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Low Temperature Growth of Tungsten Disulfide Thin Films by Atomic Layer Deposition Using Liquid Precursors

Layered transition metal dichalcogenides (TMDCs) with two-dimensional crystal structures have recently attracted remarkable attention for a number of device applications, because some TMDCs have a finite energy band gap that lacks in graphene. Among such semiconducting TMDCs, molybdenum disulfide MoS_2 has been most widely studied because of the production of natural single-crystalline minerals. Until now, many researchers have been studying TMDC field-effect transistors (FETs), whose channel layers were fabricated by mechanical exfoliation of bulk single crystals, or by thin film growth techniques such as chemical vapor deposition (CVD), molecular beam epitaxy (MBE), atomic layer deposition (ALD), etc. Among TMDC FETs, MoS_2 FET is known to show mostly n-type operation due to strong pinning of the Fermi level of source/drain metal electrodes just below the conduction band of MoS_2 [1]. On the other hand, WS_2 FET shows both n- and p-type operations [2]. Here, we report thin film growth of WS_2 by the ALD method using liquid precursors. In our ALD, bis(tert-butylimino)bis(dimethylamino)tungsten(VI) $[(t\text{-}BuN)_2W(NMe_2)_2]$ and di-tert-butyl disulfide $[(t\text{-}C_4H_9)_2S_2]$ (both supplied by Gas-Phase Growth Ltd. [3]) were used as precursors of W and S, respectively. Both precursors are volatile liquid, and less hazardous and easier to use than $W(CO)_6$, WF_6, WCl_6 or H_2S that have been used in the ALD or CVD growth of WS_2 thin films [4].

Figure 1 illustrates our home-made ALD system. Bottles of W and S precursors were heated to 80 °C and 60 °C, respectively, to supply their vapors without flowing a carrier gas. As a purging gas, a mixture of Ar (95 sccm) and H_2 (5 sccm) was injected into the ALD tube reactor. Supply of these materials were controlled by high-speed pneumatic valves. Materials supply and vacuum evacuation tubes, and ALD valves were all heated to 140 °C. The ALD system was evacuated by a rotary pump. As the substrate of WS_2 films, 285-nm-thick SiO_2/Si wafers were used. After surface cleaning by organic solvents and ozone, the substrate was introduced into the reactor. Growth temperature was investigated in the temperature range of 350−700 °C. After reaching to the growth temperature under the evacuation, ALD cycles were started. The open/close timing chart of valves is shown in Fig. 2. During the supply of W and S precursors, the vacuum valve between the reactor and the rotary pump was closed to enhance adsorption of each precursor onto the substrate. After ALD cycles, materials supply valves were closed and the reactor was naturally cooled under the evacuation. Grown WS_2 films were examined by optical microscopy, micro Raman spectroscopy, atomic force microscopy and X-ray photoelectron spectroscopy (XPS).

Figure 3 shows (a) Raman and (b) XPS spectra of a WS_2 film grown on the SiO_2/Si substrate by 200 ALD cycles at the temperature of 400 °C. Positions of two distinct Raman shift peaks at 357 cm^{-1} and 417 cm^{-1} well agree with previously observed E^1_{2g} and A_{1g} peaks on an exfoliated single-crystalline WS_2 flake, respectively [5]. The XPS measurement also reveals the growth of WS_2 by the presence of W and S peaks. Furthermore, the N_{1s} excitation peak appeared in the XPS spectrum, but the C_{1s} peak was hardly observed. From these observations, it is suggested that thin crystalline WS_2 domains can be grown by ALD at 400 °C on the SiO_2/Si substrate, although an unknown nitride compound exists in the grown film. Usually, the CVD growth of TMDC using metal oxide (MoO_3, WO_3, etc.) and elementary chalcogen needs a higher growth temperature than 700 °C to obtain a well-crystalline TMDC film. Low-temperature growth by ALD will make it possible to utilize various substrate materials which cannot endure such high-temperature growth on account of decomposition and/or sublimation. At the conference, we will also report the structural characterization of ALD-grown WS_2 films and their application to FET devices.

References

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[4] M.Bosi, RSC Adv., 5 (2015) 75500-75518.
[5] W.Zhao et al., Nanoscale, 5 (2013) 9677-9683.

Figures

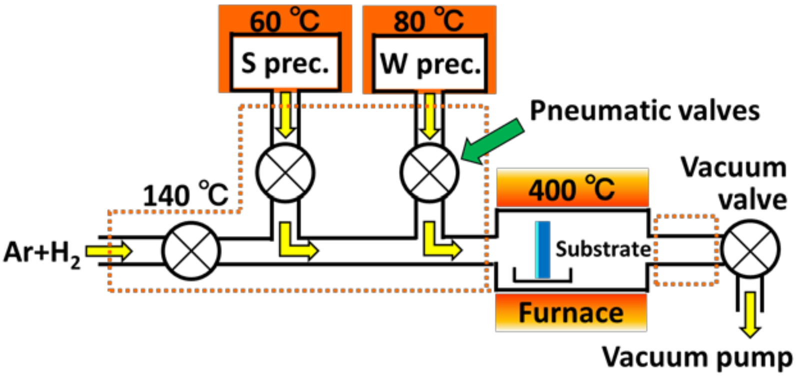

Figure 1: Schematic view of the ALD system

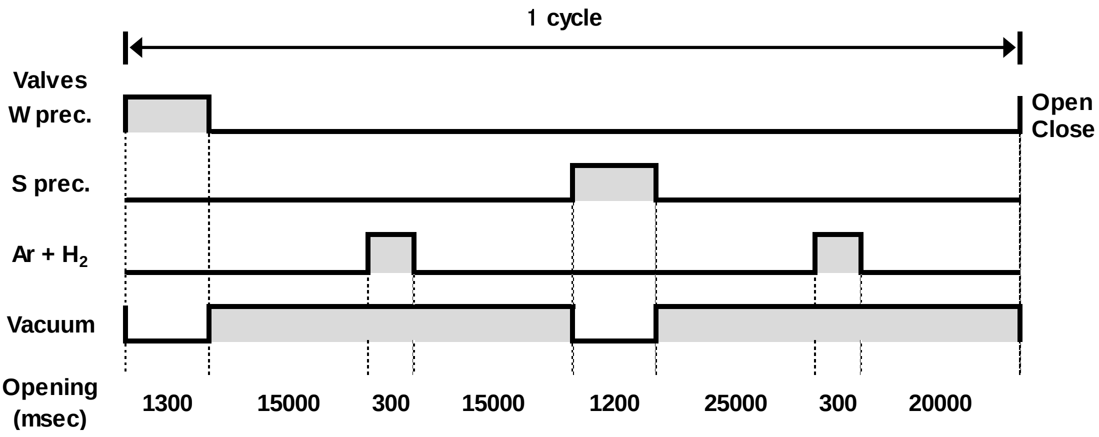

Figure 2: Open/close timing chart of ALD and vacuum valves

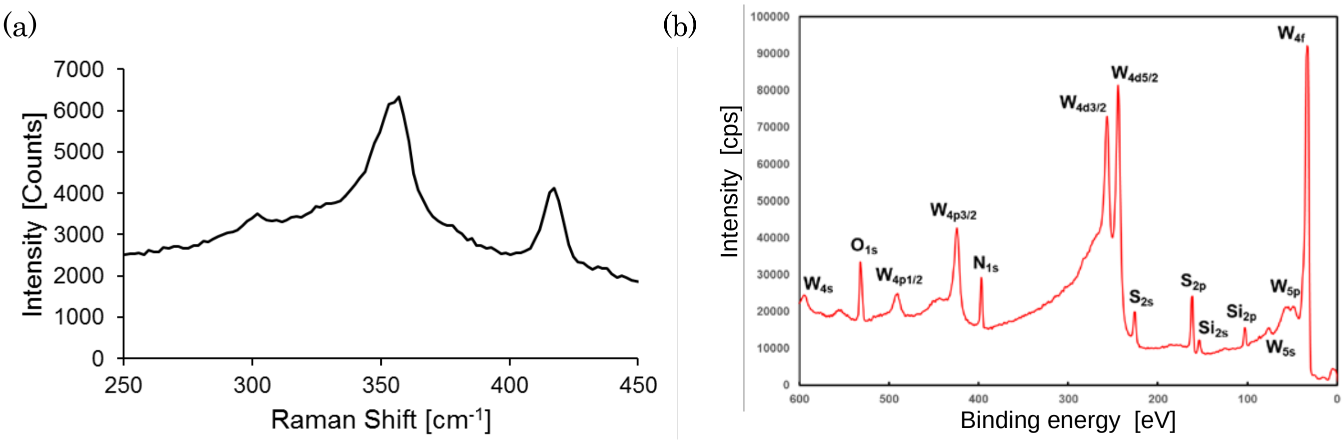

Figure 3: (a) Raman and (b) XPS survey spectra of a WS_2 thin film grown by ALD