Reflection Electron Energy Loss Spectroscopy of Semiconductors

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Understanding intrinsic electronic properties - such as bandgaps, energy-level positions and electronic excitations - is essential for advancing semiconductor research across a wide range of material classes. These quantities are typically extracted using established spectroscopic tools, including UV–vis spectroscopy and photoelectron-based techniques. In this contribution, I will discuss our ongoing efforts to evaluate reflection electron energy loss spectroscopy (REELS) as a complementary approach for probing semiconductor electronic structure, with particular emphasis on its surface sensitivity and tunable information depth.

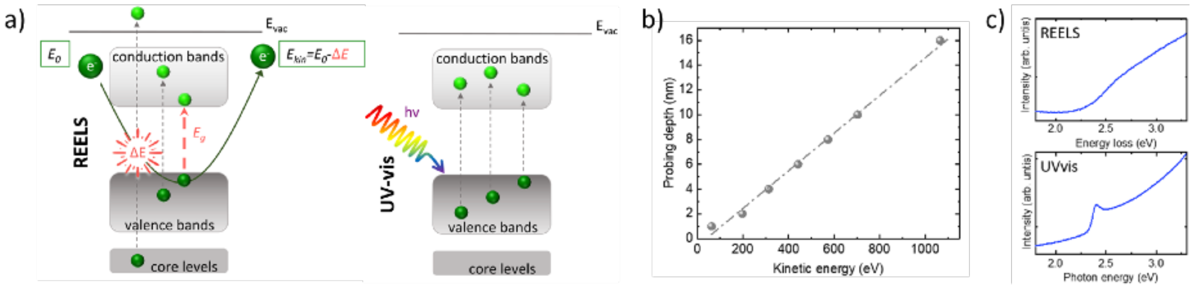

Figure 1: (a) Schematic illustration comparing the excitation of a sample with electrons in REELS and photons in UV–vis spectroscopy. (b) Measured probing depth of REELS as a function of incident electron kinetic energy. (c) Example of REELS (top) and UV–vis (bottom) spectra of the perovskite $MAPbBr_3$ illustrating a similar bandgap onset but clear differences in spectral shape.

REELS records electrons that have undergone inelastic scattering at the surface, and the resulting loss features contain signatures of electronic transitions, plasmons and other excitations. For energy losses in the range of a few eV, the information obtained is related to that from conventional UV–vis spectroscopy, as sketched in Figure 1a. However, due to the short inelastic mean free path of low-energy electrons, REELS probes only the near-surface region. We experimentally determined the energy dependence of the probing depth, shown in Figure 1b, which for the electron kinetic energies used here ranges between approximately 1 and 16 nm. This makes REELS particularly relevant for ultrathin layers, interfaces, and surface treatments, where optical techniques often provide predominantly bulk-averaged information.

I will present examples from different semiconductor and metal oxide systems, focusing on electronic transitions, to illustrate where REELS agrees with, diverges from, or expands upon conventional optical measurements. One example is shown in Figure 1c, which compares UV–vis and REELS spectra of $MAPbBr_3$. While both techniques yield a consistent bandgap onset, differences in spectral shape reflect the distinct excitation mechanisms and possibly selection rules involved.

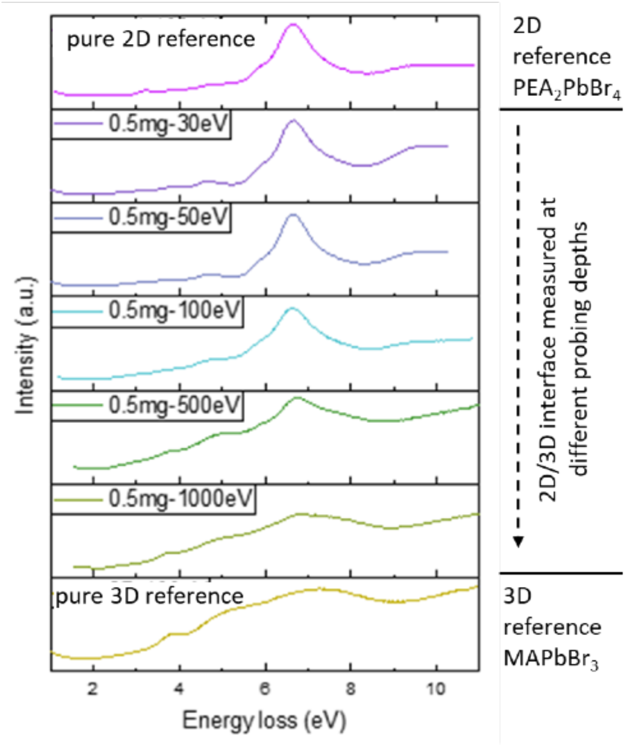

Figure 2. Example of a REELS measurement taken at different probing depth (i.e. kinetic energies) to probe a bi-layer of MAPbBr3 treated with PEABr on the surface to form a 2D capping layer. For reference, the top and bottom spectra are of the pure 2D and 3D film, respectively.

One particularly interesting application of this technique concerns 3D halide perovskite layers passivated by ultrathin 2D capping layers. As a case study, I will show $MAPbBr_3$ films treated with different concentrations of phenylethyl-ammonium bromide (PEABr) to investigate the formation of low-dimensional perovskite phases at the surface. A series of REELS spectra, shown in Figure 2, were recorded at different incident electron energies and reveal systematic changes in spectral shape. These changes can be associated with the high surface sensitivity of low-energy excitation (e.g., 50 eV electrons, dominated by the 2D capping layer), which gradually evolves toward more bulk-sensitive probing of the underlying 3D perovskite when the kinetic energy is increased up to 1000 eV. This demonstrates that REELS can sensitively detect surface phase formation and provide qualitative insight into the depth distribution of different structural motifs.

At the same time, REELS has important limitations. Prolonged electron exposure can induce irreversible changes in halide perovskite films, including the formation of degradation products such as $PbBr_2$, as confirmed by complementary XPS measurements. Careful optimization of experimental parameters is therefore essential to balance information depth, signal quality, and sample stability.

In summary, REELS is a powerful complementary tool for semiconductor characterization, bridging optical and electron spectroscopies. Its surface sensitivity, access to optically forbidden transitions, and tunable probing depth make it particularly suited for studying ultrathin layers and interfaces. With appropriate experimental control, REELS can provide unique insight into surface and near-surface electronic structure that is difficult to access by conventional methods alone.