

## Photoemission electron microscopy as a new tool to study the electronic properties of 2D crystals and inhomogeneous semiconductors

Taisuke Ohta<sup>1,2</sup>, Morgann Berg<sup>1,2</sup>, Kunttal Keyshar<sup>3,4</sup>, Jason M. Kephart<sup>5</sup>, Thomas E. Beechem<sup>1</sup>, Robert Vajtai<sup>3</sup>, Pulickel Ajayan<sup>3</sup>, Aditya D. Mohite<sup>4,6</sup>, Walajabad S. Sampath<sup>5</sup> and Calvin Chan<sup>1</sup>

<sup>1</sup>. Sandia National Laboratories, Albuquerque, New Mexico, United States.

<sup>2</sup>. Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico, United States.

<sup>3</sup>. Department of Materials Science and Nanoengineering, Rice University, Houston, Texas, United States.

<sup>4</sup>. Los Alamos National Laboratory, Los Alamos, New Mexico 87545, United States.

<sup>5</sup>. Department of Mechanical Engineering, Colorado State University, Fort Collins, Colorado, United States.

<sup>6</sup>. Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

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) [1]. PES measurements, however, remain challenging for inhomogeneous samples or 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 photoemission spectra from areas less than one micron in size [2]. Here, we present PEEM studies of the electronic structure of two inhomogeneous semiconductors, transition metal dichalcogenides (TMDs) supported on oxidized silicon wafers and polycrystalline cadmium telluride (CdTe) thin films.

The advent of atomically thin TMDs has led to the concept of designer heterostructures [3], where the lack of chemical bonding between the layers alleviates problems with lattice mismatch and chemical compatibility. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance in predicting the performance of TMD heterostructures in devices that are useful in high performance electronics and opto-electronics. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation has been reported for the wide range of 2D crystals despite their importance. Using PEEM, we successfully determined the ionization energies for three prototypical TMD monolayers – MoSe<sub>2</sub>, WS<sub>2</sub>, and MoS<sub>2</sub> – on silicon oxide (SiO<sub>2</sub>) [4]. The ionization energy changes between MoS<sub>2</sub>, WS<sub>2</sub>, and MoSe<sub>2</sub> in agreement with predictions of density functional theory calculations [5],[6],[7],[8].

Similarly using PEEM, we conducted vacuum-level mapping on mechanically polished polycrystalline CdTe thin films [12]. Polycrystalline CdTe thin films are a serious alternative to silicon photovoltaics with efficiencies reaching 21.5% [8]. A key manufacturing step is the activation of the CdTe absorber layer using cadmium chloride, which drastically improves the power conversion efficiency [9]. Past studies showed that this Cl treatment changes the microstructure of the CdTe layer through

recrystallization and grain growth [10], and the electronic properties of the CdTe grains and the grain boundaries [11]. However, to date, the notion of electronic property changes are mostly based on indirect inferences from microscopic measurements made after Cl treatment. We conducted a series of PEEM studies comparing Cl treated and air exposed samples to elucidate distinct impacts of the Cl treatment before and after air exposure. Our work illustrates the following scenarios: regrown grains with different carrier potentials help to separate the photoexcited electron-hole pairs; air exposure bends the electronic bands electrostatically at the absorber layer-electrode interface, which facilitates electron collection. The separate but coincident roles of these two processing factors have not been highlighted in the previous reports, and could point to an additional processing parameter to improve photovoltaic efficiency.

In these two case studies, PEEM measurements were conducted using lab-based deep ultraviolet (DUV) light sources. The results presented here strongly support the idea of lab-based PEEM as an emerging analytical capability to explore the electronic properties of spatially inhomogeneous materials for electronic and optoelectronic applications.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. was supported by the CINT user program and Sandia LDRD. M. B. and C. C. were supported by a U.S. DOE-EERE SunShot BRIDGE award (DE-FOA-0000654 CPS25859). K. K. was supported by the Army Research Office MURI (W911NF-11-1-0362). A. D. M. was supported by LANL LDRD. J. M. R. and W. S. S. were supported by NSF PFI:AIR-RA (#1538733). We thank R. Guild Copeland for constructing the tunable DUV light source, and Norman Bartelt for fruitful discussions. We also thank Anthony McDonald for providing photoluminescence maps of the TMD samples. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

## References:

- [1] S Hüfner in “Photoelectron Spectroscopy, Principles and Applications”, (Springer, Berlin) p. 347.
- [2] E Bauer in “Surface Microscopy with Low Energy Electrons”, (Springer, New York) p. 25.
- [3] A K Geim and I V Grigorieva, *Nature* 499 (2013), p. 419.
- [4] K Keyshar *et al*, in preparation (2017).
- [5] C Ataca *et al*, *J. Phys. Chem. C* 116 (2012), p. 8983.
- [6] J Kang *et al*, *Applied Physics Letters* 102 (2013), p. 012111.
- [7] C Gong *et al*, *Appl. Phys. Lett.* 103 (2013), p. 053513.
- [8] M A Green *et al*, *Prog. Photovoltaics* 24 (2016), p. 3.
- [9] F A Rasmussen and K. S. Thygesen, *J. Phys. Chem. C* 119 (2015), p. 13169.
- [10] H R. Moutinho *et al*, *J. Vacuum Science & Technology A* 16 (1998), p. 1251.
- [11] I Visoly-Fisher *et al*, *Advanced Functional Materials* 16 (2006), p. 649.
- [12] M Berg *et al*, in preparation (2017).