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Chemical Vapor Deposition of NbS_2 from a Chloride Source

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Abstract

NbS_2 thin films were grown on SiO_2/Si substrate by ambient pressure chemical vapor deposition (CVD) using a metal chloride source. We found that NbS_2 nanosheets can be grown directly on the SiO_2/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-NbS_2.

1. Introduction

CVD growth of MoS2 is widely studied partly because of the distinct feature of MoS_2 is its thin film growth; due to the volatile nature of the MoO_3, 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 NbS_2, suffers from the oxide impurities. We demonstrate it is possible to grow NbS_2 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-NbS_2 film.

2. Experimental

The synthesis of the NbS_2 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

H_2 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:

$NbCl_5 + 5/2H_2 + 2S \rightarrow NbS_2 + 5HCl$ (1)

Two possible reactions without H2 can be described as follows:

$NbCl_5 + 2S \rightarrow NbS_2 + 5/2Cl_2$ (2)

$NbCl_5 + 7S \rightarrow NbS_2 + 5/2S2Cl_2$ (3)

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)l;.he reaction enthalpy change of eq 1 is still much greater than that of eq 3 because the formation enthalpy of S_2Cl_2 is −59.4 kJ/mol under standard conditions. The lowest formation enthalpy of HCl among HCl, Cl_2 (0 kJ/mol), and S_2Cl_2 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 atomospheric pressure CVD using $NbCl_5$, S, and H_2.

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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).

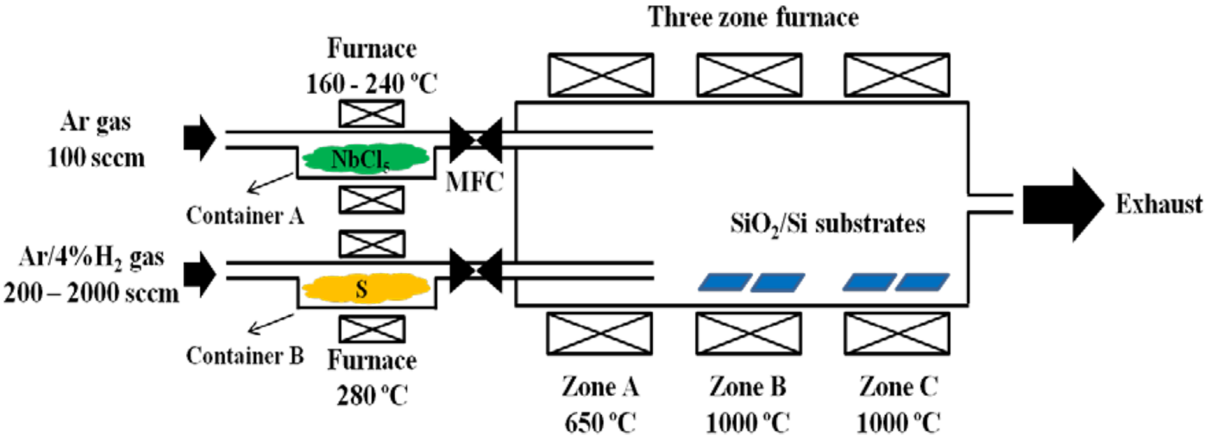
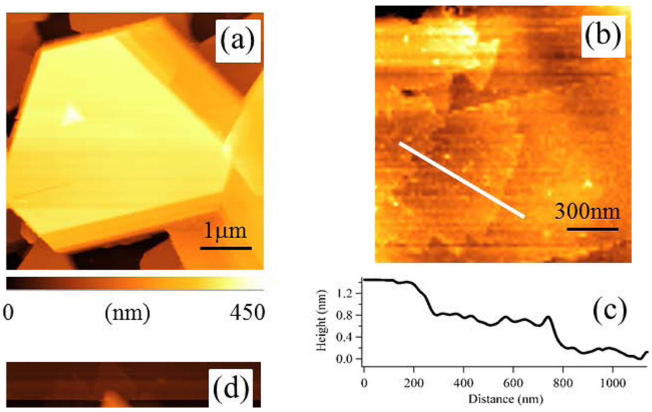


Fig.1 CVD setup



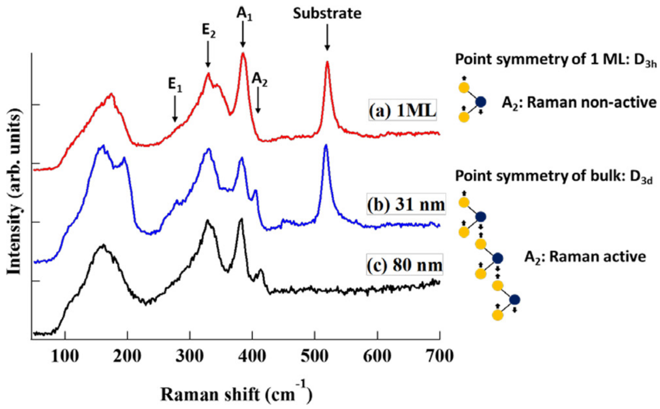


Fig.3 Raman spectra

Fig.2 AFM of NbS_2 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 NbS_2.