Optical Determination of Stacking Order in Gallium Selenide Nanosheets

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Gallium selenide is a layered transition-metal chalcogenide semiconductor with unique anisotropic optical properties. For example, the band structure of bulk GaSe presents a direct bandgap of ~2eV, but optical selection rules forbid transitions polarized in the basal plane. Owing to the weak Van der Waals interaction between constituent layers, several stable crystal polytypes with different stacking order exist. In bulk Bridgeman-grown crystals, ε-GaSe (ABA stacking) and γ-GaSe (ABCA stacking) often coexist. Given the recent interest in few-layer nanosheets of GaSe produced by micro-mechanical exfoliation of bulk crystals for electronic and optoelectronic applications, it is critical to be able to distinguish γ-GaSe and ε-GaSe nanosheets obtained by such a process.

In this study, we analyze the wave vector orientation and polarization dependence of Raman modes and second harmonic generation (SHG) as tools to determine the crystalline symmetry and stacking order of thin GaSe nanosheets.

For measurements with an E-field polarization component out of the basal-plane, several Raman modes forbidden at normal incidence appear, indicating that the dominant polytype is ε-GaSe. In addition, a strong enhancement of all Raman modes is observed due to an increased electronic coupling, as the incident fields complies with the direct gap selection rules. This is also directly observable as a squared sine dependence between the direct gap PL intensity and the E-field angle relative to the basal plane.

Polarization-resolved SHG measurements for different wave vector orientations enable a complete determination the point-group symmetry by analysis of the angular symmetries of SHG intensity. Our results confirm that our samples exhibit a D_{3h} point-group symmetry, corresponding to the ε-GaSe polytype.

In conclusion, we show that polarization- and angle-resolved Raman and SHG measurements are essential tools in the fast and accurate determination of stacking order in GaSe nanosheets.