doi:10.1017/S1431927615001300 Paper No. 0051 Microsc. Microanal. 21 (Suppl 3), 2015

Growth Morphology and Defects in 2D Heterostructures and Interfaces

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Since the successful isolation of graphene, two-dimensional materials have rapidly moved to the forefront of "next generation" materials. The many applications range from enhancing the structural properties of composite material properties,[1] to water filtration,[2] biosensing,[3] catalysis,[4] photonics,[5] and ultra-low power electronics.[6] However, none of these applications will be possible without a concerted effort to develop techniques to understand how the 2D layers are grown and their material performance.

We have developed processes to synthesize a variety of 2D materials, with an emphasis on "beyond graphene" layers.[7–9] In the case of tungsten diselenide (WSe_2), growth conditions, including temperature and total pressure, have a strong impact on the crystalline size, shape, and nucleation. Synthesis at high pressure results in a significant reduction in nucleation density and increase crystallite size, however, it also leads to the formation of particulates on the sample surface, which were subsequently identified as W-rich WSe_2 *via* cross-sectional transmission electron microscopy (TEM). The presence of such particles provided evidence that the selenium-to-tungsten (Se:W) ratio in vapor phase can be critical to achieving stoichiometric WSe_2. As a result, the Se:W ratio is a critical factor in controlling defect formation in WSe_2. This is evident in Figure 1a-d, which consists of atomic force microscopy scans of the WSe_2 surface, as a function of the Se:W ratio as it is increased from 170 to 14,000. The figure clearly demonstrates that domain size increases significantly as the Se:W ratio is increased, which is accompanied by a decrease in the density of W-rich WSe_2 particulates. Figure 1e is the cross-sectional HRTEM image of MOCVD grown multilayer WSe_2 directly on sapphire. HRTEM reveals some disorder at the WSe_2/sapphire interface suggesting a reaction during growth, which is in agreement with previous works suggesting that sapphire (Al_2O_3) is not stable.

In addition to synthesis of WSe_2, the synthesis of van der Waals heterostructures are also of increasing importance in the advancement of the field. Figure 2a shows the cross-sectional HRTEM image of CVD grown monolayer MoS_2 on bi-layer graphene and SiC substrate. The MoS_2 layer appears to be "blind" to thickness variations in the underlying graphene when there are no defects in the top layer of the graphene. However, when the top graphene layer is interrupted, the MoS_2 will also be discontinued, as indicated in the Figure 2a. Figure 2b shows HAADF image of monolayer MoS_2/WSe_2 grown tri-layer graphene and SiC substrate. The contrast in a HAADF-STEM image is approximately proportional to Z^2, where Z is the atomic number. Using HAADF, the MoS_2 and WSe_2 layers were clearly distinguished, as shown in Figure 2c. There are existing monolayer WSe_2 with brightest contrast and monolayer MoS_2 with second brightest contrast. Finally, we note that defects and edge states in the base 2D layer lead to low energy nucleation sites, and therefore multilayer growth of a top layer is highly probable at these regions, as shown in in Figure 2c.

This work was supported by the Center for Low Energy Systems Technology (LEAST), one of six centers supported by the STARnet phase of the Focus Center Research Program (FCRP), a Semiconductor Research Corporation (SRC) program sponsored by MARCO and DARPA; and the Defense Threat Reduction Agency (DTRA) under contract HDTRA1-14-1-0037.

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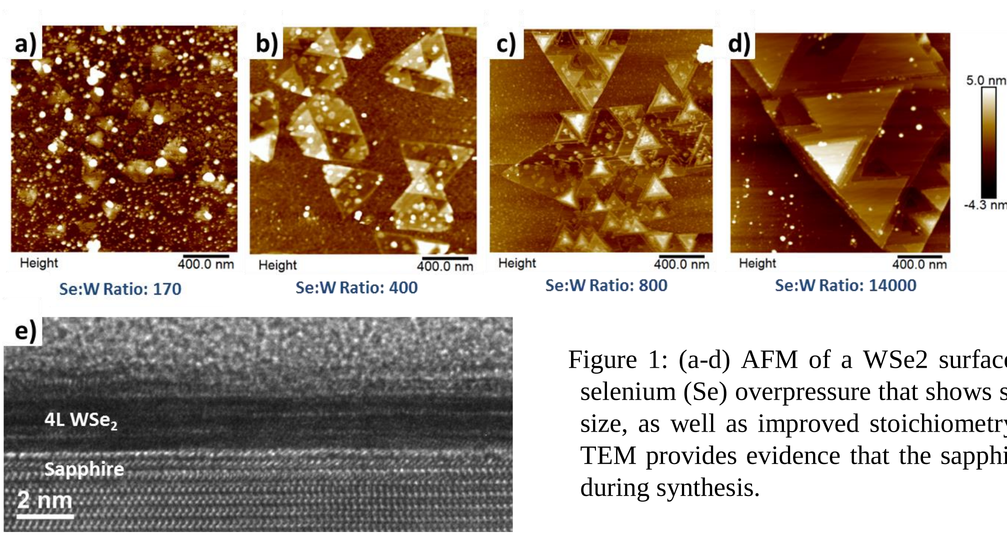

Figure 1: (a-d) AFM of a WSe2 surface as a function of increasing selenium (Se) overpressure that shows significant increase in domain size, as well as improved stoichiometry (reduction in particles). (e) TEM provides evidence that the sapphire substrate may be unstable during synthesis.

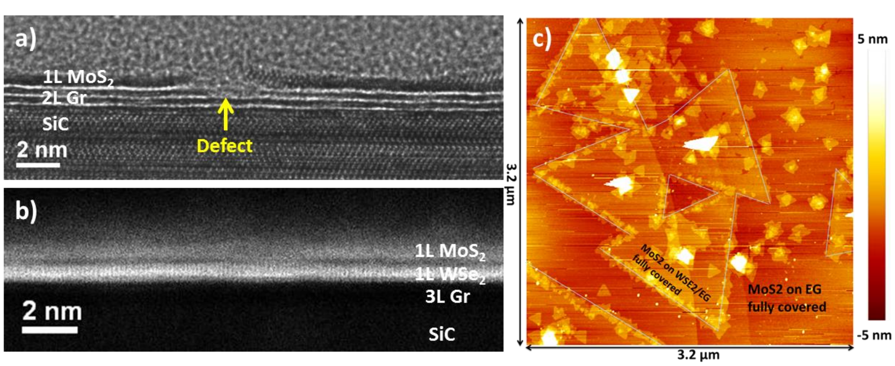

Figure 2: (a) TEM reveals that growth of 2D materials on graphene are highly sensitive to defects in the graphene. (b) TEM also provides evidence that multiple junction structures of MoS_2/WSe_2 on graphene can be directly grown, where (c) defects and edges on WSe_2 leads to multilayer MoS_2.