

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

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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 – MoSe₂, WS₂, and MoS₂ – on silicon oxide (SiO₂) [4]. The ionization energy changes between MoS₂, WS₂, and MoSe₂ 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.

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