Recrystallization Cycling and Quenching Study for the Synthesis and Characterization of Transition-Metal Dichalcogenides

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Introduction: Two-dimensional transition-metal dichalcogenides (TMDs) are a class of layered materials that have shown significant potential for applications in electronics and optoelectronics due to their unique electrical and optical properties when exfoliated down to molecular monolayers.[1] High-purity materials as well as large crystal sizes are necessary for understanding and optimizing this potential.[2] A two-step flux synthesis method has been developed to produce TMDs with significantly reduced concentrations of charged and isovalent point defects.[3] However, substitutional defect densities remain at densities greater than 10^{11} cm^{-2}, and the relatively small sizes of the resulting crystals are not ideal as they hinder exfoliation yields and device fabrication. To address these issues, this effort uses a recrystallization cycling process to attempt to further reduce point defect densities and produce larger crystals. However, the recrystallization effort is found to introduce impurities, increasing the defect density, and have minimal effect on the crystal size. Additionally, crystal growth dynamics are investigated through *ex-situ* crystal size measurements throughout the synthesis process via quenching and backlight imaging, maximizing the efficiency of the synthesis process.

Methods: High-purity tungsten (99.999%) or molybdenum (99.997%) powder and excess selenium shot (99.999%) are loaded into a quartz ampule at a 1:5 molar ratio, then sealed under vacuum. The ampules are then placed in a box furnace, ramped from room temperature to 1000˚C for 1-2 days, dwelled at 1000˚ C, and quenched in water after varying dwell times. The crystals are then transferred to a second ampule, vacuum-sealed, and annealed in a temperature gradient (T_{cold}=22˚C, T_{hot}=300˚C) to remove remaining embedded chalcogen. Resulting crystals and powders are extracted and transferred to a new ampule with additional selenium at a 1:50 molar ratio, where the ampule is again vacuum-sealed and the process is repeated for multiple cycles. Crystals are sorted and imaged using a backlight microscope, then crystal size analysis is completed using ImageJ software. Raman spectra and x-ray diffraction patterns are obtained by illuminating bulk or powdered crystals with visible light or x-rays, respectively. Monolayers are obtained by exfoliating onto a SiO_2/Si wafer with standard procedures.[4] Once identified, they are transferred to a Quantifoil™ on gold mesh grid for transmission electron microscopy (TEM) by evaporating isopropyl alcohol between the monolayer and the grid and etching the SiO_2/Si substrate with KOH.

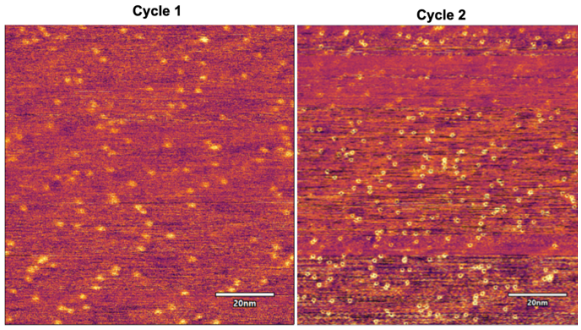

Figure 1. Conductive atomic force microscopy 100 nm x 100 nm images for two recrystallization cycles of WSe_2.

Results: The first cycle produced small WSe_2 crystals with an average size of 1 mm and essentially no $MoSe_2$ crystals as only 0.05% of the theoretical yield were converted to usable crystals. Additionally, conductive atomic force microscopy images of the starting WSe_2 crystals showed an isovalent defect density of $1.1 \cdot 10^{12}$ cm^{-2}. The second cycle, using a 1:50 molar ratio of crystal powder and selenium, also produced essentially no crystals for both WSe_2 and $MoSe_2$, with crystal yields less than 1%. X-ray powder diffraction patterns confirmed the powder product is $MoSe_2$ or WSe_2, which could be used for further cycles. Conductive atomic force microscopy images of the WSe_2 crystals following the first cycle showed an increased defect density of $2.5 \cdot 10^{12}$ cm^{-2}, suggesting that using the powder from the first cycle as the metal precursor in the second can introduce additional isovalent impurities. As a result, for the third cycle, the dwell time was increased from 3 to 7 days and the metal to selenium molar ratio was decreased to 1:10 for the third cycle. The third cycle

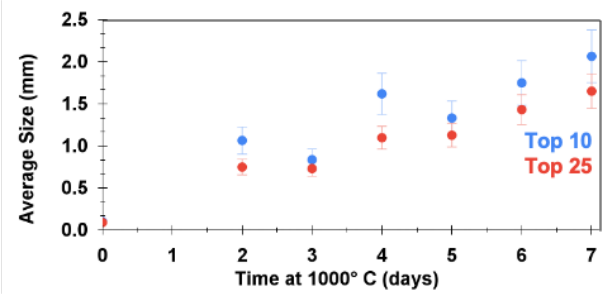

Figure 2. Average of 10 and 25 largest crystals as a function of 1000 ˚C dwell time.

produced very small crystals with average sizes of 500 µm. To investigate the effects of the dwell length on the resulting crystal size, ampules containing tungsten and selenium in a 1:5 molar ratio were ramped to 1000˚C then dwelled for varying times. Each ampule was quenched every day over the course of 7 days. The crystal size as a function of dwell time displays a direct relationship, indicating the easiest way to grow larger crystals is through longer dwells.

Table I. Defect density measurements for 2 cycles of WSe_2.

Cycle #	Defect Density (cm^{-2})
1	1.1×10^{12}
2	2.5×10^{12}

Conclusions: As reflected in Table I, using two-step flux WSe_2 powder as the metal precursor in addition cycles led to an increase in isovalent defect density. Three-day dwells are sufficient to produce WSe_2 and $MoSe_2$ powder as confirmed by x-ray diffraction analysis. However, size analysis of the three recrystallization cycles show that a dwell time longer than three days is necessary to produce a significant number of usable crystals. The results of the quenching study demonstrate that average crystal sizes of WSe_2 and dwell time over the first seven days of dwelling are directly related. Future studies are needed to investigate the relationship between dwell time and $MoSe_2$ crystal sizes, as well as whether cycling using fully formed crystals and longer dwell times produces larger crystals with less defects. Additionally, future studies can investigate the implications of more cycles, dwell times longer than seven days, and different $WSe_2/MoSe_2$ powder to selenium ratios.

References:

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