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# Facile synthesis of large-area and highly crystalline $WS_2$ film on dielectric surfaces for SERS

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ABSTRACT

A facile fabrication of high-quality and large-area tungsten disulfide ($WS_2$) layers is demonstrated using a thermal decomposition of tetrathiotungstates ($(NH_4)_2WS_4$) with two annealing process. During synthesis, the first annealing step is utilized to achieve lateral epitaxial growth of the $WS_2$ and create seamless and large-area $WS_2$ film. The second annealing step can offer an S-rich and high temperature condition, which is beneficial for the high quality of the $WS_2$ film. Scanning electron microscopy, Raman spectroscopy and atomic force microscopy confirm the presence of large-area and high-quality $WS_2$ film. The crucial role of the S, $H_2$ and the effect of the temperature during the experiment are also investigated. Furthermore, the potential application of the prepared $WS_2$ as a substrate for Raman enhancement is first discussed using R6G molecules as probe molecule.



## 1. Introduction

Recently, transition metal dichalcogenides (TMDCs) with two-dimensional (2-D) layer structure analogous to graphene has been attracting extensive scientific interests [1–13]. The TMDCs can be divided into metal, semimetal, or semiconductor due to the coordination and oxidation of the metal [8–10]. Among them, the semiconducting phases ($MoS_2$, $WS_2$, etc) have exhibited many unique properties. The optical and electronic properties of the materials are quite different such as valleytronics [14–16], when the indirect band gap in the bulk-layer form transformed into direct in the single-layer form. Molybdenum disulfide ($MoS_2$) has showed great potential applications in 2-D semiconductors with extraordinary electronic and optical properties in such materials [1], and there have been many studies about it [4–7]. Analogous to $MoS_2$, $WS_2$ layers are composed by a slab S–W–S sandwich crystallize in a Vander Waals layered structure. It possesses many remarkable characteristics such as the coupled spin and valley physics [17], the indirect-to-direct band-gap transition, high photoluminescence emission efficiency of monolayer $WS_2$ [14] and band structure tunability with strain [18]. Furthermore, the $WS_2$ layer can combine with other 2-D materials to form a large category of layered composites for further applications [19–21].

There have been various applications on $WS_2$ such as field-effect transistors (FET) [20–23], hydrogen evolution [24], and saturable absorber of mode-locked laser [25] etc. Most of applications are based on the electrical measurement, and the Raman enhancement effect on the $WS_2$ film has not been investigated up to now. The Raman enhancement effect is a practical phenomenon which is used for light-matter interaction and matter–matter interaction studies and for microanalytical applications [26]. At this time, $MoS_2$ film as a substrate for surface enhanced Raman scattering (SERS) has been proved and note that a flat surface has promising importance for further application of SERS [27]. Similar to $MoS_2$, the $WS_2$ film is a very flat and uniform substrate which may provide a good choice for SERS. We will explore potential application of the $WS_2$ as a substrate for Raman enhancement.

To cater to the needs of various applications, significant attempts have been made currently to prepare $WS_2$ thin films by different routes such as chemical exfoliation [24,28], mechanical exfoliation [14,17,29], and sulfurization of tungsten oxide films [30,31]. Nevertheless the method to synthesize large-area and

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high-quality $WS_2$ layers is still rare. Here, an approach for the large-area and high-quality deposition of the $WS_2$ thin film is offered.

It has been reported that the thermolysis of $(NH_4)_2WS_4$ in $N_2$ atmosphere for the growth of $WS_2$ nanotubes [32]. The $(NH_4)_2WS_4$ is firstly transformed into $WS_3$ at the temperature 180–280 °C as shown in aq (1). Then, the $WS_3$ will further decompose into $WS_2$ (aq2), which needs a higher temperature of ~600 °C. In this work, the $(NH_4)_2WS_4$ directly transforms to $WS_2$ under a mixture of Ar and $H_2$ carrier gas as described in eq (3) with the temperature lowered to 500 °C.

$$(NH_4)_2WS_4 \xrightarrow{180\sim280^{\circ}C} 2NH_3 + H_2S + WS_3 \quad (1)$$

$$WS_3 \xrightarrow{600^{\circ}C} WS_2 + S \quad (2)$$

$$(NH_4)_2WS_4 + H_2 \xrightarrow{500^{\circ}C} 2NH_3 + 2H_2S + WS_2 \quad (3)$$

In order to improve the crystallization quality of $WS_2$ films, it is reasonable to increase the thermolysis temperature. However, we find that the $WS_2$ easily decomposes in $H_2$ atmosphere when the temperature is higher than 500 °C. Meanwhile, the direct annealing of the $(NH_4)_2WS_4$ at a higher temperature may be affected by the presence of oxygen if there is no protection of $H_2$. Thus, two annealing process are conducted in this study.

## 2. Experimental

Fig. 1(a) schematically shows the first step for the synthesis of $WS_2$ films on $SiO_2$ substrate. The 1 ml dimethylsulfoxide (DMSO) was added into the high purity $(NH_4)_2WS_4$ (Alfa Aesar purity of 99.99%; 0.01 g) powder to form a 1wt% solution. The $(NH_4)_2WS_4$ solution was treated by sonication in ultrasonic cleaner for 20 min with the power of 80 W to break down the undissolved particles. Then we made a thin and uniform $(NH_4)_2WS_4$ film by spinning $(NH_4)_2WS_4$ solution onto $SiO_2$ substrates with a spinner at a rotating speed of 2000 rmp for one minute. The sample was put in the horizontal constant temperature zone after 20 min baking treatment at 120 °C. When the pressure was pumped to $10^{-3}$ Pa by a molecular pump, the quartz tube was heated to 500 °C at 10 °C/min for the first annealing with gas mixture ($Ar/H_2$ = 80/20 sccm) to efficiently remove the byproducts separated from the precursors. The $(NH_4)_2WS_4$ precursors were thermally decomposed into $WS_2$ after 60 min reaction. The samples were cooled to room temperature naturally to obtain lateral epitaxial structure. Then, the quartz tube was heated again until the center of the furnace reached 800 °C for the second annealing in the atmosphere of Ar/S as shown in Fig. 1(b). S powder (99.5%, Alfa Aesar; 500 mg) was placed in the low-temperature zone of about 200 °C which sublimates the S powders into sulfur vapors. Ar is used to avoid the system oxidation and carry sulphur vapors to the surface of the $WS_2$. After 30 min treatment, the samples were cooled to room temperature naturally.

### 2.1. Apparatus and characterization

Surface morphologies of the $WS_2$ were observed using scanning electron micros-copy (SEM, Zeiss Gemini Ultra-55) with energy-dispersive X-ray spectroscopy (EDX) for chemical analysis. The Raman spectroscopy was performed using a Raman spectrometer (Horiba HR Evolution 800) with laser excitation at 532 nm. The morphological changes of $WS_2$ layers were characterized by atomic force microscopy (AFM, Park XE100). The crystalline quality and the single-crystalline structure of $WS_2$ thin films were characterized by XRD (Bruker D8). The transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were carried out by a transmission electron microscopy system (Hitachi H-800).

## 3. Results and discussion

Fig. 1(a) schematically shows the first step for the synthesis of $WS_2$ films on $SiO_2$ substrate. The first annealing with gas mixture ($Ar/H_2$) make the $(NH_4)_2WS_4$ precursors thermally decompose into seamless and large-area $WS_2$ film. Then, in order to get the high crystallization quality of $WS_2$ films, the quartz tube was heated again for the second annealing in the atmosphere of Ar/S as shown in Fig. 1(b). Fig. 2(a) exhibits SEM image of the $WS_2$ thin layers after the second annealing at 800 °C. The edge region of the $WS_2$ film is clearly observed which can visually identify the presence of the large-area, uniform and continuous $WS_2$ films. In order to observe the surface morphology clearly, SEM image of $WS_2$ film at a higher

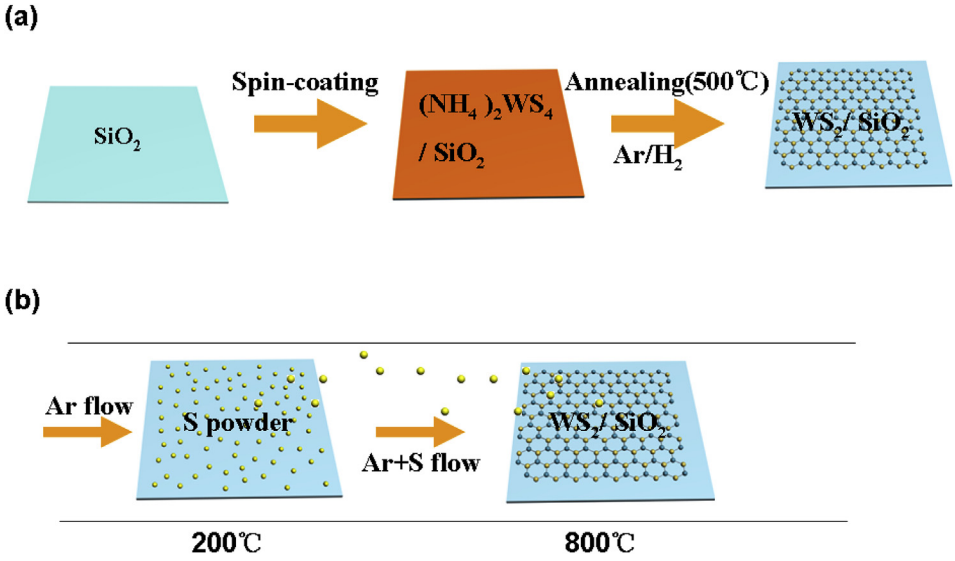


**Fig. 1.** (a) Schematic illustration of the first process for the synthesis of $WS_2$ films on $SiO_2$ substrate. (b) the second annealing in the (Ar+S) gas environment with the $WS_2$ in the high-temperature zone and a boat of S powders in the low-temperature zone.