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TERS for Functional Thin Films: Nanoscale Insights into Polymeric, Semiconductor, and Smart Materials

Probing the chemical structure of functional thin films at the nanometer scale under ambient conditions – without labeling or inducing damage – remains a major challenge in materials science. Tip-enhanced Raman spectroscopy (TERS) offers an effective solution by enabling label-free vibrational imaging with spatial resolution down to 10 nm. In this talk, I will present recent advances from our laboratory that showcase the capabilities of TERS in revealing molecular-level insights into a range of technologically relevant thin-film systems.

We first examine phase-separated polystyrene (PS)–poly(methyl methacrylate) (PMMA) polymer blend films, which are employed as templates or patterned surfaces in solar cells, catalysis, and biomedical devices. Using correlative TERS, AFM, confocal Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS), we uncover both lateral and vertical phase separation within the top 20 nm of the surface. Remarkably, TERS and XPS data indicate PMMA presence within 9.2 nm of the surface and PS at the subsurface, confirming vertical stratification otherwise inaccessible to conventional methods [1]. These findings establish TERS as a sensitive analytical tool for probing nanoscale composition and organization in soft matter systems.

Next, we apply TERS to study interfacial regions in inorganic Sb_2Se_3-based thin film solar cells, where interface chemistry plays a crucial role in charge carrier dynamics and overall device efficiency. Hyperspectral TERS imaging at 10 nm resolution reveals an unexpectedly diffuse and chemically intermixed interface between the Sb_2Se_3 absorber and CdS buffer layers [2]. This interfacial region, with a thickness of nearly 300 nm, is attributed to roughness and undesired reactions during chemical bath deposition. Additionally, we identify the presence of ZnO within the Sb_2Se_3-rich region – experimentally confirmed here for the first time – underscoring the power of TERS in exposing subtle yet significant compositional intermixing in complex heterostructures.

Finally, we turn to thermochromic VO_2 thin films, known for their temperature-driven metal-insulator transition near 68 °C and their potential use in smart window coatings. TERS imaging of pristine VO_2 and VO_2/TiO_2 bilayers reveals nanocrystalline heterogeneity, grain boundary networks, and localized strain – all of which influence the transition temperature and optical behavior [3]. In the bilayer system, we detect phase coexistence in TiO_2 (anatase and brookite) and chemical intermixing at the interface, further evidencing how nanoscale structure and chemistry modulate functional performance. These results highlight the utility of TERS in advancing our understanding and design of functional materials through nanoscale structural and interfacial insights.

References

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