

Quantification of Dopant Distribution and the Local Band Gap in Selenium-Doped Molybdenum Disulfide

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Ternary two-dimensional dichalcogenide alloys exhibit compositionally modulated electronic structure. For example, we have recently shown that by substituting sulfur atoms with Se, the bandgap of MoS₂ could be linearly tuned between 1.85 and 1.60 eV as a function of Se doping level [1]. Therefore, controlled doping and *quantification* of the local dopant distribution becomes critical for understanding the doping behavior and its influence on the local electronic properties. However, high-accuracy and high-efficiency dopant mapping at the single atom level remains a key challenge [2], and discriminating the dopant distribution in bilayer 2D materials has not previously been achieved.

Here we describe a one-step synthesis of monolayer and bi-layer Se-doped MoS₂ and demonstrate the fine-tuning of the bandgap via controlled doping [1]. Next, using atomic resolution Z-contrast imaging on an aberration-corrected scanning transmission electron microscope (STEM), we provide direct observation and quantification of individual Se dopant atoms in the MoS₂ lattice, as shown in Figure 1. We develop a robust image analysis method that allows locating and quantifying the Se dopant distribution with single-atom resolution and *single-layer* discrimination for the first time. Furthermore, using a calibration between bandgap and doping level obtained from photoluminescence spectroscopy measurement and density- functional theory calculations, the doping level quantified via STEM imaging can be converted into bandgaps, and thus provides a measure of the local band gaps at the 10 nm scale.

We show that Se dopants can randomly substitute S atoms in the lattice up to 75% dopant level, and there is no preference for forming any particular Se and S configuration in nearest neighbor chalcogen sites. Furthermore, in an AB stacking bilayer structure, we find that each layer contains similar Se doping levels, randomly distributed, suggesting a possible concurrent growth, instead of sequential growth, of bi-layer MoSe_{2(1-x)}S_x alloy under our synthesis conditions. The methodology for quantitative local band gap mapping developed in this study can also be applied to other 2D materials in general.

References:

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[2] D.O. Dumcenco *et al.*, *Nat. Commun.* **4**, 1351 (2013).

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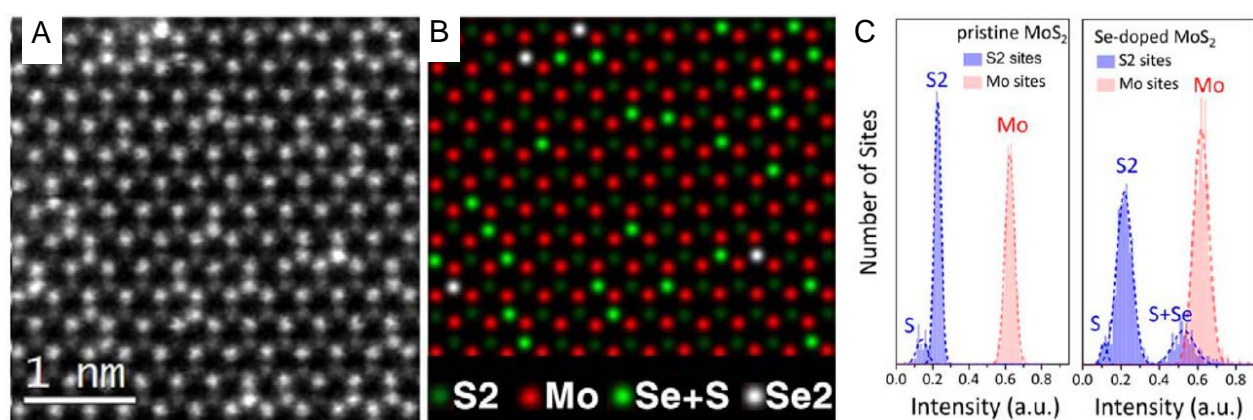


Figure 1. Atom-by-atom dopant analysis in monolayer MoS₂ adapted from Ref. [1]. (A) ADF image of Se-doped MoS₂. (B) Structure model obtained from histogram analysis showing the distribution of single- and double-Se substituted S₂ sites. Red, Mo sites; dark green, S₂ sites; bright green, Se + S sites; white, Se₂ sites. (C) Site-separated image intensity histogram analysis of pristine and Se-doped MoS₂ monolayers. The dashed lines are Gaussian fits to the intensity peaks.