Native and Irradiation-Induced Defects in Two-Dimensional Inorganic Materials

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Two-dimensional (2D) materials such as graphene, hexagonal boron nitride, transition metal dichalcogenides (TMDs) and silica bilayers have recently received lots of attention due to their unique properties and numerous potential applications. All these materials have defects, which naturally affect their characteristics. Moreover, defects and impurities can deliberately be introduced by irradiation or chemical treatment to tailor the properties of these systems.

In my talk, I will present the results of our first-principles theoretical studies [1-7] of defects in 2D systems, compare them to the experimental transmission electron microscopy data, and discuss how defect and impurities can be used to engineer the electronic structure of 2D materials. Specifically, we showed that vacancies produced by the electron beam agglomerate and form line structures, which can be used for engineering material properties [2]. In some chalcogen-deficient TMDs, rotational defects appear under electron beam [4], which eventually give rise to formations of new grains inside the material. We further demonstrated that TMDs can be doped by filling the vacancies with impurity atoms or introducing impurities during the growth stage [1,3].

We also studied the atomic scale morphology of non-stoichiometric 2D TMDe $MoSe_{2-x}$ and showed that a Se-deficit in single layers of $MoSe_2$ grown by molecular beam epitaxy gives rise to a dense network of mirror-twin-boundaries (MTBs) decorating the 2D-grains [5]. Using density functional theory calculations, we further demonstrated that MTBs are thermodynamically stable structures in Se-deficient sheets. These line defects host localized states close to the valence band minimum thus giving rise to enhanced conductance along straight MTBs.

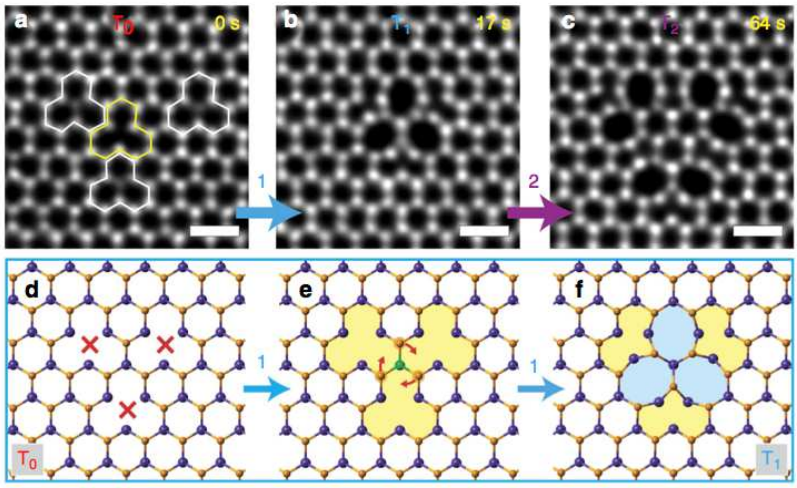

Figure 1: Structure, formation and evolution of rotational defect in WSe_2. The filtered experimental TEM images of WSe_2 of (a) Se single vacancy (SV, white polygon) and Se double vacancy (DV, yellow polygon), (b) Rotational T1 defect and (c) T2 defect. (d–f) The atomic model of T0 to T1 transformation including the creation of three DV Se (red crosses) (d) and a 60° rotation of three pairs of W–Se bonds around the W atom (green) e to form T1 with three octagons (blue; f).

I will also touch upon our simulations of defect production under ion [8,9] and electron [1] irradiation. For the former, the Ehrenfest dynamics and time-dependent density functional theory was shown to be an accurate approach beyond the adiobatic approximation to calculate electronic stopping power in graphene [9]. The latter (specifically the knock-on damage) can quantitatively be described [1] by density-functional theory-based molecular dynamics and McKinley-Feshbach formalism. I will also touch upon Stone-Wales transformations in graphene and silica bilayers [10], 2D materials with the hexagonal symmetry, and address the equivalent transformations in 2D materials with the trigonal symmetry, such as BN or TMDs [4]. I will present the theoretical data on defect evolution, migration and agglomeration and compare the theoretical results to the available experimental data.

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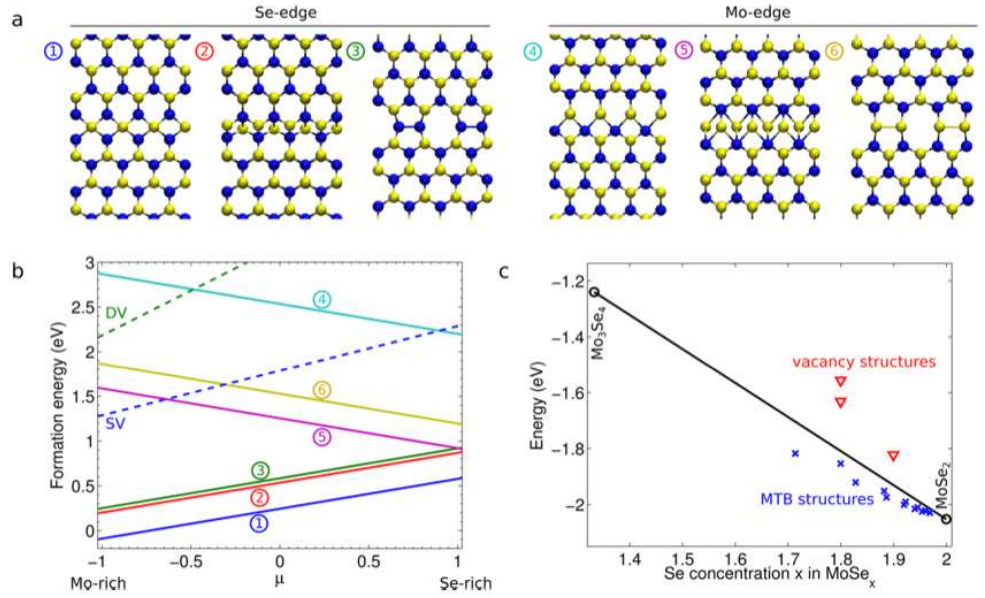

Figure 2: Calculated energetics of twin boundary structures (a) Atomic structures of the MTB candidates considered. The structures are grouped depending on whether they are constructed from Mo- or Se-edges. (b) The calculated formation energies of all MTBs as well as single (SV) and double vacancy (DV) lines as a function of the Se chemical potential. (c) Heats of formation of defective MoSe2 systems compared to the energies of the bulk MoSe2 and Mo_3Se_4 phases. The chemical potentials for Mo and Se are taken from the reference phases. The calculated energies are scaled to the number of Mo atoms in the system and plotted as a function of their Se/Mo fraction.