**Article**

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# Deposition of $ReS_2$ Thin Films Using Aerosol-Assisted Chemical Vapor Deposition

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## Abstract

Transition metal dichalcogenides (TMDCs) have remarkable properties, which can make these materials as a source alternative to graphene. The new member of TMDCs family $ReS_2$ has got interest because its unique property. Synthesis $ReS_2$ still needs a high temperature to deposit; the high deposition temperature makes $ReS_2$ materials highly cost to produce. In this work the rhenium carbamate complex ($[Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4]$) which have a high thermal stability was used to synthesis $ReS_2$ thin films by reducing the deposition temperature to 525 °C, 25 °C less from previous study. The produced thin films were deposited using Aerosol-Assisted Chemical Vapor Deposition (AA-CVD). Films have been characterized firstly by p-XRD which confirmed that $ReS_2$ thin films were successfully prepared, then the morphology of thin film were investigated by SEM and the results showed morphology was smooth and uniformed.

## Introduction

Transition-metal dichalcogenides (TMDCs) field has attracted the interest of research groups due to their wide application; therefore, it is a promising field. The TMDCs such as $WS_2$, $WSe_2$ $MoS_2$ and $MoSe_2$, in bulk form have indirect band gab, however, if monolayer for they have direct band gap. This feature is giving different application in transistors devices, electroluminescent and photodetectors [1]. The new member in TMDCs family rhenium disulfide ($ReS_2$) is a rare transition metal dichalcogenide. It is rare because it's found at only one location in the Kudriavy volcano on Iturup Island in the Kuril Islands, off the west coast of Russia [2]. $ReS_2$ has a direct bandgap, which remains in bulk materials and monolayers unlike most other TMDCs. The material still has a direct band gap semiconductor by transferring from bulk to monolayer [3, 4], with values from 1.47 eV in case of bulk to 1.61 eV in a monolayer, with evidence of birefringent behavior [5]. Rhenium sulfide has a complicated structure more than other metal dichalcogenides such as $MoS_2$ [6]. Rhenium disulfide has a distorted 1*T* triclinic structure and weaker interlayer coupling, different from most of others TMDCs, which have 2*H* structure. And because of this unique feature in the crystal structure $ReS_2$ possess many different characteristics [3]. So, because of these extraordinary properties that $ReS_2$ has, it can potentially be use in different applications such as transistors [7], digital electrocatalysts [8], inverters [9], and photodetectors [10]. The larger interlayer distance bulk material 0.614 nm and weak interlayer coupling [11], can be used to improve the electrochemical performance for Lithium-ion batteries [12, 13]. Different techniques have been used to synthesis $ReS_2$ by MOCVD at high-temperature (650 to 80 °C) has been used to produce $ReS_2$ nanoparticles were successfully synthesised [14], using CVD $ReS_2$ monolayers were produced [1, 15]. A thermal-evaporation method was used to synthesis few layers of $ReS_2$ [16]. $ReS_2$ nanosheets have been produced using a facile hydrothermal method,

and suggested that $ReS_2$ could be a promising candidate to lithium-ion batteries [17].

A few layers thickness nanosheets of $ReS_2$ were produced using two different methods the aerosol assisted chemical vapor deposition (AACVD) followed by top-down LPE technique [18]. Rhenium disulfide is a unique material because of it has attractive properties among the 2D materials. The rhenium carbamate complexes have a high thermal stability as a result it needs a high temperature to decompose and deposit on the substrate. In this study we have deposited $ReS_2$ using carbamate rhenium precursor at 525 °C reduced the deposition temperature or these complexes by 25 °C from previous study [19].

## Experimental

**Chemicals:** The chemical reagents were purchased from Sigma-Aldrich and Biochem, used without further purification. Bis(diethylthiocarbamoyl)disulfide (≥97.0%), tetraethyl ammonium bromide (99%), acetonitrile anhydrous (99.8%), ammonium perrhenate (≥99.0%) were purchased from Sigma-Aldrich. Acetonitrile (99.9%), dichloromethane (99.0%), methanol (99.9%), diethyl ether (99.8%), ethanol absolute, sulfur (≥99%), ammonium sulfide (20 wt.% in water), hexane (99.0%), were purchased from Biochem. All reactions were carried out under

### Deposition of thin films using aerosol-assisted chemical vapor deposition (AACVD).

AA-CVD was used to deposit the rhenium or cobalt sulfide thin films by employing ($[Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4]$), 0.1 mmol concentrations of 0.1 mmol in 30 mL of THF at 525 °C. Argon was used as inert gas carrier with flow rate 200 sccm into the furnaces where the precursor mist will decompose then deposit on a clean glass substrate (1 × 2 cm), with depositions typically lasted for ca. ~ 150 min.

## Synthesis of tetraethylammonium tetrathioperrhenate ([$(Et_4N)ReS_4$]) Complex

This complex has been reported previously [20]. Briefly, 100 mL of ammonium sulfide was used to dissolve 0.7 g elemental sulfur, then solution stirred quickly for 10 minutes, to produce a deep orange colour. After that, 6.3 g tetraethyl ammonium bromide and 3.9 g of ammonium perrhenate [$NH_4ReO_4$] were added respectively, and the reaction stirred for 20 h at room temperature. The product precipitated and isolated using vacuum filtration. The precipitate was washed with different ratios of a mixture of ethanol, diethyl ether, methanol, and deionised water by the rate (1:2:3:3) respectively, to produce a dark violate powder, which was dried in vacuum oven overnight to yield crude compound (90.4 %). Then 2.85 g of the crude product was then recrystallized from a mixture of acetonitrile 400 mL which reduced by heating to 200 mL. Then 200 ml of toluene has been added, followed by further by heating to 200 mL then the solution was allowed to ice bath very slowly for 30 minutes at room temperature to yield dark-green crystals, which were collected by suction filtration and washed with 50 mL of toluene (50 mL) and diethyl ether (50 mL) and dried in vacuum oven.

## Synthesis of ([$Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4$]) Complex

The compound was synthesized as reported previously [21]. [$(Et_4N)\ ReS_4$] (1.1 g, 2.5 mmol) was reacted with bis (diethylthiocarbamoyl) disulfide (1.1g, 3.37 mmol) in dry acetonitrile (50 mL) for 27 h. The green precipitate was filtered and washed three portions with equal amount (50 ml) of hexane and (50 ml) dichloromethane, finally dried in vacuum oven overnight.

## Results and Discussion

Thermogravimetric analysis (TGA), which have been explained in previous study [19]. The thermal decomposition range of complex ([$Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4$]) was determined using thermogravimetric analysis. Rhenium

Precursor decomposed in three steps the first two steps are in the temperature ranges from 127 °C to 705 °C. The first started at 127 °C to 465 °C, while the second step started from 565 °C to 705 °C. Then in last step, the precursor goes in slow decomposition process to1000 °C. The residue of ([$Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4$]) precursor after being held at 1000 °C corresponded to rhenium sulfide.

The p-XRD patterns of $ReS_2$ film show five peaks (figure 1), which correspond to the (001), (002), (230), and (313) crystal planes of 1T-$ReS_2$, are located in 2θ positions 14.463, 29.165, 44.356, and 60.508, respectively. It was possible to directly measure the *d*-spacing of (001) plane in $ReS_2$ from p-XRD data, and it was is (6.11928 Å)

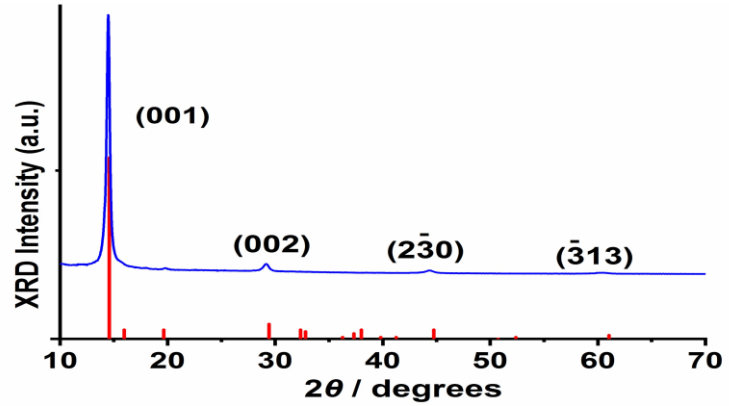


**Figure 1: The P-XRD pattern of rhenium disulfide deposited by AACVD using ([$Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4$]) (1) at 525 °C.**

The surface morphology of the $ReS_2$ films deposited by AA-CVD at 525 °C were investigated using SEM. The morphologies of $ReS_2$ that observed was a lamellar morphology. Rhenium sulfide have been synthesized with different morphologies, teardrops [22], lamellar[18], flowers [23], hexagonal [15], and microspheres[17, 24, 25]. Figure 2 shows a smooth and uniform morphology of the synthesized $ReS_2$ films. In this work we have reduced the deposition temperature of $ReS_2$ using carbamite complex from 500 °C in previous study [19], to 525 °C in

this study. Reducing the deposition temperature is important for less cost and reduces the probability of oxidizing the metal sulfide.

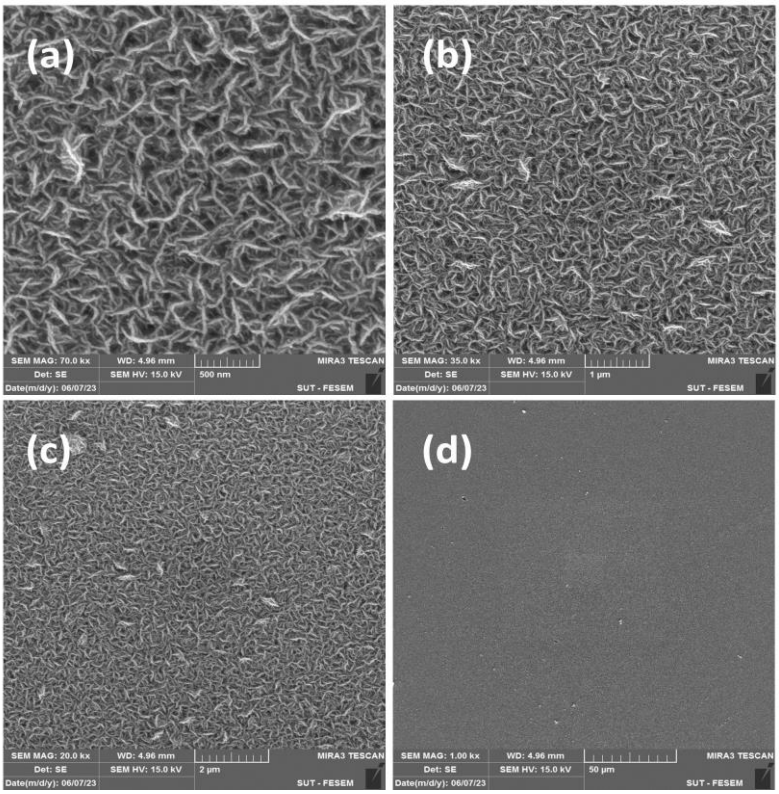


**Figure 2: Secondary electron SEM images (10 kV) of rhenium sulphide ($ReS_2$) thin films deposited by AA-CVD at 525 °C. Scale bars represent: (a) 500; (b) 1 µm; (c) 2 µm; (d) 50 µm.**

## Conclusion

In this work $ReS_2$ thin film was produced using aerosol-assisted chemical vapor deposition (AA-CVD) using single source precursor ($[Re_2(\mu\text{-}S)_2(S_2CNEt_2)_4]$) at 525 °C. These types of precursors have a high thermal stability. Therefore, it needs a high temperature so can be deposited on a substrate. Reducing the deposition temperature is important for less cost and reduces the probability of oxidizing the metal sulfide. The produced materials have been characterized firstly by p-XRD which confirmed that $ReS_2$ thin films were successfully prepared, then the morphology of thin film was investigated by SEM and the results showed morphology was smooth and uniformed.

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