Quantitative Scanning Transmission Electron Microscopy Study of Monolayer $Re_xMo_{1-x}S_2$

Shize Yang[1], Yongji Gong[2], Andy Lupini[1], Mark Oxley[1], Pulickel M. Ajayan[2], Matthew F. Chisholm[1], Wu Zhou[1].

[1.] Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831, United States.
[2.] Department of Materials Science and NanoEngineering, Rice University, 6100 Main Street, Houston, Texas 77005, United States

Two-dimensional transition-metal dichalcogenides (TMDs, chemical formula MX_2) are promising candidates for flexible nanoelectronics, as many of them in their monolayer form are direct bandgap semiconductors. TMD alloys can be achieved via chemical doping at the metal or chalcogen sites, and their optical and electronic properties can be tuned by controlling the composition and dopant distribution [1, 2, 3].

An interesting TMD alloy system is $Re_xMo_{1-x}S_2$, where the two end components, i.e. pure MoS_2 and ReS_2 monolayers, have different stable 1H and diamond 1T (DT) structures, respectively. The structure models and the corresponding atomic resolution scanning transmission electron microscope medium anglge annular dark field (STEM MAADF) images of 1H MoS_2, DT ReS_2 and Mo doped DT ReS_2 are shown in Figure 1 (a, b), (c, d) and (e, f), respectively. As Re has one more valence electron than Mo, the structure evolution of this ternary alloy as a function of composition is largely controlled by the electron doping. Understanding the distribution and behavior of Re atoms in this system can, thus, reveal how local electron density triggers phase transformation in TMD materials.

Single layer $Re_xMo_{1-x}S_2$ samples were prepared using chemical vapor deposition (CVD). The as-grown $Re_xMo_{1-x}S_2$ samples with a range of Re concentration were transferred onto TEM grids for electron microscopy analysis. The atomic structure and structure dynamics were studied by STEM MAADF imaging and electron energy-loss spectroscopy (EELS) using a Nion UltraSTEM-100 microscope at 60 kV.

Atom finding algorithms written in Python were used to locate the atomic positions in the images. Two dimensional Gaussian functions were then applied for fitting of local intensities to increase precision. MAADF image intensity of a single atom is highly sensitive to its atomic number Z. Thus, quantification of MAADF image intensity allows for atom-by-atom identification in monolayer $Re_xMo_{1-x}S_2$. To identify Re and Mo atoms in the images, statistical histograms of site intensities are plotted, in which Re and Mo atoms should generate two distinct intensity peaks. Additionally, the coordination numbers for both Re and Mo can be determined by analyzing the local atomic neighbors. Figure 2 shows the atomic resolution STEM ADF images used for analysis and the corresponding bonding configurations used for calculation of alloying degree [2, 3]. In order to evaluate the resistance of the alloy to phase separation, an alloying degree of solubility of Re (Mo) is defined. The alloying degree of Re is defined as average Mo coordination number over six divided by the Mo content and vice versa. The alloying degree of both Re and Mo are plotted in Figure 2(c). For all the experimental images analyzed, the alloying degree is around 100%. This shows that the samples with different contents tend to form one single phase with random distribution of solute atoms. There is no phase separation over the

Re content range we've analyzed. Thus there might be a threshold content value separating the two phases and this will be further studied by DFT simulations.

References:

[1] Kutana, A., E. S. Penev and B. I. Yakobson, Nanoscale 6(2014), 5820-5825.
[2] D. O. Dumcenco, H. Kobayashi, Z. Liu et al, Nat Commun 4 (2013), 1351.
[3] Gong, Y. J., Z. Liu, A. R. Lupini et al., Nano Lett 14(2014), 442.
[4] The work is supported by the U.S. Department of Energy, Office of Science, Basic Energy Science, Materials Sciences and Engineering Division and through a user project at ORNL's Center for Nanophase Materials Sciences (CNMS).
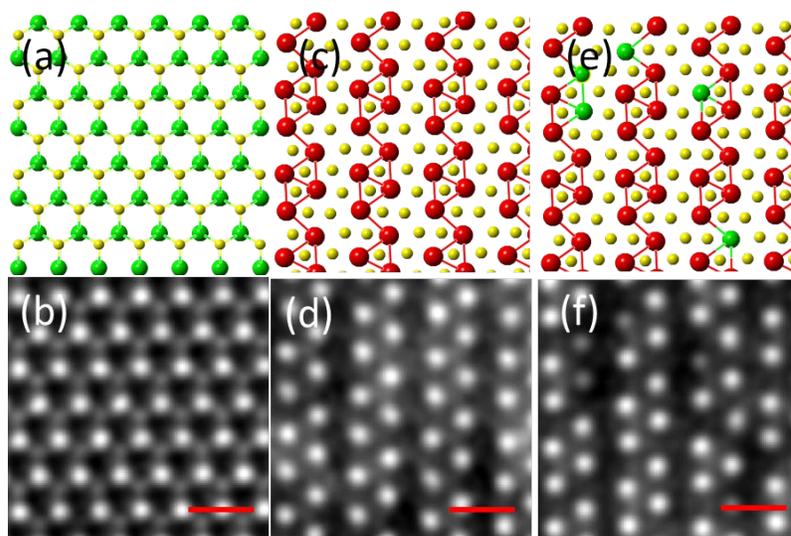
Figure 1. The structure models and corresponding atomic resolution STEM ADF images of 1H MoS_2, DT ReS_2 and Mo doped DT ReS_2 are shown in (a, b), (c, d) and (e, f), respectively. Scale bars: 0.5 nm.
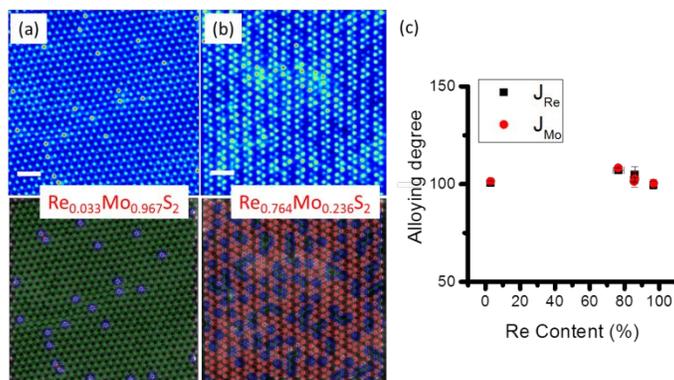

Figure 2. (a) top: ADF image of 1H phase $Re_{0.033}Mo_{0.967}S_2$, bottom: illustration of bonding used for analysis of alloying degree, with Re-Re bonding in red, Re-Mo bonding in blue and Mo-Mo bonding in green; (b) top: ADF image of DT phase $Re_{0.764}Mo_{0.236}S_2$, bottom: illustration of bonding; (c) alloying degree for both Re and Mo; scale bar 1nm.