Twist Angle Dependent Chemical Reactivity of 2D Molybdenum Disulfide (MoS_2) in Nitridation Conversion

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Introduction

Background

- MoS_2 is a member of the transition metal dichalcogenide (TMD) family of two-dimensional (2D) materials

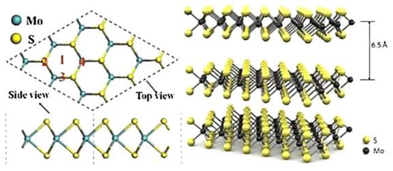

Figure 1. Crystal structure of MoS_2 [1]

- In addition to its mechanical and band structure properties, MoS_2 gains unique characteristics when layers are twisted
- Twisting MoS_2 generates Moiré superlattices, based on the twist angle

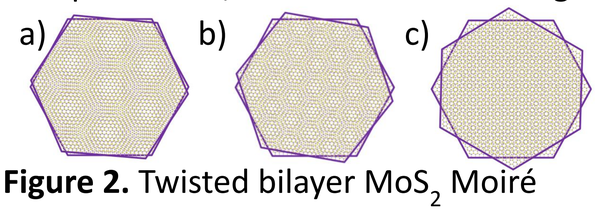

Figure 2. Twisted bilayer MoS_2 Moiré superlattices at a) 5°, b) 15°, and c) 30° angles

Objective

- To gain a deeper understanding of how Moiré superlattices affect the chemical properties of MoS_2

Methods

Sample Preparation

- MoS_2 flakes were prepared through gold-assisted exfoliation and deposited on Si / SiO_2 substrates
- Twisted 2L+2L MoS_2 samples were fabricated via a dry transfer process using Poly (Bisphenol A carbonate) (PC)

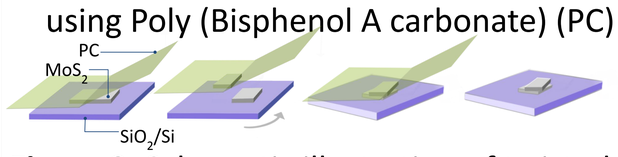

Figure 3. Schematic illustration of twisted MoS_2 dry transfer fabrication.

Nitridation Reaction

- Nitridation of twisted MoS_2 samples was performed in a quartz furnace tube filled with ammonia and argon gas, each at a flow rate of 50 sccm, and heated to a temperature of 680 °C.

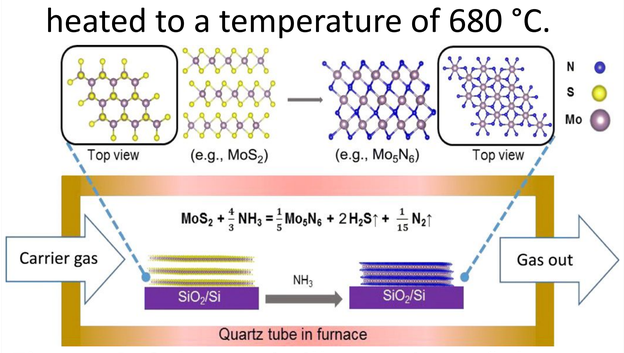

Figure 4. Schematic illustration of the nitridation of MoS_2 to Mo_5N_6 [2]

Raman Spectroscopy

- Renishaw inVia microscope was used, laser excitations at 532 nm setting

Results

Optical Microscopy Imaging

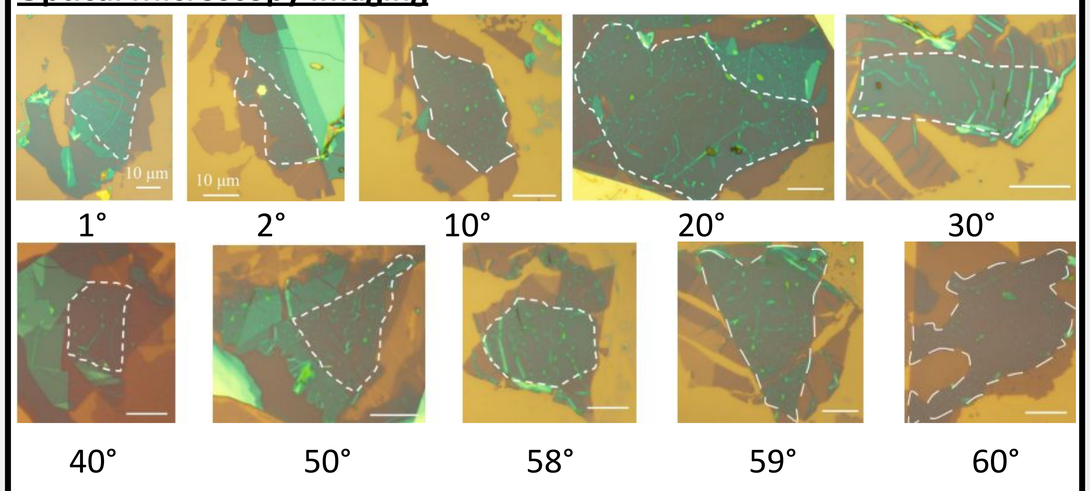

Figure 5. Optical images of twisted MoS_2 samples at different twist angles. Twisted regions are indicated by white dash lines.

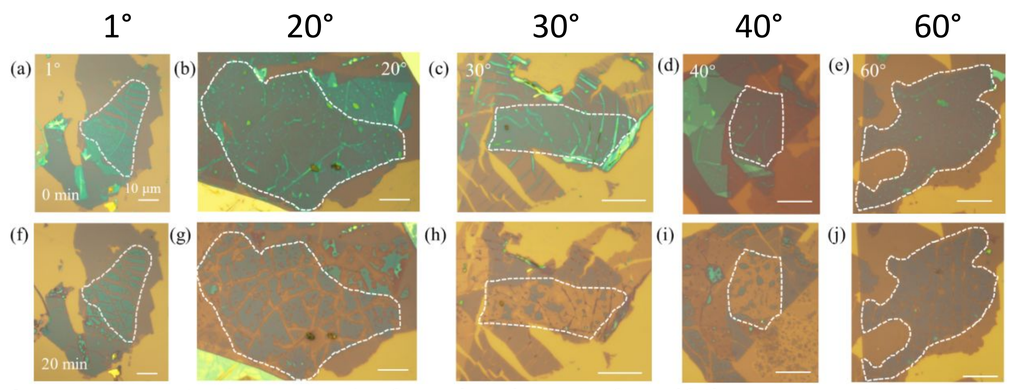

Figure 6. Optical images before (a-e) and after (f-i) running the nitridation reaction for 20 minutes.

Raman Spectra and Mapping

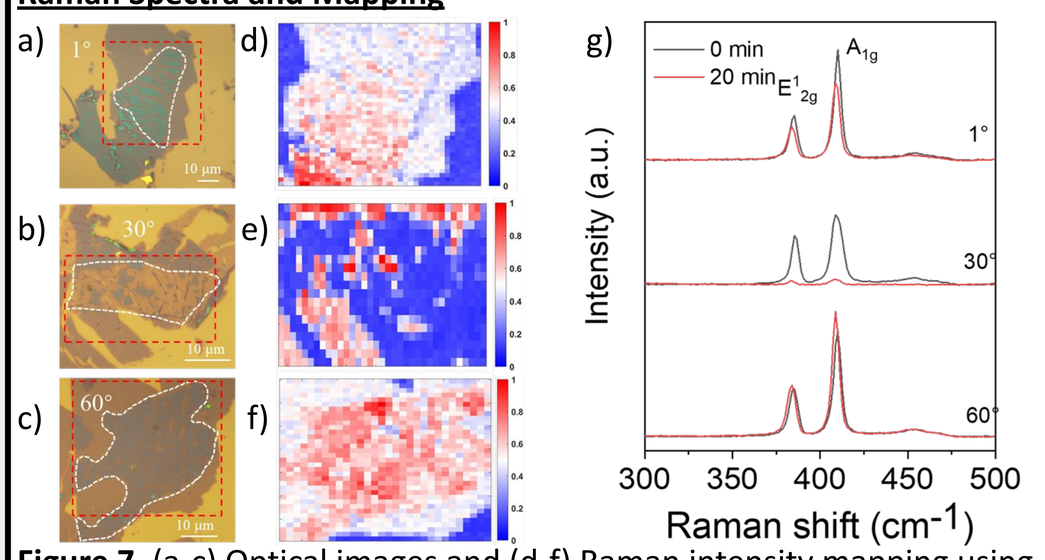

Figure 7. (a-c) Optical images and (d-f) Raman intensity mapping using E^1_{2g} mode of MoS_2 for 1°, 30° and 60° samples after conversion. (g) Raman spectra comparison of the samples before and after the conversion reaction. The red dashed lines label the regions where the Raman mappings were taken.

Twist Angle Dependent Reactivity

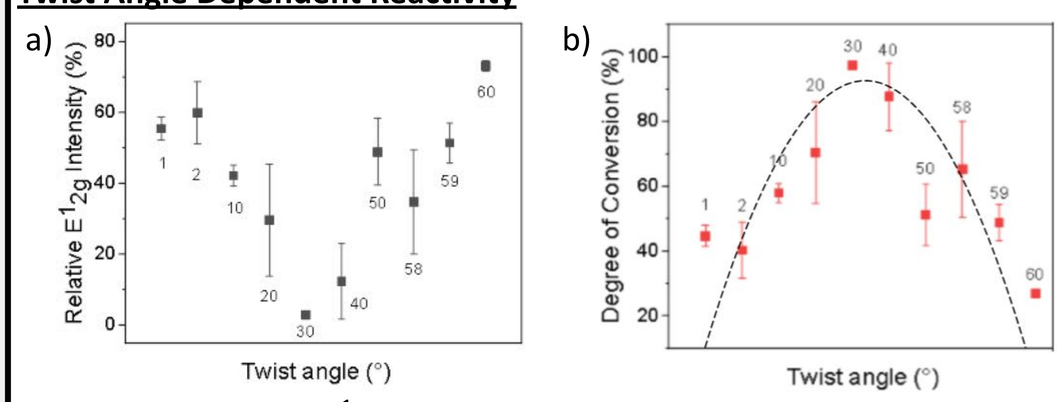

Figure 8. (a) Relative E^1_{2g} peak intensity of the samples after conversion, calculated using **Equation 1**. (b) Degree of conversion of the samples, calculated using **Equation 2**.

Equation 1:

$$\text{Relative Intensity (RI)} = \frac{(I_{E2g\ final} / I_{Si\ final})}{(I_{E2g\ initial} / I_{Si\ initial})} \times 100\%$$

Equation 2:

$$\text{Degree of Conversion (DoC)} = 1 - \text{RI}$$

Discussion

Summary of Results

- Samples with twist angles around 30° exhibit higher reaction rate than the others, showing a volcano plot-like relationship of nitridation reactivity to twist angles from 0° to 60°.
- This data suggests that it is lattice mismatch, not numerical twist angle, which affects twist MoS2 's reactivity
- Moiré superlattices generated at each twist angle therefore affect the homostructure's chemical properties

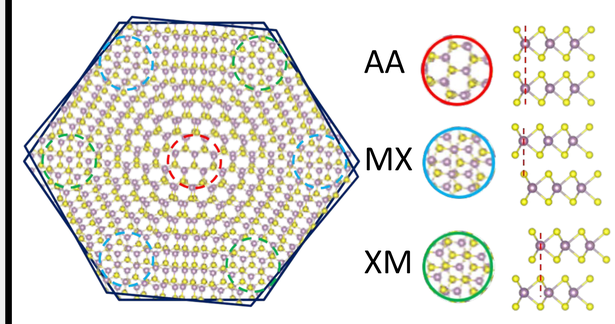

Figure 9. Localized stacking configurations within the twisted MoS_2 Moiré superlattice

Future Plans

- Extend the study to larger twist angles up to 120° to further reveal the relationship between nitridation reactivity and twist angle of MoS_2
- Further analysis into how the twist angle dependent Moiré superlattice's local stacking structures (as in Fig. 9) affect atomic substitution reactions
- Performing transmission electron microscopy (TEM) on crystal structures of the twist nitridation products, which might provide us deeper understanding of the chemical reactivity phenomena

References

[1] He, Z.; Que, W. "Molybdenum Disulfide Nanomaterials: Structures, Properties, Synthesis and Recent Progress on Hydrogen Evolution Reaction." *Applied Materials Today* **2016**, *3*, 23–56.
[2] Cao, J.; Li, T.; Gao, H.; Lin, Y.; Wang, X.; Wang, H.; Palacios, T.; Ling, X. "Realization of 2D Crystalline Metal Nitrides via Selective Atomic Substitution." *Science Advances* **2020**, *6* (2).

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