Tuning the bandgap of exfoliated InSe nanosheets by quantum confinement

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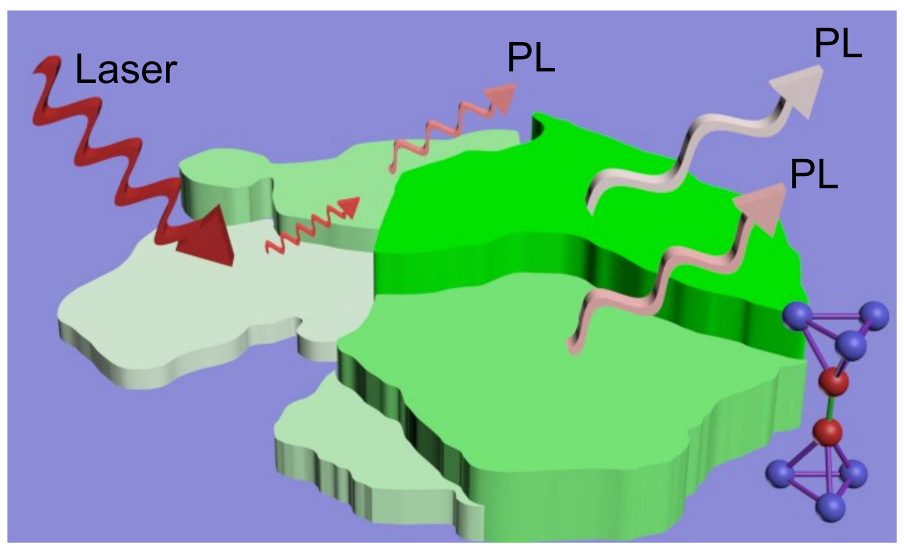
1. Introduction

We investigate the optical properties of thin, exfoliated layers of γ-rhombohedral InSe, a semiconductor with a direct band gap. The room temperature near-band edge photoluminescence (PL) peak and absorption-induced photoconductivity strongly blue-shift to higher photon energies with decreasing *L*. This is consistent with 2D-quantum confinement of photo-excited carriers by atomically flat interfaces when *L* < 30 nm. The quenching of the PL signal for *L* < 6 nm points to a direct-to-indirect band gap crossover that contrasts with the indirect-to-direct band gap transition reported for transition metal dichalcogenides as the film thickness is decreased [1-3]. The quantum confinement energies for the direct exciton in these InSe nanoflakes are one order of magnitude larger than those reported for III-VI compound GaSe [4].

2. Indium Selenide

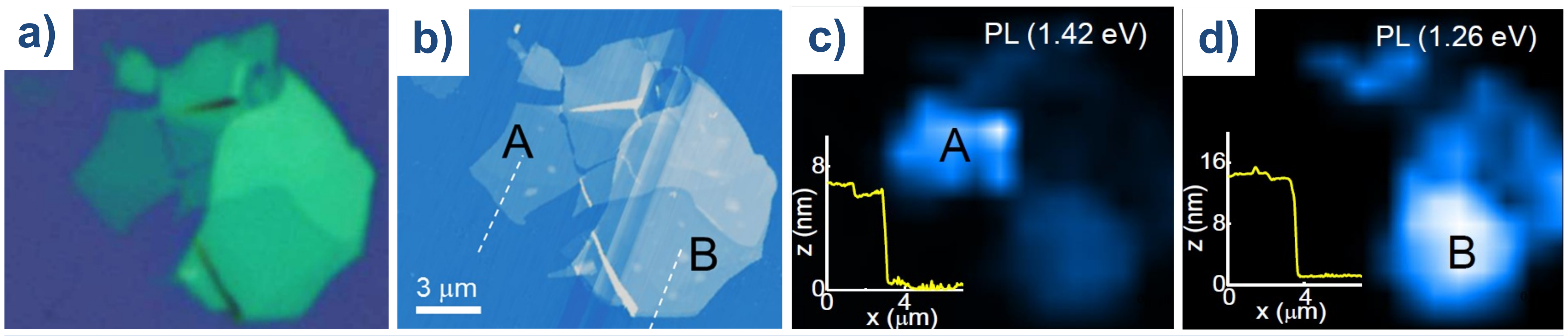
InSe nanofilms, a new member of the 2D crystal family!



- InSe: E_g(300 K) = 1.26 eV.
- γ-rhombohedral Bridgman grown crystal.
- Group III-VI compound.

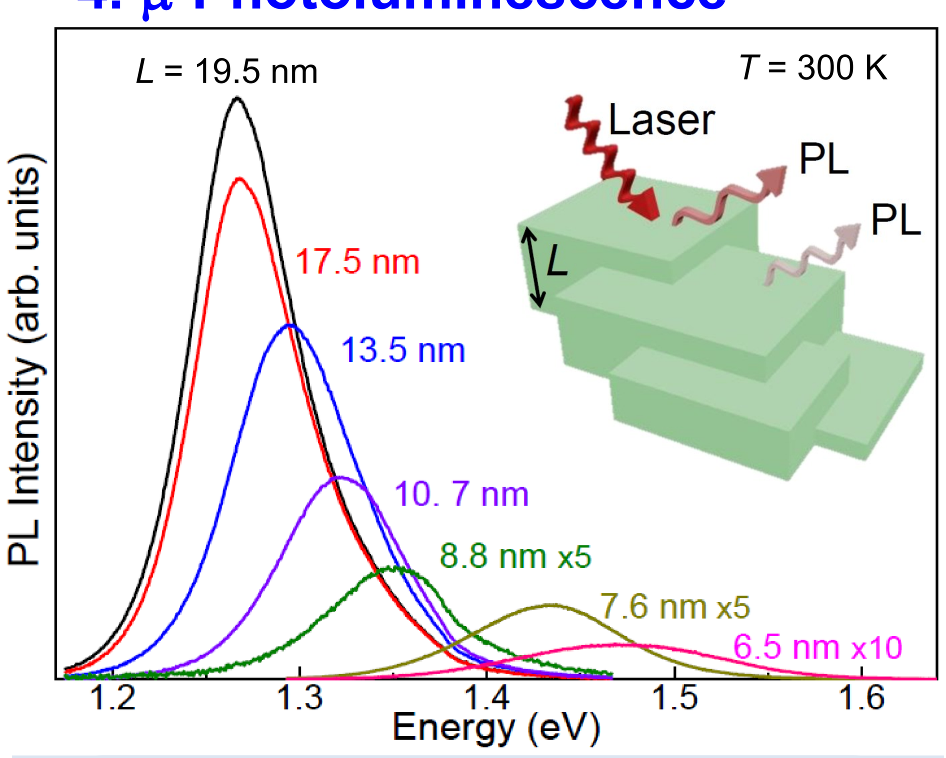
3. Investigating InSe Nanoflakes

Micromechanical exfoliation of as-grown InSe crystals with adhesive tape produces thin layers from 1 to 10^3 μm^2 in size. Layers were deposited on various substrates (SiO_2, mica) and examined under an optical microscope **(a)**. The appearance of assorted contrasts reveals flakes of multiple layers.



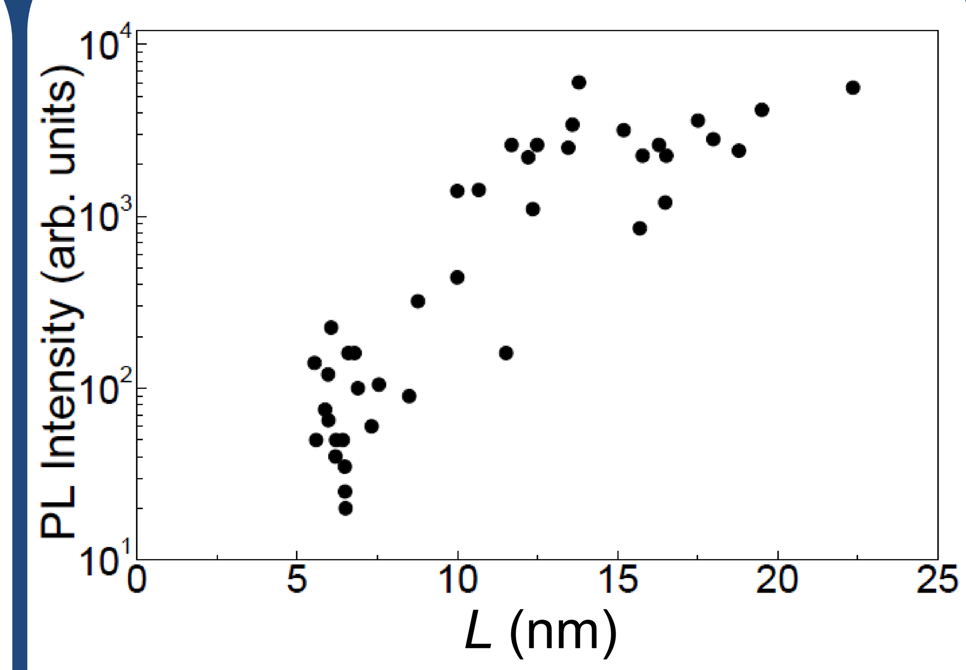
- Non-contact atomic force microscopy (AFM) produced images of the nanoflake surface topography **(b)**.
- Apparent height z-scans revealed InSe layers of multiple layers (~ down to 4 nm) and single monolayer steps (~1 nm).
- Confocal μ-photoluminescence (PL) maps and spectra were obtained at room temperature **(c-d)**.
- Maps represent the PL intensity centred around specific photon energies at *hν* = 1.42 eV and 1.26 eV, revealing blue shift in PL emission associated with decreasing layer thickness.

4. μ-Photoluminescence



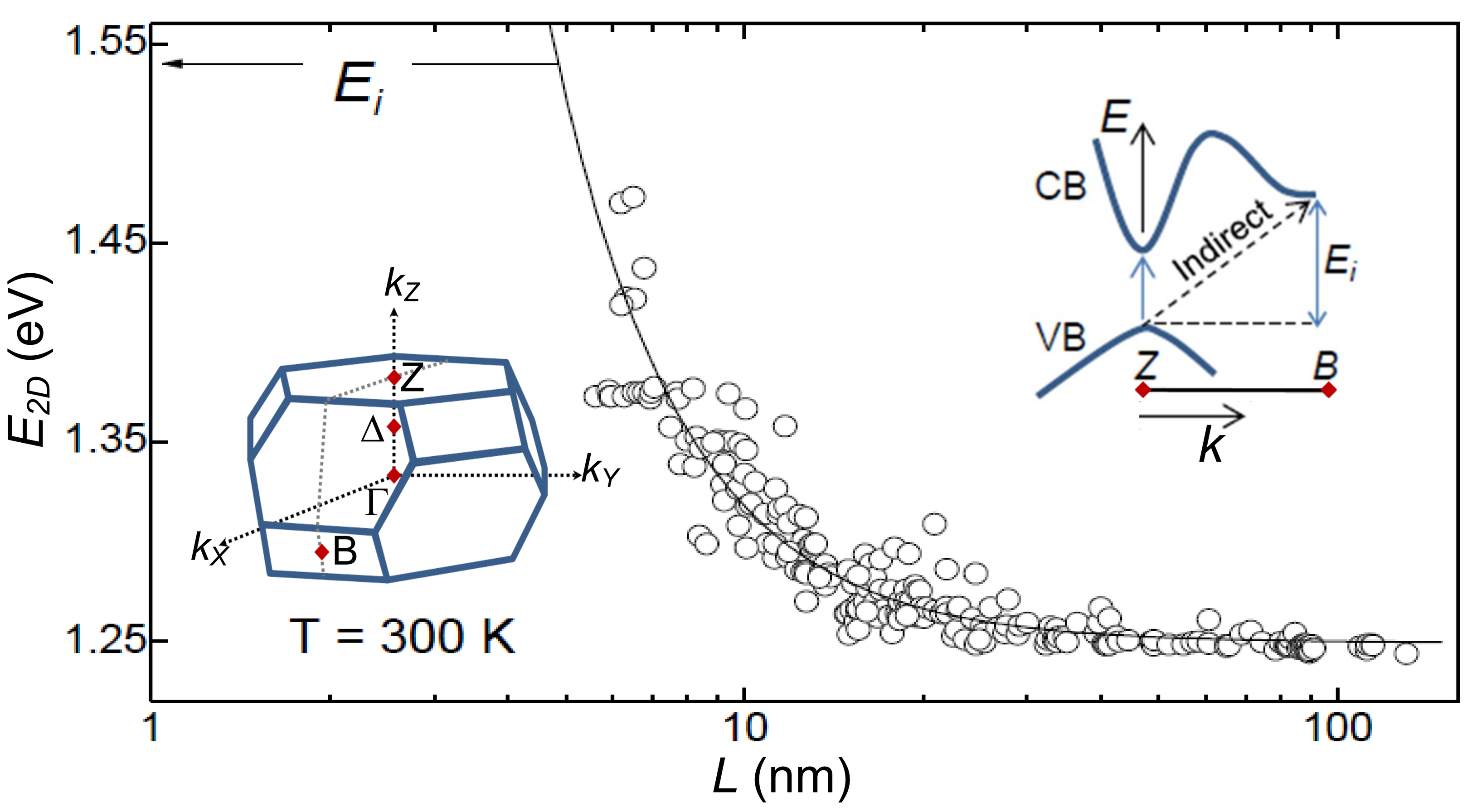
- Reducing *L* causes PL emission to blue shift to photons of higher energies by up to 200 meV.
- Such a shift is consistent with planar quantum confinement of photo-excited carriers by the external surfaces of the flakes.
- The thinnest flakes identified by PL have *L* = 6 nm (~7 monolayers) with room temperature emission peaked at E_{2D} = 1.45 eV.
- Thinner flakes were measured by AFM, however no PL emission was detected from these layers.

5. μPL Quenching



- Quenching of the PL emission is always observed for flakes at small *L* (< 6 nm).
- PL integrated intensity decreases by a factor of > 10.
- The observed reduction in PL emission intensity is greater than what would be expected for loss of absorption due to a decrease in absorbing material.
- Such behaviour is attributed to a direct-to-indirect crossover, analogous to that induced in bulk γ-InSe by hydrostatic pressure [5].

6. Blue Shifted μPL and Direct-to-Indirect Crossover



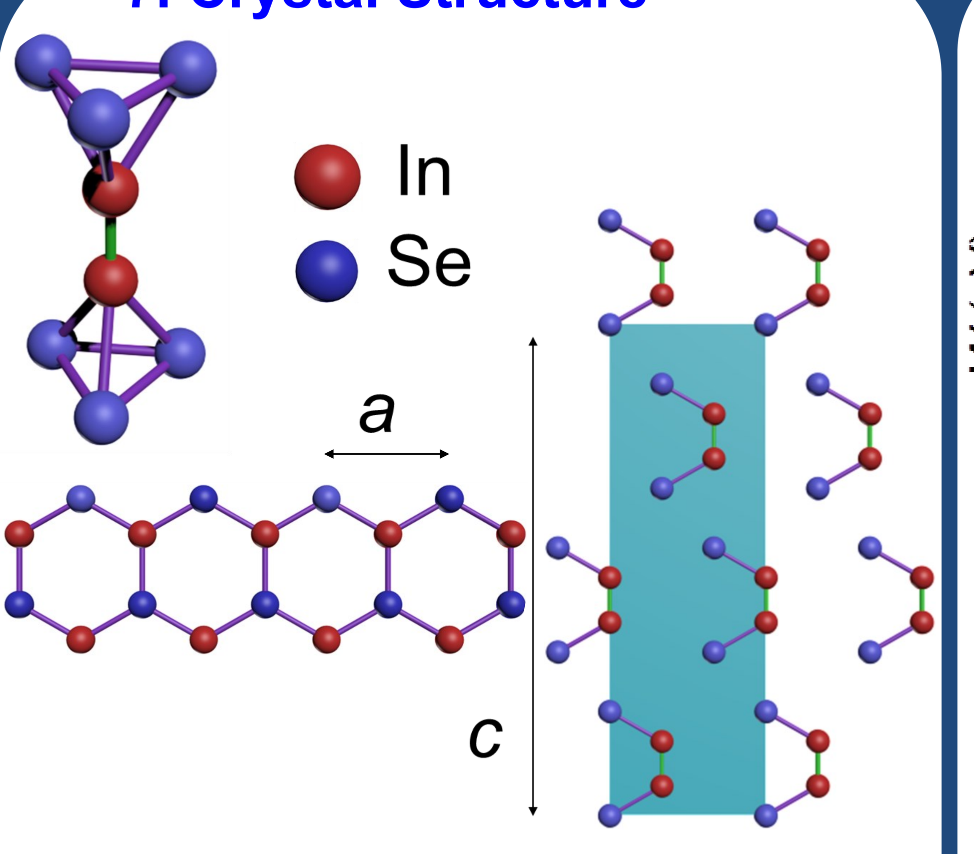
- Combining the results of PL and AFM studies on more than 100 flakes gives the dependence of the band-to-band direct edge transition, E_{2D}, on flake thickness *L*.
- E_{2D} can be modelled using a square quantum well potential of infinite height.

$$E_{2D} = E_g - E_b + \pi^2 \hbar^2 / 2L^2 \mu_{//c}$$

⇒ E_b = exciton binding energy (= 15 meV)
⇒ $\mu_{//c}$ = exciton effective mass (along c-axis) (= 0.054m_e)

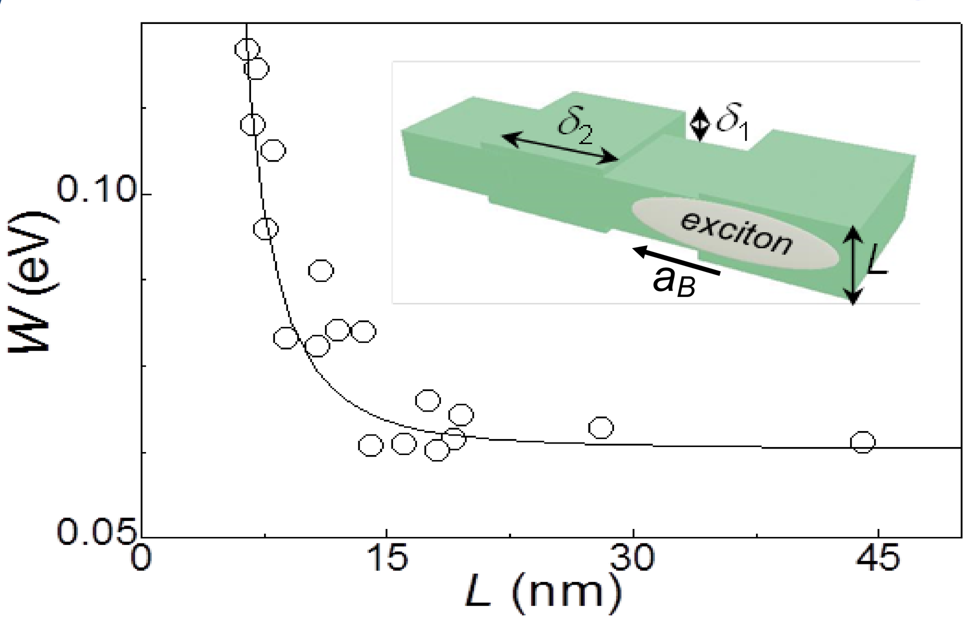
- The scatter in the data suggests the presence of a thin surface film, such as an oxidised layer [5], preventing the penetration of carrier wavefunctions.
- The direct-to-indirect crossover is estimated to occur at a critical layer thickness *L* = 5 nm by the model E_{2D} curve, consistent with the quenching of the PL peak emission for nanoflakes with *L* < 6 nm (E_i = 1 .54 eV).
- Quantum confinement due to small *L* transfers the lowest conduction band minima at the z-point of the Brillouin zone to the upper B-minimum. The upper B-minimum is less sensitive to the effects of quantum confinement due to its larger electron effective mass.

7. Crystal Structure



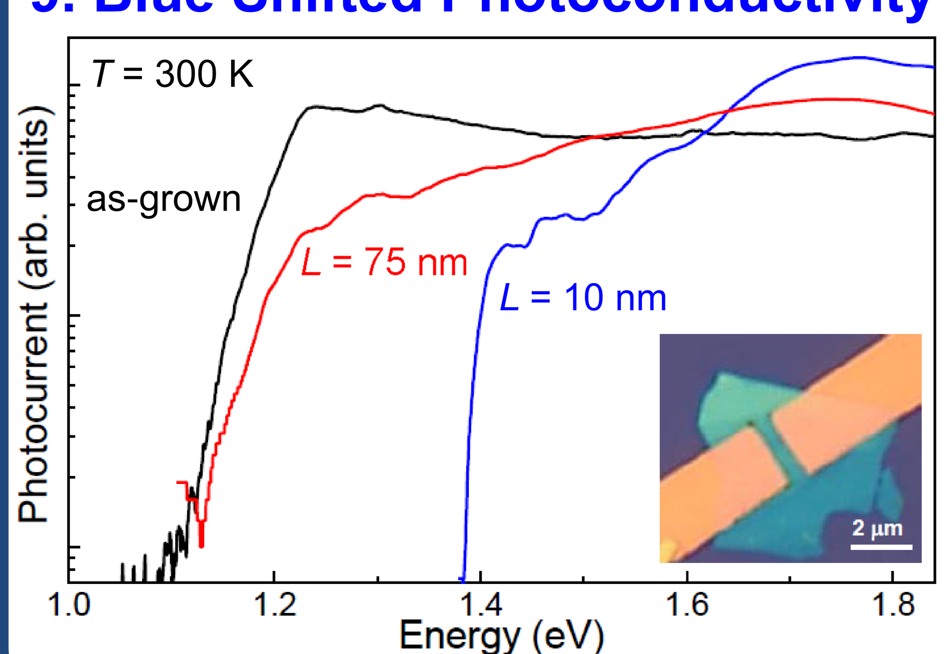
- γ-rhombohedral Bridgman grown crystal.
- Lattice *a* = 0.405 nm; *c* = 2.495 nm.
- Weak interlayer van der Waals forces leads to easy exfoliation.

8. Exciton Linewidth Broadening



- PL studies show a systematic increase (x2) of the FWHM, *W*, of the PL emission with decreasing *L* (below 15 nm).
- Strong quantum confinement effects make the linewidth quite sensitive to the surface roughness.
- This broadening can be explained with a statistical model of PL emission that compares the exciton Bohr radius, a_B, with the roughness of the layers and considers the dependence of E_{2D} on *L*.

9. Blue Shifted Photoconductivity



- Photoconductivity spectra of 2-terminal Ti/Au/InSe samples for as-grown crystals, bulk (*L* = 75 nm) and thin (*L* = 10 nm) flakes at *T* = 300 K.
- Absorption edge of as-grown and bulk layer (*L* = 75 nm) is at photon energies of ~1.2 eV.
- Absorption edge of thin (*L* = 10 nm) is at photon energies of ~1.4 eV.
- A blue shift of ~0.2 eV, in comparison to thicker flakes, confirms strong 2D carrier confinement for *L* < 15 nm.

10. Conclusion

⇒ Combining μPL and AFM studies reveals a dependence of the band-to-band direct edge transition E_{2D}, on the flake thickness *L*.
⇒ Thinnest flakes identified by μPL have their peak emission blue shifted by ~200 meV up to photon energies of *hν* ~ 1.45 eV (*L* ~ 6 nm).
⇒ μPL emission quenching for *L* < 6 nm indicates a direct-to-indirect bandgap crossover, opposite to the behaviour of transition metal dichalcogenide MoS_2 and III-VI compound GaSe which exhibit indirect-to-direct crossover for small *L*.
⇒ Model of E_{2D} vs. *L* indicates a direct-to-indirect crossover occurs at a critical thickness *L* = 5 nm for InSe.
⇒ μPL linewidth broadening highlights the strong sensitivity of carrier recombination to small surface roughness for *L* < 15 nm, and the presence of a thin surface layer possibly due to oxidation.
⇒ Photoconductivity measurements confirm the strong 2D quantum confinement of carriers as shown by the blue shift of the absorption edge by 0.2 eV for *L* = 10 nm.

11. References

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