# Activated Reduction Plasma Assisted Sulfurization in Layered $WS_2$ Synthesis

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## Abstract

CVD process is known as a promising method in large domain size and continuous 2D film synthesis. Sulfurization of Group VIB contained precursor (metal or metal oxide) for sulphide formation were widely studied. Sulfur is also reported as reduction agent of metal oxide at initial stage. In some cases, $H_2$ flew along with sulfur vapor during reduction time in MOCVD [1] and ALD [2] process. $H_2$ could be beneficial in the impurity removal and to enlarge the domain size effectively.

Plasma source in vacuum technology is useful especially in lowering the process temperature and for increasing the precursor decomposition efficiency in CVD or ALD process. R. Morrish et al., revealed that a and longer than 30 min at 500°C for sulfurization process using 10% $H_2S$ plasma could reduce the activation energy between $WO_3$ and $H_2S$ [3]. The presence of energetic radicals such as atomic S and H during sulfurization, the temperature and the exposure time are important.

In this study, we demonstrated the sulfurization process by two steps: (1) The energetic hydrogen (H*) generated by ICP plasma in $WO_3$ reduction at early stage, (2) Reaction between the activated hydrogen (H*) and sublimated sulfur vapor for $WS_2$ formation. The hydrogen concentration, plasma exposure time, the reaction temperature and duration time are evaluated for the sulfurization of $WO_3$.

$WO_3$ film was deposited on Si substrate covered by 90 nm thermal dry oxide. Samples were sulfurized in a 4 inch inductively coupled plasma (ICP) reactor with copper coil connected to a 13.56 MHz RF power supply. The reaction temperature varied from 700 to 900°C. Raman and PL spectrum were adopted for the film quality inspection. The surface roughness of formed $WS_2$ layers were examined by AFM. The best condition performed when the reaction temperature was 850°C with 5% $H_2$ plasma pre-treatment for 20min. Higher H% is harmful for film formation, which was similar to the report by K. N. Kang et al. that sulfurization can etch the damage of the film [4]. Raman and photoluminescence (PL) spectroscopy were taken with 532 nm excitation. The uniform Raman signals and PL spectrum within 4 $cm^2$ are shown and the center of the PL peak was at 629 nm (1.97 eV).

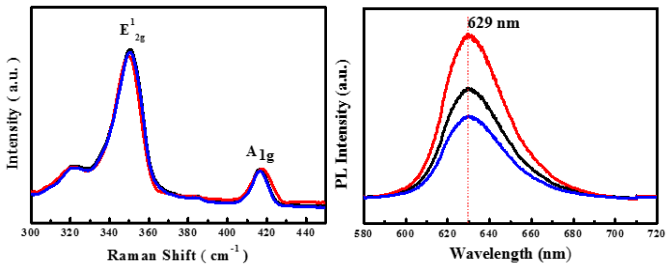


Figure 1. The Raman and PL spectrum of optimal $WO_3$ sulfurization in this study. The three color lines obtained from different position of the sample within 4 $cm^2$ of the as prepared $WS_2$.

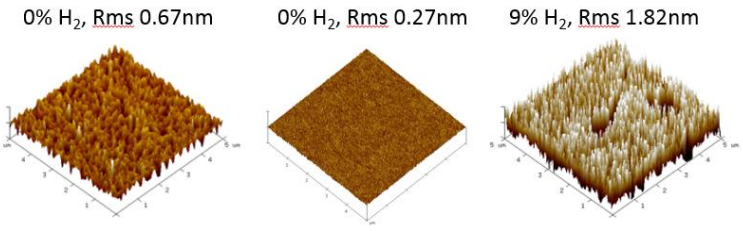


Figure 2. AFM images of as prepared $WS_2$ sulfurized with different hydrogen concentration.

**Reference:**

[1] K. Kang et al, Nature, 520, 656 (2015).
[2] Y. Kim et al, Sci rep., 6, 18754 (2016)
[3] R. Morrish et al., Chem. Mater. 26, 3986−3992 (2014)
[4] K. N. Kang et al., Scientific Reports, 5, 13205 (2015)