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Electronic Structure and Coupling of Re Clusters In Monolayer MoS_2

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Two dimensional materials like BN and transition metal dichalcogenides have promising optical applications. How local atomic structure controls optical, electrical and magnetic property is both interesting and critical for further engineering of those materials. MoS_2 in the monolayer or thin layer form has been widely explored for exotic optical, electrical and catalytic applications. In the monolayer form, MoS_2 is a direct bandgap (1.9 eV) semiconductor. Re doping has been introduced as a method to improve the electrical conductivity [1] and explore the possible phase transformation [2]. And directe exchange between single Re and Mo atoms are also observed [3]. The electronic structure and coupling of Re dopants in monolayer MoS_2 are important to further utilize the doping strategy.

The Re doped monolayer MoS_2 samples were grown via a chemical vapor deposition method. Molybdenum oxide, sulfur powder and ammonium perrhenate were used as the Mo, S and Re sources, respectively. The samples were first grown on Si/SiO_2 (285 nm) wafers and then transferred onto a Quantifoil TEM grid. The samples were baked at 150 ^{0}C in vacuum before observation by scanning transmission electron microscopy (STEM) at 60 kV.

Atomic resolution STEM images with different Re cluster structures are taken. Atom identification was achieved by a python code implemented in pycroscopy [4]. Re clusters with different numbers and structures are identified. Analysis were also carried out over different regions to get statistical population of different Re clusters. Monte Carlo based simulations were carried out to simulate the growth process considering the occupation of Mo and Re atoms.

Density functional theory (DFT) simulations were carried out to understand the electronic structure of different Re clusters and possible coupling of Re atoms (Figure 1). DFT results show that the coupling is strong when the Re distances are below two times lattice constant. A single isolated Re dopant shows a shallow donor defect level near the conduction band. The defect levels of Re clusters move toward the middle of the bandgap with increasing number of Re atoms. Binding energies show that Re clusters with a larger number is energetically favored. It was also found that Re clusters favors the formation of sulfur vacancies and this was confirmed in the STEM images.

To summarize, we carried out systematical study on the structure and population of Re clusters. The coupling between Re atoms were studied by DFT, population analysis of Re clusters and Monte Carlo simulations. Those results provide insights for further control of dopants in monolayer MoS_2 [5].

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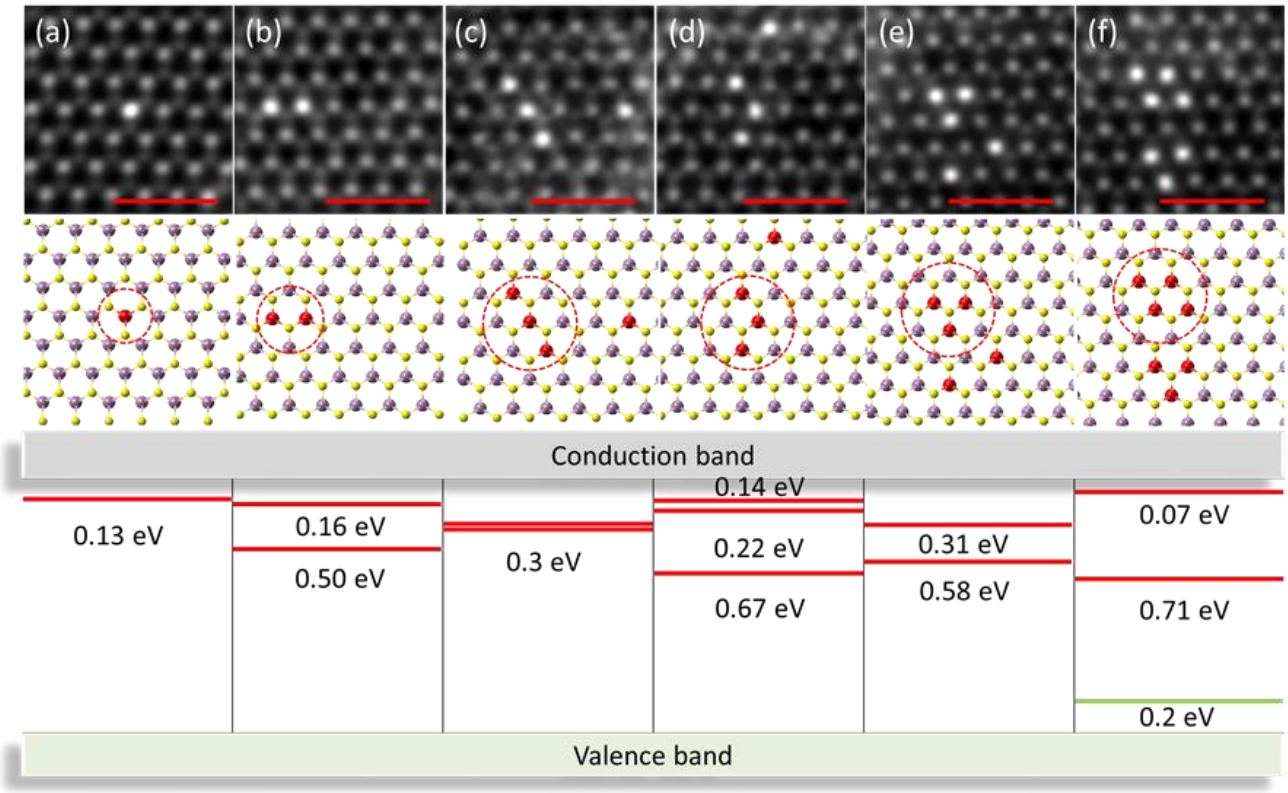

Figure 1. Re cluster structures in MoS_2. The MAADF image (upper panel), structural model (middle panel) and defect levels in the bandgap (lower panel) of single isolated Re atom (a), Re dimers (b), linear Re cluster (c), L shaped Re cluster (d), triangle shaped cluster with sulfur site at center (e) and Re quad cluster (f). Scale bar 1nm.

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