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Epitaxial growth of ReS$_2$(001) thin film via deposited-Re sulfurization

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In this paper, we present the formation of large-size rhenium disulfide (ReS$_2$) films via the sulfurization of Re films deposited on sapphire substrates. The effects of sulfurization temperature and pressure on the crystal quality were investigated. A [001]-oriented single crystal of ReS$_2$ films with $6 \times 10^{-5}$mm$^2$ area was realized. By sulfurizing Re films at 1100 °C, ReS$_2$ films with well-defined sharp interfaces to c-plane sapphire substrates could be formed. Below and above the sulfurization temperature of 1100 °C, incomplete sulfurization and film degradation were observed. The twofold symmetry of the monocrystalline in-plane structure composed of Re–Re bonds along with Re–S bonds pointed to a distorted 1T structure, indicating that this structure is the most stable atomic arrangement for ReS$_2$. For a S/Re compositional ratio equal to or slightly lower than 2.0, characteristic Raman vibrational modes with the narrowest line widths were observed. The typical absorption peak of ReS$_2$ can be detected at 1.5 eV.

1. Introduction

Layered two-dimensional (2D) materials such as graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (h-BN) have received much attention owing to their potential applications in novel, high-performance, low-cost, and/or flexible optoelectronic devices. Such layered 2D materials can be easily transferred to any substrate, since the stacked layers in these materials are bound by van der Waals force. By transfer methods, a heterostructure consisting of a layered 2D material with other materials can be formed without dislocations and defects at the interface, which originate, respectively, from the lattice mismatch and structural difference between the two materials. In principle, an unlimited number of combinations between such materials is possible; however, such heterostructures should be precisely tailored to control a clean and abrupt interface at the junction.

Rhenium disulfide (ReS$_2$) has received much attention as a novel 2D direct energy bandgap optoelectronic material, which can be potentially used as a channel material in field-effect transistors and light-detecting devices, especially because a very high carrier mobility (~5000 cm$^2$V$^{-1}$s$^{-1}$) under conditions of strain has been predicted for this material. 2D-ReS$_2$ films have been generally prepared by mechanical exfoliation from bulk single crystals grown by chemical vapor transport. In most cases, these exfoliated ReS$_2$ films have a small size on the order of several square micrometers with random distribution thicknesses. Recently, the chemical vapor deposition (CVD) growth of large-size films using Re precursors such as NiH$_4$ReO$_4$, ReO$_3$, and Re–Te eutectic alloy has been reported. Although monolayer or bilayer ReS$_2$ films on SiO$_2$/Si and sapphire substrates can be formed by CVD, these films are mostly polycrystalline with small grains of several micrometers. It has been noted that polycrystalline films lead to poor device performance. Thus, for device applications, it is important to investigate the growth of large-size high-crystalline-quality materials.

An initial step in the preparation of large-size ReS$_2$ films with high crystalline quality is the formation of single-crystal ReS$_2$ films with [001] orientations, since this structure is found to be the most stable. As reported in the case of TMDCs, van der Waals epitaxy has been performed on other TMDCs and mica substrates. However, large-size films with planes oriented along the [0001] direction are difficult to obtain owing the low-temperature growth. On the other hand, the sulfurization of Mo films deposited on MgO(111) and c-plane sapphire substrate has been reported for the epitaxial growth of large-size MoS$_2$, which is called vapor–solid growth and has been extended to ReS$_2$ for the preparation of large-size crystalline films of TMDCs. In this regard, however, note that the vapor–solid growth method has yet been used to grow ReS$_2$ thin films, and the experimental knowledge of this process is important for the applications of ReS$_2$ thin films in devices. In this paper, we have investigated the formation of ReS$_2$ thin films on c-plane sapphire substrates via vapor–solid growth. High-quality ReS$_2$ thin films with [001] orientation have been successfully formed by controlling the sulfurization temperature and pressure. It is assumed that the stoichiometry (S/Re) ratio and line widths of Raman signals are related to crystal quality, in accordance with previous works. The typical absorption peak was detected at 1.5 eV, which is attributed to exciton absorption at the Γ point of ReS$_2$. Thus, we show that the vapor–solid growth method used for MoS$_2$ can be extended to ReS$_2$ for the preparation of large-size crystalline films with the desired orientation.

2. Experimental procedure

All ReS$_2$ samples were fabricated via the sulfurization of deposited Re films. First, epi-ready c-plane substrate (Optostar, ~10 × 15 mm$^2$) were cleaned with acetone, methanol, and ultrapure water by ultrasonic washing. Next, a Re film was deposited at room temperature (25 °C) by e-beam evaporation (ANELVA 980-7104) using a metallic Re pellet (3N, Kohsei) as the source. The chamber pressure was ~1 × 10$^{-3}$ Pa during the deposition. The deposition rate was set to approximately 15 Å/min and the deposition time was 4 min. Then, the Re deposited sapphire substrate and S powder (5N, Furuiuchi Chemical) were placed in a quartz tube, which was pumped down to ~3 × 10$^{-3}$ Pa from the open end using a rotary pump and a diffusion pump, after which...
the tube was sealed by high-temperature welding as shown in Fig. 1. The sealed quartz tube was placed inside an electrical furnace and heated to a temperature in the range of 1000–1150 °C at the heating rate of 15 °C/min. After the reaction, the quartz tube was cooled using the following protocol; the cooling rate was 2 °C/min up to 650 °C to suppress the exfoliation of the film, followed by natural cooling at room temperature. The S pressures in the sealed quartz tube were 0.5, 1.0, and 1.5 atm as determined from the vapor pressure curve while taking into account the tube volume and the amount of S powder. The sulfurization time was fixed to 1 h.

The surface morphology of the films was observed by optical microscopy and atomic force microscopy (AFM) in the non contact mode (Shimadzu SPM-9500J3). ReS2 thin films were characterized by the α/2θ curve of X-ray diffraction (XRD) measurement (Rigaku SmartLab) with symmetrical and asymmetrical diffraction conditions. Detailed experimental conditions are given in the supplementary data (Fig. S1 in the online supplementary data at http://stacks.iop.org/JJAP/57/02CB07/mmedia). X-ray photoelectron spectroscopy (XPS) analysis (PHI Quantera II) was carried out to characterize the bonding states of Re and S. The compositions of Re and S were determined by XPS signal intensities. Microscopic Raman spectroscopy (LabRAM HR Evolution) was performed to characterize the ReS2 layer by analyzing E2g (around 162 cm−1), E1g (around 307 cm−1), and A2g (around 212 cm−1) peaks, which are attributed to the in-plane (E2g and E1g) and out-of-plane (A2g) vibrational modes.24) The 532 nm line of a diode-pumped solid-state laser was used for optical excitation. The Raman signal was dispersed in an 800 mm monochromator and a cooled charge-coupled device (Synapse). The absorbance spectrum was obtained using a visible/near-infrared spectrophotometer (JASCO V-630) with a conventional setup and the measurement area was 4 × 8 mm².

3. Results and discussion

Figure 2(a) shows the photograph of a typical ReS2 thin film grown at 1100 °C, indicating successful large-size growth with an area of 6 × 10 mm²; the surface of the film is smooth with a mirror like appearance. Figure 2(b) shows the optical microscopy image of the ReS2 thin film, where a continuous large-size film on the substrate is seen. Figure 2(c) shows the step edge between the ReS2 thin film and the c-plane sapphire substrate measured by AFM. From the height profile of the step edge, the thickness of the ReS2 thin film is estimated to be 16–19 nm. This ReS2 thin film corresponds to 25–30 layers, since the thickness of a single layer is approximately 0.64 nm.25)

Wide-range α/2θ curves of symmetrical XRD measurement on four samples of ReS2 are shown in Fig. 3(a). For all the samples, diffraction peaks only from the 001 family of planes of the ReS2 films and the 0006 diffraction peak of the c-plane sapphire substrate were observed, indicating the formation of a ReS2 single crystal oriented in the [001] direction. These diffraction peaks show good agreement with a PDF2plus database of 1T ReS2 (00-024-0922). Diffraction peak intensities for ReS2 films were stronger for the sulfurization temperature of 1100 °C, as compared with other sulfurization temperatures. At sulfurization temperatures of 1000 and 1050 °C, an incomplete sulfurization could have occurred since the decomposition temperature of the Re oxide is in the range of 1000–1050 °C.26) Therefore, to achieve the epitaxial growth of the ReS2 film, the sulfurization of the Re film should be carried out above 1050 °C. Besides, the film thickness was decreased for the temperature of 1150 °C owing to the decomposition of Re–S bonds and the desorption of Re during the sulfurization process. Thus, our results suggest that the appropriate sulfurization temperature of deposited Re films to avoid both incomplete sulfurization and film degradation was around 1100 °C. Additionally, Pendellösung oscillations (fringes) are clearly observed around the 001 diffraction peak for the ReS2 sample grown at 1100 °C as shown in Fig. 3(b). This observation indicates the presence of a markedly abrupt interface between the ReS2 films and the c-plane sapphire substrate. A film thickness of 16 nm was estimated from the distance between the Pendellösung oscillations, which is in good agreement with the thickness evaluated by AFM scan.

For the ReS2 sample grown at 1100 °C, XRD measurements with 0112 sapphire and 103 and 013 ReS2 across the full range of Φ = 360° under the asymmetrical condition were carried out; the results are shown in Fig. 3(c). The diffraction profile clearly shows three periodic peaks corresponding to...
the 0112 reflections originating from c-plane sapphire, indicating a threefold symmetry in the Φ direction. For ReS₂, two profiles are measured for 013 and 013 reflections showing twofold symmetry. The lattice constants of a- and b-axes were 6.45 and 6.39 Å, respectively. Also, the profiles for the a- and b-axes of ReS₂ are broader than those for the sapphire substrate. It has been proposed that the atomic arrangement in ReS₂ corresponds to a distorted octahedral structure (1T), because the hexagonal (H) phase is unstable, whereas the 1T phase goes through Peierls distortion. Consequently, a structure with parallel zigzag Re chains and buckled S layers with the unit cell in the form of a parallelogram has been reported, where the b-axis is along the zigzag Re chains and the angles between the a- and b-axes are 118.97° and 61.03°. The twofold symmetry and broad profiles have been advocated in the proposed structure. Our XRD measurements have indicated the growth of single-crystal ReS₂ with a distorted 1T structure.

Figure 4(a) shows the whole XPS spectrum of the ReS₂ thin film sulfurized at 1100 °C. The peaks originating from Re 4f and S 2p levels can be clearly observed. In addition, Al, O, and C peaks are seen, which can be attributed to signals from the sapphire substrate and surface contamination. The detailed Re and S spectra are shown in Fig. 4(b). For Re, two typical peaks from 4f⁷/₂ and 4f⁵/₂ core levels located at 41.0 and 43.5 eV, respectively, were observed; each of these is made up of two peaks as confirmed from the results of deconvolution. For S, an asymmetric peak originating from 2p³/₂ and 2p₁/₂ core levels located at 161.4 and 162.5 eV, respectively, was observed; the spectral positions of these core levels indicate the absence of an inherent Re oxide. In the deconvoluted 4f⁷/₂ and 4f⁵/₂ spectra, the separation of the two peaks is 0.5 eV, which implies that these peaks originate from (Re–)Re–S and S–Re–S type bonds. This means that, in addition to the typical S–Re–S bonds in the distorted ReS₂ structure, zigzag Re chains (Re–Re) can exist in the basal plane as described above. Therefore, the results of our XPS analysis support the formation of single-crystal ReS₂ with a distorted structure. Additionally, the stoichiometry of the ReS₂ thin film was also determined by XPS analysis. Figure 4(c) shows the dependence of the S/Re elemental ratio on the sulfurization temperature.
pressure. The sulfurization temperature was 1100 °C. It is seen that the S/Re ratio first increases with sulfurization pressure. At sulfurization pressures of more than 1 atm, the S/Re ratio remained stable at 2.1. This leads to the generation of point defects involving S interstitials accompanied by the formation of unstable bonds. At 1 atm or less, the S/Re ratios are below the ideal stoichiometry (i.e., S/Re = 2.0), suggesting that point defects involving S vacancies are generated. However, note that the realistic (distorted) octahedral structure of TMDCs is prone to deficiency in chalcogen atoms compared with the ideal stoichiometry.\textsuperscript{30,31}

Figure 5(a) shows the dependence of Raman spectra with a particular orientation on the sulfurization pressure. The sulfurization temperature was 1100 °C. Several sharp peaks were observed with more than 10 active vibrational modes in the 100–400 cm\textsuperscript{-1} range, which are attributed to symmetry splitting in the distorted structure and coupling to acoustic phonons.\textsuperscript{14,27} These vibrational modes are shown in the supplementary data (Fig. S2 in the online supplementary data at http://stacks.iop.org/JJAP/57/02CB07/mmedia). In particular, the prominent characteristic peaks at approximately 162, 307, and 212 cm\textsuperscript{-1} correspond to the in-plane E\textsubscript{2g} and E\textsubscript{1g} and the out-of-plane A\textsubscript{1g} vibrational modes,\textsuperscript{27} To correlate the Raman spectroscopy data with film quality, the full widths at half maximum (FWHMs) of these characteristic peaks (E\textsubscript{2g}, E\textsubscript{1g}, and A\textsubscript{1g}) were estimated from the fitted spectra as shown in Fig. 5(b). The FWHMs of E\textsubscript{2g}, A\textsubscript{1g}, and E\textsubscript{1g} were respectively decreased to 2.0, 3.1, and 5.5 cm\textsuperscript{-1} for the samples prepared with a sulfurization pressure of 1.0 atm. These values are comparable to those of exfoliated ReS\textsubscript{2} thin films,\textsuperscript{32} indicating that the highest quality crystal is obtained under this condition. In association with stoichiometry as determined by XPS analysis, it is found that the S/Re ratio at 2.0 or slightly below is appropriate for obtaining high-quality crystals.

Figure 6 shows the absorption spectrum of the ReS\textsubscript{2} thin film sulfurized at 1100 °C. A typical absorption peak at around 1.5 eV was observed, corresponding to absorption from multilayer or bulk ReS\textsubscript{2} films.\textsuperscript{33} This peak is related to excitonic absorptions at the Γ point in momentum space (direct bandgap) in the band structure of ReS\textsubscript{2}.\textsuperscript{34,35}
addition, a peak at around 1.9 eV was observed. As of now, the origin of this peak remains unclear and could possibly be the (1) free carrier transition at the band edge and (2) excited Rydberg excitons from low-lying states. A more detailed investigation including photoluminescence excitation and decay measurements to investigate the carrier dynamics is required.

4. Conclusions

In this paper, we present the epitaxial growth of ReS₂ thin films on c-plane sapphire substrates via a vapor-solid growth process that consisted of the deposition and sulfurization of Re films. Symmetrical XRD measurements showed that the sulfurization temperature should be set to approximately 1100 °C to achieve highly ordered ReS₂ films oriented along the (001) plane and forming an abrupt interface with the substrate. Additionally, asymmetrical XRD measurements of the 103 and 013 reflections in ReS₂ revealed a twofold symmetry for the in-plane distorted 1T structure, indicating that the most stable atomic arrangement involves Peierls distortion, as reported previously. The Re–Re and Re–S bonding states were also elucidated by XPS analysis, supporting the formation of a crystal structure of ReS₂ with a distorted 1T structure. The appropriate stoichiometry (S/Re ratio) to achieve the highest crystal quality was found to be 2.0 or slightly lower, as determined from the FWHMs of the characteristic vibrational modes in Raman spectra. The typical absorption spectrum of ReS₂ with the excitonic absorption peak located at 1.5 eV was detected.

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