Atomic-level Structure Determines the Nonlinear Optical Properties of 2D Polar-Metal Heterostructures

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Using correlative light and electron microscopy (CLEM), both quantitative and mechanistic descriptions of the nonlinear optical responses of hexagonal two-dimensional polar metals (gallium and indium) and their alloys were obtained. The optical responses of these systems are intimately linked to the material's interfacial structure at the atomic level. These results are unexpected because symmetry arguments would suggest that these materials should not exhibit strong second harmonic signals. Nonetheless, they generate the largest known near-infrared second-order susceptibilities. Using cross-sectional electron microscopy, we show that the atomic-level, interfacial structure is not what it seems – out-of-plane symmetry breaking over approximately two atomic layers, which causes a change in metal-to-metal bond distances of 0.2 angstroms, leads to extremely large nonlinear optical signals. Through correlative polarization-resolved second-harmonic imaging and electron microscopy, we also show that the rotation of metal atoms at interfacial step edges results in a well-defined modulation of the harmonic light polarization plane. To our knowledge, such a strong correlation between interfacial structure and nonlinear frequency conversion has not been reported for any material system. These findings open completely new directions for nonlinear optical switching and frequency mixing applications, which can now be tailored with atomic-level structural precision.