

Chemical Vapor Deposition of NbS₂ from a Chloride Source

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Abstract

NbS₂ thin films were grown on SiO₂/Si substrate by ambient pressure chemical vapor deposition (CVD) using a metal chloride source. We found that NbS₂ nanosheets can be grown directly on the SiO₂/Si substrate with the aid of hydrogen gas mixed in the carrier gas. It appears that the major cause of the misorientation is the off-stoichiometry with surplus Nb. The quality of the films was evaluated by X-ray diffraction and Raman spectroscopy as well as resistivity measurements at low temperatures. They showed a resistivity minimum at the same temperature of the charge density wave (CDW) transition for a bulk single crystal of 3R-NbS₂.

1. Introduction

CVD growth of MoS₂ is widely studied partly because of the distinct feature of MoS₂ is its thin film growth; due to the volatile nature of the MoO₃, the oxide impurities are automatically removed during the chemical vapor deposition (CVD). This makes it possible to fabricate large area atomic layer crystals using a rather crude setup. Other metal chalcogenides, such as NbS₂, suffers from the oxide impurities. We demonstrate it is possible to grow NbS₂ from the chloride source, NbCl₅, and elemental S with the aid of hydrogen (H₂) gas mixed in the carrier gas. Chlorides are easily available, easy to purify, and free from possible contamination due to byproducts in the decomposed organometallic sources. We show the separate-flow CVD system has eliminated several weak points of the singleflow CVD system such as the mutual contamination of sources, and successfully synthesized a high-quality 3R-NbS₂ film.

2. Experimental

The synthesis of the NbS₂ thin films was carried out using a separate flow APCVD apparatus[1,2] including a three-zone furnace, an outer quartz tube with an inner diameter of 22 mm and two inner quartz tubes, two small one-zone furnaces, and two source containers as illustrated in Figure 1. The grown film was characterized by optical microscope, AFM, SEM-EDS, Raman and resistivity measurement between 300K to 1.7K.

3. Results

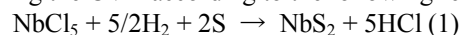
H₂ gas flow was very important to make c-axis oriented films with large domain. At the optimized condition, well-defined hexagonal crystal was observed by AFM (Fig.2 (a)). The magnified image of the top surface exhibited layer-by-layer structure with the unit thickness of 0.6nm

(Fig. 2(b) and (c)). Raman spectra shown in Fig. 3 and XRD pattern shows the growth of 3R-NbS₂.

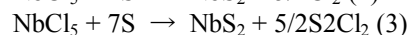
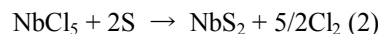
The resistivity measurement of the film showed minimum at 22K (Fig. 4). This behavior is reported for 3R-NbS₂ bulk single crystal.

4. Discussions

The role of hydrogen is to increase the reducing power during the CVD according to the following reaction:



Two possible reactions without H₂ can be described as follows:



The reaction enthalpy change of eq 1 is greater than that of eq 2 due to the negative formation enthalpy of HCl (−92.30 kJ/mol under standard conditions); the reaction enthalpy change of eq 1 is still much greater than that of eq 3 because the formation enthalpy of S₂Cl₂ is −59.4 kJ/mol under standard conditions. The lowest formation enthalpy of HCl among HCl, Cl₂ (0 kJ/mol), and S₂Cl₂ indicates eq 1 was the major reaction during the CVD, while eqs 2 and 3 were minor reactions.

4. Conclusions

We successfully prepared NbS₂ thin films by thermal atmospheric pressure CVD using NbCl₅, S, and H₂.

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References

- [1] T.Yanase, S. Watanabe, M. Weng, M. Wakeshima, Y. Hinatsu, T.Nagahama, , T.Shimada, Cryst.Growth & Design 16, 4467(2016).

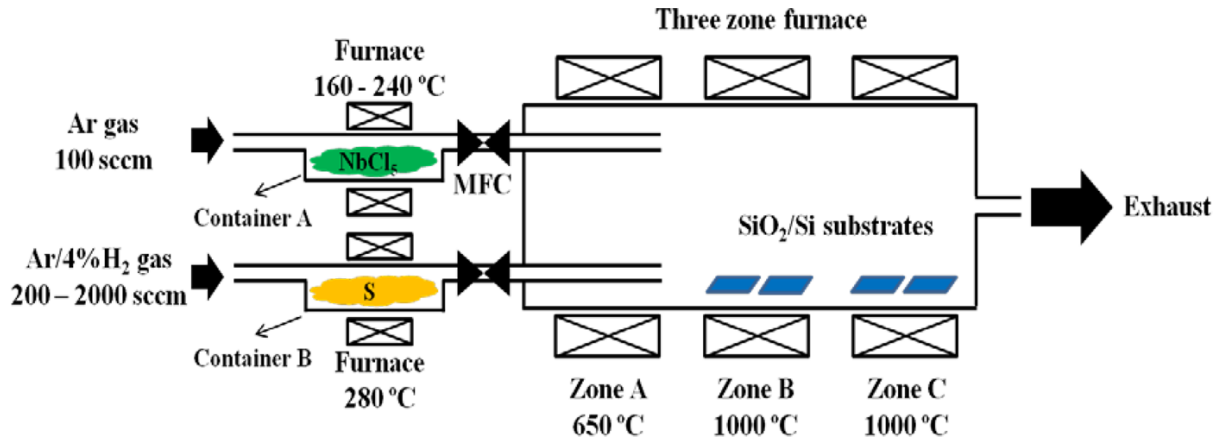


Fig.1 CVD setup

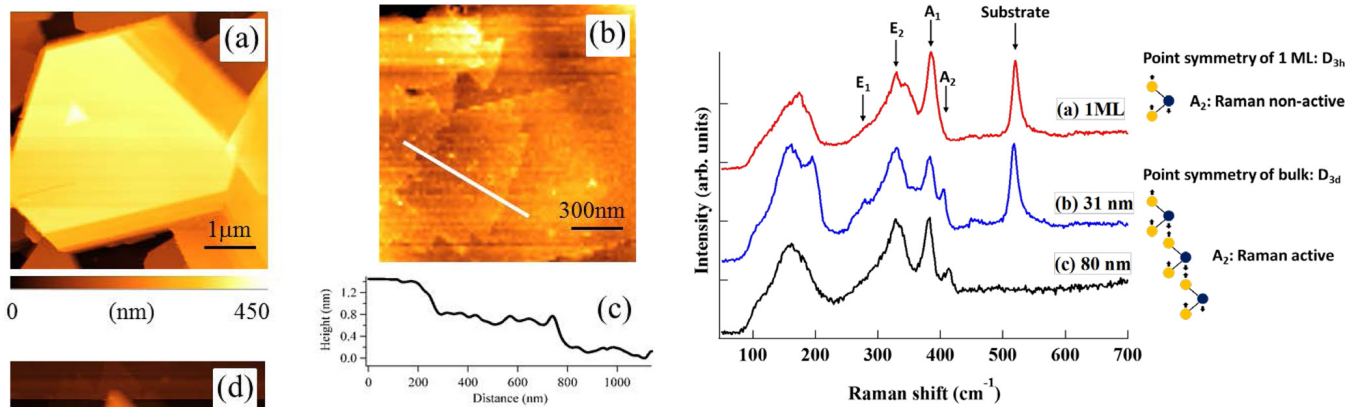


Fig.3 Raman spectra

Fig.2 AFM of NbS₂ films grown at optimized contion. (a) a hexagonal domain (b) Layered structure of the top of the terrace. (c) thickness of the layer is about 0.6nm, which is in agreement of unit layer thickness of NbS₂.