

Exchange of Re and Mo atoms in MoS₂ driven by Scanning Transmission Electron Microscopy

Shi-Ze Yang¹, Weiwei Sun^{2,1}, Yu-Yang Zhang², Yongji Gong³, Matthew F. Chisholm¹, Sokrates T. Pantelides^{2,1}, Wu Zhou¹

¹ Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA

² Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA

³ Department of Materials Science & NanoEngineering, Rice University, Houston, Texas 77005, USA

Two-dimensional materials exhibit unique properties that can be used for novel applications. These properties are adversely affected or positively promoted by different types of defects. “Defect engineering” is thus employed as a tool to control material functionality. For example, Lin et al. used a STEM’s electron beam to sculpt and simultaneously image nanowires that are only three-atoms thick in transition-metal dichalcogenide monolayers[1]. Ishikawa et al. reported the direct observation of the migration of Ce and Mn dopant-atoms in a bulk AlN crystal[2]. Scanning transmission electron microscopy has proven to be an effective tool to study defect structures.

We study the dynamic structure evolution of Re dopants in MoS₂ through atomic level scanning transmission electron microscopy. In our experiments, samples were grown by chemical vapor deposition. The as-grown sample was transferred onto a TEM grid by the solution method, and afterwards the sample was baked at 160 °C for eight hours. Imaging was performed with an aberration-corrected scanning transmission electron microscope (Nion UltraSTEM 100) operated at 60 kV using medium angle annular dark field (MAADF, inner angle 50 mrad) with a beam current of 9 pA.

Exchange between Re and Mo atoms was observed by electron microscopy. The direct exchange migration process is shown in Figure 1, where nearby Mo and Re atoms were found to exchange their positions. The images in Fig. 1a and 1b are the sum of twelve consecutive images with single frame time of 1.18 second. It was found that the exchange event occurred within two frames (1.18 second). No cation vacancies were found to be involved in the process and thus it is concluded that the migration process is through direct exchange.

Further experiments were carried out to account for the poor time resolution (1.18 second). Migration processes mediated by cation vacancies were observed and recorded. It was found that the cation vacancy is highly mobile under similar imaging conditions. Although surface cation atoms moved around, no surface cations were observed to move to the cation vacancy site and fill the vacancy. This behavior is further support for the conclusion that Re and Mo exchange their positions.

The effect of sulfur vacancies was carefully studied. In the experiment, under a constant electron beam irradiation, sulfur vacancies are being created, and a nearly linear relationship between electron beam dose and sulfur vacancy density has been found. By linear fitting, 10⁸ electrons of 60 kV over 8 nm by 8 nm area create one single sulfur vacancy. DFT simulations also show that local sulfur vacancies can greatly reduce the energy barrier for diffusion, but the net barrier is still much larger than the energy that can be transferred to a Mo or Re atom by the electron beam. Further calculations find that the presence of sulfur vacancies and displacements of the Re atom lead to dynamically changing localized energy

levels in the band gap. These levels can facilitate extensive electron-hole recombination processes which transfer energy to local phonons and enable the direct exchange (a form of “explosive” recombination enhanced migration). Based on the above results, we propose that spectator sulfur vacancies play a critical and multifaceted role in the observed direct exchange process. If similar structures (Fig. 1) can be created, the exchange process can thus be reproduced. In these experiments, we parked the electron beam at the chosen positions to control sulfur vacancy creation. So far, our efforts have been limited to reproducing the exchange event. The reproducibility further supports our hypothesis that sulfur vacancies can be used to control the exchange of neighboring cations in MoS₂ experimentally [3].

References:

- [1] Lin, J., *et al.* Nat. Nano. **9** (2014), p. 436.
 [2] Ishikawa Ryo, *et al.* Physical Review Letters **113** (2014), p. 155501.
 [3] This work was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division and by Award DE-FG02-09ER46554(VU).

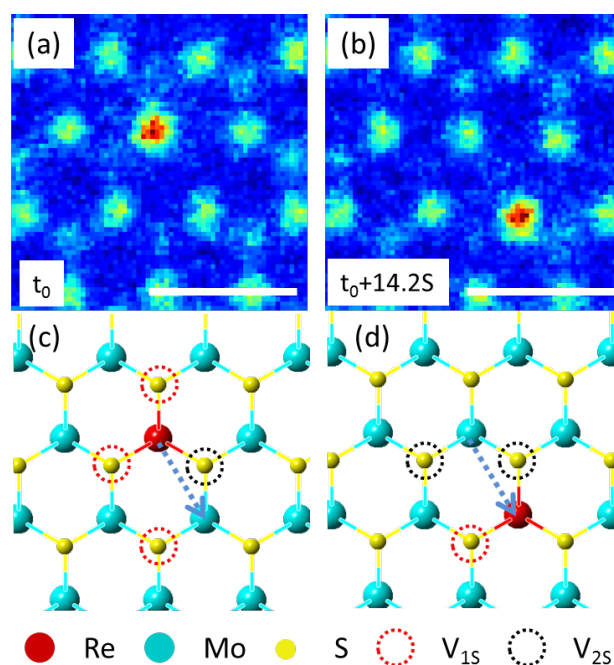


Figure 1. (a) the image before the exchange event, obtained from Re doped MoS₂ in the 1H phase and recorded at 60 kV from the medium-angle annular dark field (MAADF) image at time t_0 ; (b) the image recorded 14.2 seconds after the exchange event. The atoms showing slightly weaker brightness than Re are Mo atoms and atoms with the lowest contrast (least brightness) are sulfur atoms. The exchange of Re and Mo atoms are highlighted by blue dash arrows, while sulfur mono-vacancies are highlighted by dash circles. Sulfur vacancies are highlighted by dash circles in the structure model below the MAADF images: Re atoms are in red, Mo in cyan, and sulfur in yellow.