Role of Annealing Atmosphere Towards Stoichiometry and Chemical Integrity of Solution-Processed MoS_2 Thin Films

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1. Introduction

Among various approaches, solution process is one of the quickest and simplest methods to produce MoS_2 thin films, compared to other techniques such as chemical vapor deposition (CVD), atomic layer deposition (ALD), and mechanical exfoliation [1-3]. However, their stoichiometry and chemical integrity are typically affected by sulfur vacancies (V_s) that serve as reactive sites for oxygen incorporation and cause degradation in device performance [4]. Annealing in sulfur vapor (S-vapor) represents a promising technique toward the restoration of stoichiometry through sulfur replenishing and concurrent oxidation suppression. Herein, we demonstrate the solution-based synthesis of MoS_2 films on Si_3N_4 surfaces with various precursor concentrations (5, 12, 16, 20, 25, and 30 mM) followed by annealing in argon (Ar) and sulfur vapor (S-vapor) at 700 °C. S-vapor annealed films achieved a near-ideal S/Mo ratio (~2:1) with significantly lower oxidation than Ar-annealed films, indicating the strong influence of annealing atmosphere on the stability of MoS_2 .

2. Experimental Procedure

Molybdenum disulfide (MoS_2) films were prepared from a precursor solution via a single-step annealing in Ar and S-vapor atmospheres. The precursor solution was obtained by dissolving ammonium tetrathiomolybdate [$(NH_4)_2MoS_4$, 99.999%, Sigma Aldrich] in a solvent mixture of dimethylformamide (DMF), isopropanol (IPA), and ethanolamine with the 3:5:3 (v/v) ratio. The solution was stirred for 2 h, and spin-coated on clean Si_3N_4 surfaces at 500 rpm for 10 s and 3000 rpm for 30 s. The Si_3N_4 surfaces were treated with 0.5% HF for 60s followed by rinse with DI water. The films were pre-annealed at 180 °C for 30 min and annealed at 700 °C for 1 h under 1 slm Ar flow using a lamp annealing system. S-vapor annealing procedures are demonstrated in Fig.1. The fabricated MoS_2 films were characterized using transmission electron microscopy (TEM), Raman spectroscopy, x-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS) respectively.

3. Results and Discussion

To assess the stoichiometry and sulfur vacancy (V_s) of the MoS_2 films, X-ray photoelectron spectroscopy (XPS) measurements were performed on both the surface and after 15 s etching, as illustrated in Fig. 2. At 5 mM, both films show sulfur deficiency (S/Mo ~2:1), but Ar-annealed films (Fig. 2a) remain sub-stoichiometric across all concentrations. In contrast, S-vapor annealed films (Fig. 2b) approach the ideal 2:1 ratio with increasing concentration and achieve homogeneous stoichiometry above 12 mM. These results confirm the effectiveness of S-vapor annealing in mitigating sulfur vacancies [5], despite minor surface oxidation upon air exposure.

The Mo^{6+}/Mo^{4+} ratios of Ar and S-vapor annealed MoS_2 films were obtained from the Mo 3d XPS spectra (Fig. 3). Ar-annealed MoS_2 films (Fig. 3a) undergo significant oxidation, with Mo^{6+}/Mo^{4+} ratios reaching a maximum at ~0.45 around 16 mM and persisting even after etching, indicating interfacial defects and oxygen incorporation. In contrast, S-vapor annealing keeps the ratio below 0.2 (slightly higher at the surface), yielding stoichiometric and chemically stable films above 12 mM as illustrated in Fig. 3b. These results confirm the superior oxidation resistance of S-vapor annealed MoS_2. Sulfur vacancies in MoS_2 strongly affect its electronic properties and also promote environmental degradation through oxidation. To investigate the impact of these vacancies and the subsequent adsorption of O_2 and H_2O molecules, density functional theory (DFT) calculations were performed as shown in Fig. 4. PDOS analysis shows that pristine MoS_2 with a band gap (E_g) of 1.7 eV, has a S-3p dominated valence band and a Mo-4d dominated conduction band with no mid-gap states. Introducing a sulfur vacancy reduces the band gap to 1.3 eV and creates Mo 4d defect states near the Fermi level. O_2 adsorption slightly recovers the gap (1.5 eV) but leaves residual states, indicating poor passivation. In contrast, H_2O adsorption restores the gap to 1.74 eV, effectively suppressing defect states and providing better passivation.

4. Conclusions

In conclusion, S-vapor annealing is essential for repairing sulfur vacancies, suppressing oxidation, and achieving near-stoichiometric, crystalline MoS_2 films. This post-synthesis treatment offers a reliable route to structurally and chemically stable MoS_2 for future electronic applications.

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References

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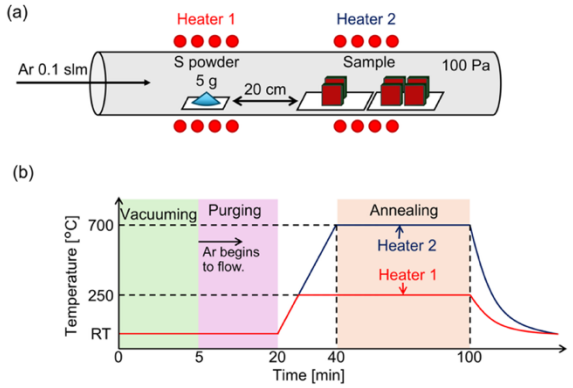

Fig. 1: (a) Schematic of the two-zone furnace setup used for sulfur annealing of MoS_2 films and (b) Temperature vs time profile of annealing process.

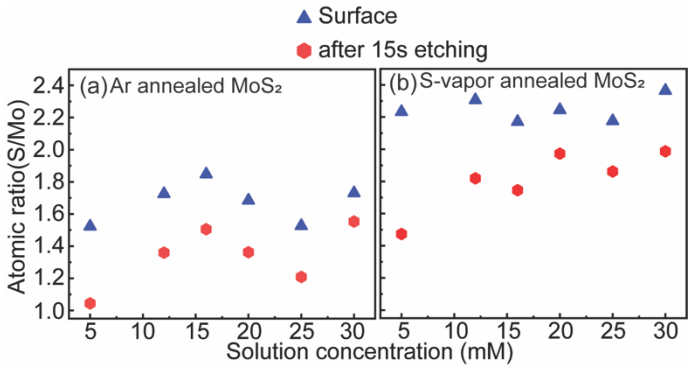

Fig. 2: Sulfur-to-molybdenum (S/Mo) atomic ratio of MoS_2 films as a function of precursor concentration, extracted from XPS of Mo 3d: (a) Ar-annealed and (b) S vapor-annealed films at 700 °C.

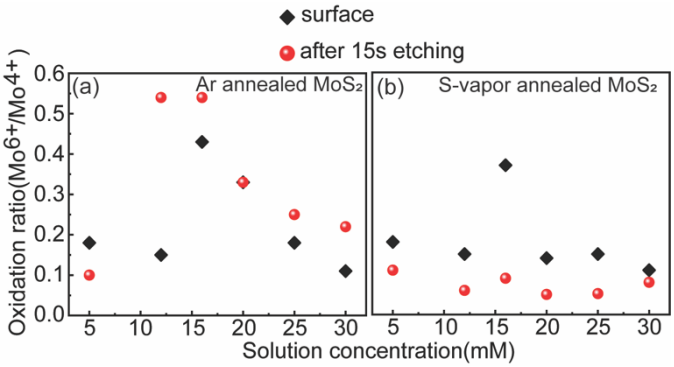

Fig. 3: Mo^{6+}/Mo^{4+} ratio as a function of solution concentration, extracted from Mo 3d XPS spectra of MoS_2 films grown on Si_3N_4 surfaces using (a) Ar annealing and (b) S vapor annealing at 700 °C.

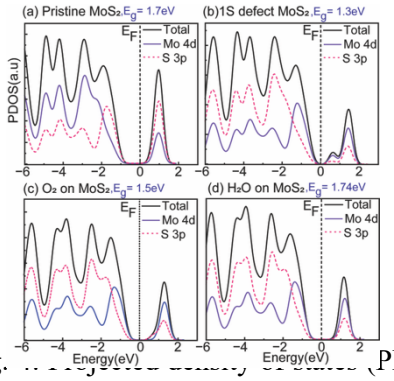

Fig. 4: Projected density of states (PDOS) (a) Pristine MoS_2 (b) Sulfur defect (1S) defect MoS_2 (c) O_2 adsorbed MoS_2 and H_2O adsorbed MoS_2 respectively.