending, two-dimensional, semiconductors, photovoltaics, ultrafast, spatiotemporal imaging
Abstract: van der Waals materials exhibit naturally passivated surfaces and an ability to form versatile heterostructures to enable an examination of carrier transport mechanisms not seen in traditional materials. Here, we report a new type of homojunction termed a “band-bending junction” whose potential landscape depends solely on the difference in thickness between the two sides of the junction. Using MoS2 on Au as a prototypical example, we find that surface potential differences can arise from the degree of vertical band bending in thin and thick regions. Furthermore, by using scanning ultrafast electron microscopy, we examine the spatiotemporal dynamics of charge carriers generated at this junction and find that lateral carrier separation is enabled by differences in the band bending in the vertical direction, which we verify with simulations. Band-bending junctions may therefore enable new optoelectronic devices that rely solely on band bending arising from thickness variations.
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Article Title: Scanning ultrafast electron microscopy reveals photovoltage dynamics at a deeply buried p-Si/SiO2 interface
Authors: S. R. Ellis, N. C. Bartelt, F. Léonard, K. C. Celio, E. J. Fuller, D. R. Hughart, D. Garland, M. J. Marinella,
Keywords: scanning ultrafast electron microscopy, photocarrier dynamics, buried interface
Abstract: The understanding and control of charge carrier interactions with defects at buried insulator/semiconductor interfaces is essential for achieving optimum performance in modern electronics. Here, we report on the use of scanning ultrafast electron microscopy (SUEM) to remotely probe the dynamics of excited carriers at a Si surface buried below a thick thermal oxide. Our measurements illustrate a novel SUEM contrast mechanism, whereby optical modulation of the space-charge field in the semiconductor modulates the electric field in the thick oxide, thus affecting its secondary electron yield. By analyzing the SUEM contrast as a function of time and laser fluence we demonstrate the diffusion mediated capture of excited carriers by interfacial traps.
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Article Title: Transient strain induced electronic structure modulation in a semiconducting polymer imaged by scanning ultrafast electron microscopy
Authors: Taeyong Kim, Saejin Oh, Usama Choudhry, Carl Meinhart, Michael Chabinyc, Bolin Liao
Keywords: scanning ultrafast electron microscope, photocarrier dynamics, semiconducting polymer
Abstract: Understanding the opto-electronic properties of semiconducting polymers under external strain is essential for their applications in flexible devices. While prior studies have highlighted the impact of static and macroscopic strains, assessing the effect of a local transient deformation before structural relaxation occurs remains challenging. Here, we employ scanning ultrafast electron microscopy (SUEM) to image the dynamics of a photo-induced transient strain in the semiconducting polymer poly(3-hexylthiophene) (P3HT). We observe that the photo-induced SUEM contrast, corresponding to the local change of secondary electron emission, exhibits an unusual ring-shaped profile. We attribute the observation to the electronic structure modulation of P3HT caused by a photo-induced strain field owing to its low modulus and strong electron-lattice coupling, supported by a finite-element analysis. Our work provides insights into tailoring opto-electronic properties using transient mechanical defo
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Article Title: Characterizing Microscale Energy Transport in Materials with Transient Grating Spectroscopy
Authors: Usama Choudhry, Taeyong Kim, Melanie Adams, Jeewan Ranasinghe, Runqing Yang, Bolin Liao
Keywords: energy transport, transient grating spectroscopy, ballistic phonon transport, spin transport
Abstract: Microscale energy transport processes are crucial in microelectronics, energy harvesting devices, and emerging quantum materials. To study these processes, methods that can probe transport with conveniently tunable length scales are highly desirable. Transient grating spectroscopy (TGS) is such a tool that can monitor microscale energy transport processes associated with various fundamental energy carriers including electrons, phonons, and spins. Having been developed and applied for a long time in the chemistry community, TGS has regained popularity recently in studying different transport regimes in solid-state materials. In this Tutorial, we provide an in-depth discussion of the operational principle and instrumentation details of a modern heterodyne TGS configuration from a practitioner’s point of view. We further review recent applications of TGS in characterizing microscale transport of heat, charge, spin, and acoustic waves, with an emphasis on thermal transport.
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Article Title: Persistent hot carrier diffusion in boron arsenide single crystals imaged by ultrafast electron microscopy
Authors: Usama Choudhry, Fengjiao Pan, Taeyong Kim, Ryan Gnabasik, Geethal Amila Gamage, Haoran Sun, A
Keywords: ultrafast electron microscopy, photocarrier diffusion, boron arsenide
Abstract: Cubic boron arsenide (BAs) is promising for microelectronics thermal management due to its high thermal conductivity. Recently, its potential as an optoelectronic material is also being explored. However, it remains challenging to measure its photocarrier transport properties due to small sizes of available high-quality crystals. Here, we use scanning ultrafast electron microscopy (SUEM) to directly visualize the diffusion of photoexcited charge carriers in BAs single crystals. Surprisingly, we observed ambipolar diffusion at low optical fluence with persistent hot carrier dynamics for above 200 picoseconds, which can be attributed to the large frequency gap between acoustic and optical phonons, the same feature that is responsible for the high thermal conductivity. At higher optical fluence, we observed spontaneous electron-hole separation. Our results show BAs is an attractive optoelectronic material combining high thermal conductivity and excellent photocarrier transport properties.
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Article Title: Impact of photoexcitation on secondary electron emission: a Monte Carlo study
Authors: Wenkai Ouyang, Xiangying Zuo, Bolin Liao
Keywords: secondary electron emission, ultrafast electron microscopy, Monte Carlo simulation
Abstract: Understanding the transport of photogenerated charge carriers in semiconductors is crucial for applications in photovoltaics, optoelectronics and photo-sensing. While recent experimental studies using scanning ultrafast electron microscopy (SUEM) have demonstrated that the local change of the secondary electron emission induced by photoexcitation enables direct visualization of the photocarrier dynamics in space and time, the origin of the corresponding image contrast still remains unclear. Here, we investigate the impact of photoexcitation on secondary electron emissions from semiconductors using a Monte Carlo simulation aided by time-dependent density functional theory (TDDFT). Particularly, we examine two photo-induced effects: additional inelastic electron scattering in the bulk due to photocarriers, and the surface photovoltage (SPV) effect. Using doped silicon as a model system and focusing on primary electron energies below 4 keV, we found that the SPV effect plays a predominant
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Article Title: In situ imaging of photo-induced ion migration in organic-inorganic hybrid halide perovskites
Authors: Taeyong Kim, Soyeon Park, Vasudevan Iyer, Qi Jiang, Usama Choudhry, Ryan Gnabasik, Benjamin La
Keywords: halide perovskite, ion migration, in situ imaging, photovoltaics
Abstract: Organometallic halide perovskite solar cells (PSCs) exhibiting electronic properties comparable to those of inorganic materials are of fundamental and practical interest, owing to visible absorption, tunability, and low manufacturing cost. Recent works have reported unusual the current–voltage characteristics hysteresis occurring in the PSCs under light soaking, which can affect the device performance along with the lifetime for the long term stability. While prior extensive investigations have suggested that ion migration is a plausible origin of the hysteresis, detailed understanding of the microscopic transport properties of the ion has been missing. Here, we report an in-situ elemental mapping of the ions to study the migration effect under the light, combining energy-dispersive X-ray spectroscopy (EDS), secondary electron imaging and cathodoluminescence mapping.
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Partners

,

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Signature: Bolin Liao
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Supplementary Material

(Detailed description and context of each figure is included in the "Accomplished" section)

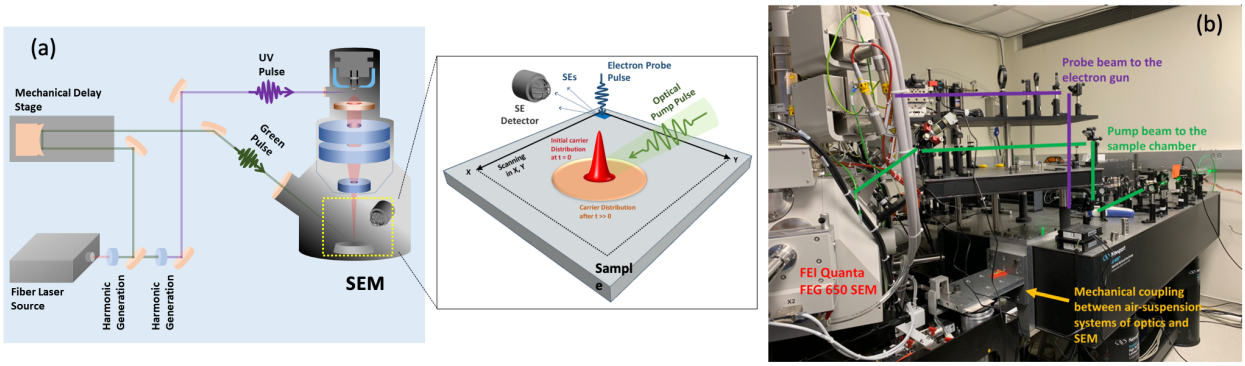

Figure 1. Description of the SUEM Instrumentation Project. Panel (a) shows a schematic of the SUEM setup. The output from a femtosecond laser is split into a pump beam and a probe beam. The pump beam is frequency converted to 515 nm (green) and focused onto the sample to initiate a photophysical process. The probe beam is converted to 257 nm (UV) and focused onto the electron gun (a ZrO-coated tungsten tip) to generate short electron pulses. The pulsed electron beam is accelerated to 30 keV and focused onto the surface of the sample to image the surface changes as a result of the optical pump pulse. Panel (b) shows a picture of the actual SUEM setup at UCSB.

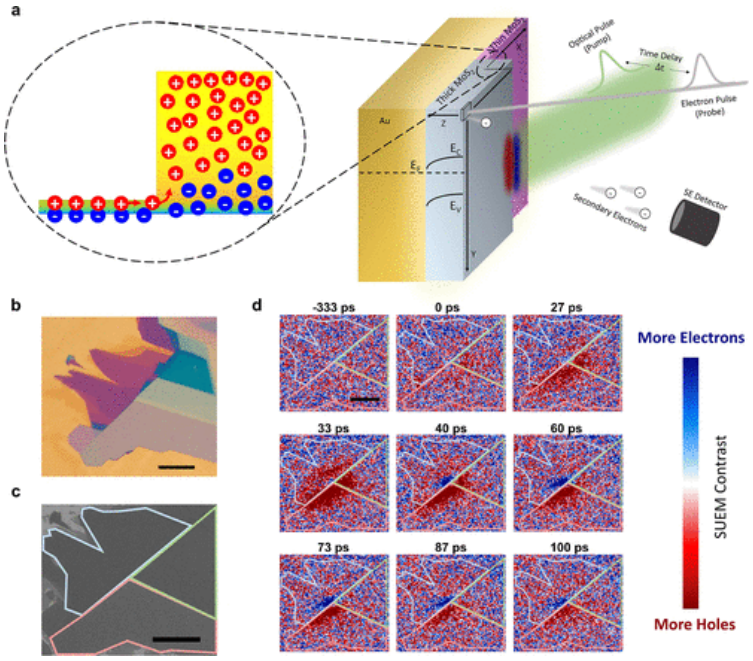

Figure 2. SUEM imaging of charge separation in a 2D "band-bending junction". (a) Schematic of the experiment showing the surface-potential-driven charge separation. (b) & (c) Optical and SEM images of the band-bending junction formed by MoS_2 regions with different thicknesses. (d) SUEM contrast images showing the separation of photo-induced electrons and holes at the junction. [Publication: Nano Letters, 21, 5745, 2021]

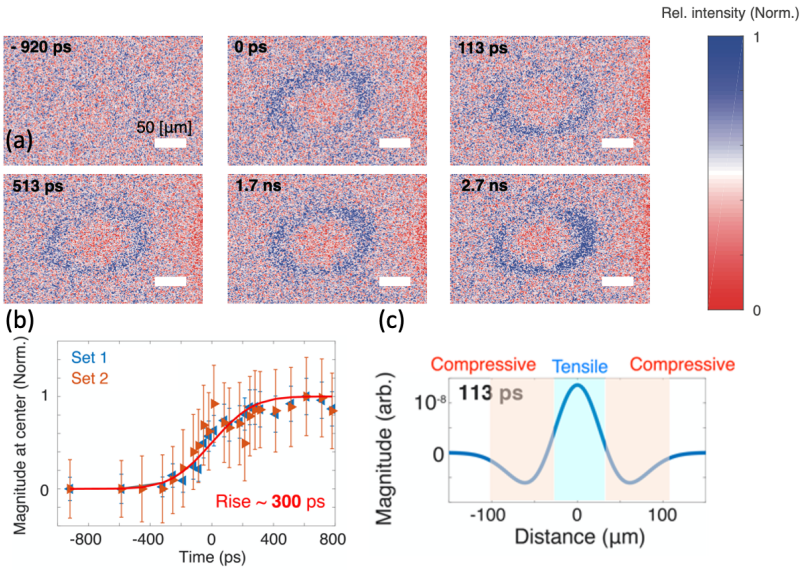

Figure 3. Time-resolved SUEM images of photoexcited semiconducting polymer P3HT. The goal of this study is to probe the impact of photo-induced strain on the electronic properties of semiconducting polymers. Panel (a) shows the characteristic "ring-shaped" contrast feature in semiconducting polymers that is attributed to photo-induced transient strain. The photo-induced strain modulates the electronic structure of the polymers, which further lead to changes in the secondary electron yield that are observed in the SUEM images. Panel (b) shows the rise time of the SUEM contrast. The relatively slow rise time (300 ps) indicates that the observed contrast is of photoinduced elasticity nature. Panel (c) shows a schematic of the photo-induced strain profile that generates the observed ring-shaped contrast in SUEM images. [Publications: Nano Letters, 21, 9146, 2021]

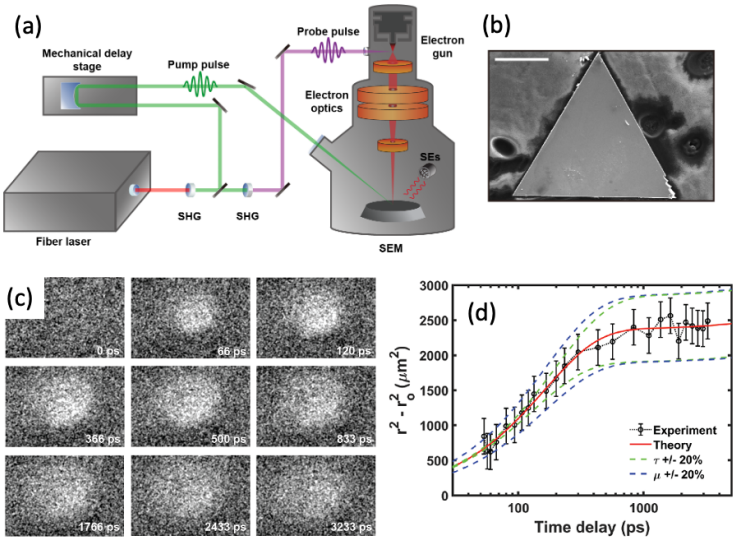

Figure 4. Persistent hot carrier diffusion in cubic boron arsenide imaged by SUEM. The goal of this project is to measure the hot photocarrier transport time in a III-V semiconductor boron arsenide single crystal. This material has ultrahigh thermal conductivity due to a large frequency gap between optical and acoustic phonons, which we hypothesize will also lead to a phonon bottleneck effect and thus long hot carrier lifetime. For this purpose, we used SUEM to image small flakes of boron arsenide flakes. Panel (a) shows the schematic of the SUEM experiment and panel (b) shows a normal SEM image of the boron arsenide single crystal that we studied. Panel (c) shows the SUEM contrast images showing the initial fast superdiffusion of photocarriers in boron arsenide after photoexcitation. Panel (d) shows how the radius of the photocarrier distribution evolves with the delay time, indicating clearly two regimes: a fast superdiffusion regime and a normal slow diffusion regime. The hot carrier lifetime can be extracted from this measurement. We measured very long hot carrier lifetime (> 200 ps) in this material, the longest in a semiconductor to the best of our knowledge. [Under review in Matter. arXiv: 2206.12712, 2022]

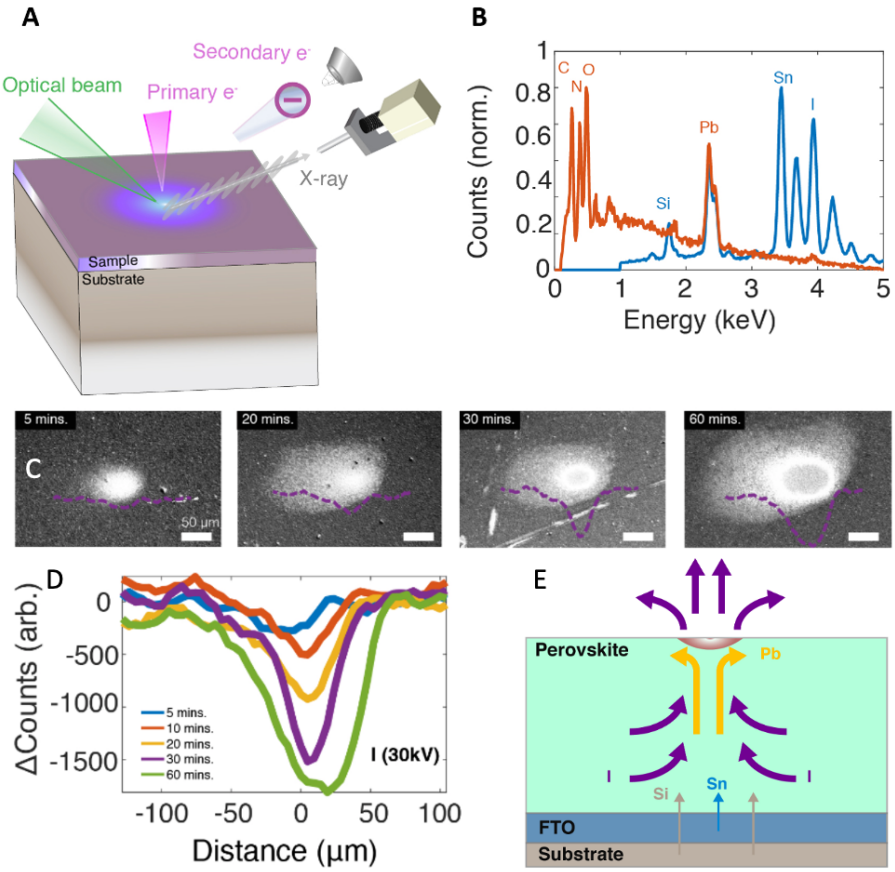

Figure 5. Imaging photo-induced ion migration in halide perovskites. The goal of this project is to understand ion migration processes in hybrid halide perovskite induced by light exposure. This process is crucial to understanding the device instability issue of perovskite-based solar cells. We used SUEM to *in situ* characterize ion migration in perovskites. Panel (a) shows a schematic of the experiment, where we use a combination of optical, electron and x-ray characterization to study photo-induced ion migration. Panel (b) shows a typical x-ray spectroscopy showing the local composition of the hybrid perovskite material. Panel (c) shows the evolution of the secondary-electron contrast as a function of optical exposure time, correlated to the ion distribution profile measured by x-ray energy dispersive spectroscopy, demonstrating long-ranged photo-induced ion migration. Panel (D) shows a quantitative analysis of the ion distribution profile as a function of exposure time, from which the ion diffusivity can be extracted. Panel (e) shows a conceptual picture of the ion migration processes revealed by our study. This picture is of significant importance in understanding and improving the stability of perovskite-based solar cells. [Submitted to Science]

Publications Supported by this Award

1. **Title:** S.-Y. Yue, R. Q. Yang and B. L. Liao, Controlling thermal conductivity of two-dimensional materials via externally induced phonon-electron interaction, *Physical Review B*, **100**, 115408, 2019.

Abstract:
Phonon scattering by electrons, or "phonon-electron scattering," has been recognized as a significant scattering channel for phonons in materials with high electron concentration, such as thermoelectrics and nanoelectronics, even at room temperature. Despite the abundant previous studies of phonon-electron scattering in different types of three-dimensional bulk materials, its impact on the phonon transport, and thus the heat transfer properties, of two-dimensional (2D) materials has not been understood. In this work, we apply *ab initio* methods to calculate the phonon-electron scattering rates in two representative 2D materials, silicene and phosphorene, and examine the potential of controlling the thermal conductivity of these materials via externally induced phonon-electron scattering by electrostatic gating. We also develop an analytical model to explain the impact of reduced dimensionality and distinct electron and phonon dispersions in two dimensions on phonon-electron scattering processes. We find that over 40% reduction of the lattice thermal conductivity can be achieved in silicene with an induced charge-carrier concentration around 10^{13} cm^{-2}, which is experimentally achievable. Our study not only generates new fundamental insights into phonon transport in 2D materials but also provides practical guidelines to search for 2D materials with strong phonon-electron scattering for potential thermal switching applications.

2. **Title:** Y. Li, U. Choudhry, J. Ranasinghe, *A. Ackerman* and B. L. Liao, Probing surface photovoltage effect using photo-assisted secondary electron emission, *Journal of Physical Chemistry A*, **124**, 5246, 2020.

Abstract:
While the properties of surfaces and interfaces are crucial to modern devices, they are commonly difficult to explore since the signal from the bulk often masks the surface contribution. Here we introduce a methodology based on scanning electron microscopy (SEM) coupled with a pulsed laser source, which offers the capability to sense the topmost layer of materials, to study the surface photovoltage (SPV) related effects. This method relies on a pulsed optical laser to transiently induce an SPV and a continuous primary electron beam to produce secondary electron (SE) emission and monitor the change of the SE yield under laser illumination. We observe contrasting behaviors of the SPV-induced SE yield change on n-type and p-type semiconductors. We further study the dependence of the SPV-induced SE yield on the primary electron beam energy, the optical fluence, and the modulation frequency of the optical excitation, which reveal the details of the dynamics of the photocarriers in the presence of the surface built-in potential. This fast, contactless, and bias-free technique offers a convenient and robust platform to probe surface electronic phenomena, with great promise to probe nanoscale effects with a high spatial resolution. Our result further provides a basis to understand the contrast mechanisms of emerging time-resolved electron microscopic techniques, such as the scanning ultrafast electron microscopy.

3. **Title:** S. R. Ellis, N. C. Bartelt, F. Léonard, K. C. Celio, E. J. Fuller, D. R. Hughart, D. Garland, M. J. Marinella, J. R. Michael, D. W. Chandler, B. L. Liao and A. A. Talin, Scanning ultrafast electron microscopy reveals photovoltage dynamics at a deeply buried p-Si/SiO_2 interface, *Physical Review B*, **104**, L161303, 2021.

Abstract:
The understanding and control of charge carrier interactions with defects at buried insulator/semiconductor interfaces is essential for achieving optimum performance in modern electronics. Here, we report on the use of scanning ultrafast electron microscopy (SUEM) to remotely probe the dynamics of excited carriers at a Si surface buried below a thick thermal oxide. Our measurements illustrate a previously unidentified SUEM contrast mechanism, whereby optical modulation of the space-charge field in the semiconductor modulates the electric field in the thick oxide, thus affecting its secondary electron yield. By analyzing the SUEM contrast as a function of time and laser fluence we demonstrate the diffusion mediated capture of excited carriers by interfacial traps.

4. **Title:** J. Wong, A. R. Davoyan, B. L. Liao, A. Krayev, K. Jo, E. Rotenberg, A. Bostwick, C. Jozwiak, D. Jariwala, A. Zewail and H. A. Atwater, Spatiotemporal imaging of thickness-induced band bending junctions, *Nano Letters*, **21**, 5745, 2021.

Abstract:
van der Waals materials exhibit naturally passivated surfaces and an ability to form versatile heterostructures to enable an examination of carrier transport mechanisms not seen in traditional materials. Here, we report a new type of homojunction termed a "band-bending junction" whose potential landscape depends solely on the difference in thickness between the two sides of the junction. Using MoS_2 on Au as a prototypical example, we find that surface potential differences can arise from the degree of vertical band bending in thin and thick regions. Furthermore, by using scanning ultrafast electron microscopy, we examine the spatiotemporal dynamics of charge carriers generated at this junction and find that lateral carrier separation is enabled by differences in the band bending in the vertical direction, which we verify with simulations. Band-bending junctions may therefore enable new optoelectronic devices that rely solely on band bending arising from thickness variations to separate charge carriers.

5. **Title:** T. Kim, S. Oh, U. Choudhry, C. Meinhart, M. Chabinyc and B. L. Liao, Transient strain induced electronic structure modulation in a semiconducting polymer imaged by scanning ultrafast electron microscopy, *Nano Letters*, **21**, 9146, 2021.

Abstract:
Understanding the optoelectronic properties of semiconducting polymers under external strain is essential for their applications in flexible devices. Although prior studies have highlighted the impact of static and macroscopic strains, assessing the effect of a local transient deformation before structural relaxation occurs remains challenging. Here, we employ scanning ultrafast electron microscopy (SUEM) to image the dynamics of a photoinduced transient strain in the semiconducting polymer poly(3-hexylthiophene) (P3HT). We observe that the photoinduced SUEM contrast, corresponding to the local change of secondary electron emission, exhibits an unusual ring-shaped profile. We attribute the observation to the electronic structure modulation of P3HT caused by a photoinduced strain field owing to its low modulus and strong electron–lattice coupling, supported by a finite-element analysis. Our work provides insights into tailoring optoelectronic properties using transient mechanical deformation in semiconducting polymers and demonstrates the versatility of SUEM to study photophysical processes in diverse materials

6. **Title:** U. Choudhry, T. Kim, M. Adams, J. Ranasinghe, R. Q. Yang and B. L. Liao, Tutorial: characterizing microscale energy transport in materials with transient grating spectroscopy, *Journal of Applied Physics*, **130**, 231101, 2021.

Abstract:
Microscale energy transport processes are crucial in microelectronics, energy-harvesting devices, and emerging quantum materials. To study these processes, methods that can probe transport with conveniently tunable length scales are highly desirable. Transient grating spectroscopy (TGS) is such a tool that can monitor microscale energy transport processes associated with various fundamental energy carriers including electrons, phonons, and spins. Having been developed and applied for a long time in the chemistry community, TGS has regained popularity recently in studying different transport regimes in solid-state materials. In this Tutorial, we provide an in-depth discussion of the operational principle and instrumentation details of a modern heterodyne TGS configuration from a practitioner's point of view. We further review recent applications of TGS in characterizing microscale transport of heat, charge, spin, and acoustic waves, with an emphasis on thermal transport.

7. **Title:** U. Choudhry, F. J. Pan, T. Kim, R. Gnabasik, G. A. Gamage, H. R. Sun, A. Ackerman, Z. F. Ren and B. L. Liao, Persistent hot carrier diffusion in boron arsenide single crystals imaged by ultrafast electron microscopy, submitted, arXiv: 2206.12712, 2022.

Abstract:
Cubic boron arsenide (BAs) is promising for microelectronics thermal management due to its high thermal conductivity. Recently, its potential as an optoelectronic material is also being explored. However, it remains challenging to measure its photocarrier transport properties due to small sizes of available high-quality crystals. Here, we use scanning ultrafast electron microscopy (SUEM) to directly visualize the diffusion of photoexcited charge carriers in BAs single crystals. Surprisingly, we observed ambipolar diffusion at low optical fluence with persistent hot carrier dynamics for above 200 picoseconds, which can be attributed to the large frequency gap between acoustic and optical phonons, the same feature that is responsible for the high thermal conductivity. At higher optical fluence, we observed spontaneous electron-hole separation. Our results show BAs is an attractive optoelectronic material combining high thermal conductivity and excellent photocarrier transport properties. Our study also demonstrates the capability of SUEM to probe photocarrier transport in emerging materials.

8. **Title:** W. K. Ouyang, X. Y. Zuo and B. L. Liao, Impact of photoexcitation on secondary electron emission: a Monte Carlo study, submitted, 2022.

Abstract:
Understanding the transport of photogenerated charge carriers in semiconductors is crucial for applications in photovoltaics, optoelectronics and photo-sensing. While recent experimental studies using scanning ultrafast electron microscopy (SUEM) have demonstrated that the local change of the secondary electron emission induced by photoexcitation enables direct visualization of the photocarrier dynamics in space and time, the origin of the corresponding image contrast still remains unclear. Here, we investigate the impact of photoexcitation on secondary electron emissions from semiconductors using a Monte Carlo simulation aided by time-dependent density functional theory (TDDFT). Particularly, we examine two photo-induced effects: additional inelastic electron scattering in the bulk due to photocarriers, and the surface photovoltage (SPV) effect. Using doped silicon as a model system and focusing on primary electron energies below 4 keV, we found that the SPV effect plays a predominant role in changing the secondary electron yield (SEY), suggesting that the major SUEM image contrast mechanism in doped semiconductors is the change in the surface band bending induced by light. Our work provides insights into electron-matter interaction under photoillumiation and paves the way towards quantitative interpretation of the SUEM contrasts.

9. **Title:** T. Kim, S. Park, V. Iyer, Q. Jiang, U. Choudhry, R. Gnabasik, B. Lawrie, K. Zhu and B. L. Liao, In situ imaging of photo-induced ion migration in organic-inorganic hybrid halide perovskites, submitted, 2022.

Abstract:
Organometallic halide perovskite solar cells (PSCs) exhibiting electronic properties comparable to those of inorganic materials are of fundamental and practical interest, owing to visible absorption, tunability, and low manufacturing cost. Recent works have reported unusual the current–voltage characteristics hysteresis occurring in the PSCs under light soaking, which can affect the device performance along with the lifetime for the long term stability. While prior extensive investigations have suggested that ion migration is a plausible origin of the hysteresis, detailed understanding of the microscopic transport properties of the ion has been missing. Here, we report an in-situ characterization of the photo-induced ion migration in organic-inorganic halide perovskite using scanning electron microscope and an energy-dispersive X-ray spectroscopy (EDS). Particularly for $FAPbI_3$ (FA = formamidinium [CH(NH2)2]+), we observe an occurrence and spatial expansion of bright secondary electron (SE) contrast over hundreds-of-micrometer distances, along with a subsequent formation of a dark SE contrast under higher optical exposure. Considering an additional in-situ EDS elemental analysis, we attribute our observation to the electronic property changes due to the light-assisted accumulation and depletion of halide and metal ions across the bulk to the surface. Our work provides insights into understanding fundamental photo-induced ion migration processes in the PSC devices that are useful for various applications.