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Synthesis and Characterization of MoS_2 Amorphous Nano Thin Films by Three Temperature Zone CVD System

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Abstract

Low-dimensional material molybdenum disulfide (MoS_2) is a promising candidate for nanoelectronic device. It has attracted many attempts to produce MoS_2 via chemical and mechanical exfoliation of bulk material. To synthesis nanoscale material molybdenum disulfide, a separated three-temperature zone CVD system has been utilized. Magnetron-sputtered thin film Mo and powder sulfur were used as the precursor. 30 nm MoS_2 thin film deposited on Si substrates which was revealed by high resolution TEM. The crystal structure was amorphous which was carefully characterized by XRD. A showed smooth surface morphology (rms=1.356nm) was reviewed by AFM.

Keywords

Molybdenum Disulfide (MoS_2); Three-temperature Zone CVD System; Low Dimension Material.

1. Introduction

Low dimensional nanomaterials have been receiving great attention in recent years because they show unusual physical properties, which is the result of a quantum size effect associated with their ultra-thin structure. The foundation of grapheme opened the door for the research of two-dimension materials in 2004[1-4]. Before this, extensive research believed that this kind of material was unable to exist because of the thermodynamic instability. Grapheme created the legend and attracted many attentions after it has been discovered. Recently, many experimental and theoretical efforts have focused on grapheme and it is determinate that grapheme has excellent properties, such as electrical, optical, intensity, thermal conductivity etc. Therefore, it brought vast application research. However the bandgap of grapheme is zero, which can’t be used as a semiconductor material[5-7]. Another material molybdenum disulphide (MoS_2) has similar properties as grapheme in addition to having a direct band gap. Recent studies have found that when the MoS_2 material is thin to a certain extent, the band gap will increase with the reduction of the number of MoS_2 layers. The band gap of a single-layer MoS_2 is 1.90eV, and the indirect band gap of the bulk material changes to the direct band gap of the single-layer material. This shows that the single-layer MoS_2 material can be applied in the field of microelectronic devices, but also is suitable for the production of optoelectronic devices[8-11].

Nano-MoS_2 has broad application prospects in many fields and its next development will be large-scale industrial production, the first step to achieve this goal is how to quickly easily and economically complete the large-scale production[12-13]. There are various methods for preparing MoS_2 nanomaterials, which can be divided into solid phase method, liquid phase method and gas phase method according to the different preparation states. Solid phase method mainly includes solid phase decomposition method, mechanical grinding method and self-propagating combustion method. Liquid phase method mainly includes chemical precipitation method, electrochemical method, micro

emulsion method, hydrothermal synthesis method, sol-gel method and so on. The gas phase method mainly includes gas phase reaction method, gas phase deposition method, magnetron sputtering method and template method. MoS_2 with various morphologies can be synthesized by the above methods, such as nanotubes, nanorods, nanowires, nanospheres, nanoflowers, and nanopolyhedra. In recent years, many research groups at domestic and overseas have carried out research work on the preparation of MoS_2 by CVD method[14-15]. Among the various synthetic methods, chemical vapor deposition (CVD) has the advantages of short process steps, no filtration and drying, the lowest sulfur and molybdenum molar ratio and no waste water. The composition of waste gas is simple and easy to recycle. CVD method also has the advantages of continuous and large-scale industrial scale-up value, and the easiest to achieve the growth of large-area films.

2. Experimental Procedures

MoS_2 nano-thin films were synthesized by CVD method in this experiment, and the main experimental instruments used in the experiment were listed in Table 1. The experimental process was separated to two parts.

Table 1. Main experimental instrument

Instrument	Type	Manufacture
TEM	TECNAIF20S-TW2N	FEI
SEM	Hitachi-3400N	HITACHI
XRD	ULTIMA-3	Rigaku
CVD	BTF-1200C	Anhui BYQ
UHV-Sputter&IBS	FJL560	SKY Technology Development
PIPS II	MODEL 695	Gatan
AFM	Cypher	ASYLUM RESEARCH

2.1 Preparation of Mo Layer

Firstly, the Mo layer was sputtered on Si substrate and Si substrate with SiO_2 oxide layer by magnetron sputtering with 30W power and 20sccm flow of argon. The first substrate was Si, sputtering time was 10 minutes. The second substrate is Si with thermally grown SiO_2, sputtering time 8 minutes. No.3 substrate was Si, sputtering time was 5 minutes. No. 4 substrate is Si with thermally grown SiO_2, and the sputtering time is 3 minutes. The schematic diagram is shown in Figure 1.

Figure 1. Substrate preparation

2.2 Growth of MoS_2 Layer

The No. 1 substrate and 3g sulfur powder were put into two quartz boats respectively and placed in temperature zone one and zone three in the furnace body of CVD device. The substrate was heated

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to 500℃ and the sulfur powder was heated to 140℃, then N_2 was passed through with 2sccm. Sulfur powder was easy to sublimate. After repeatedly exploration of parameters, the pressure and heating temperature were set at 1Pa and 140℃ respectively, so that the complete sublimation time of 3g sulfur powder was about 50min at the carrier gas flow rate of 2sccm. The sublimated S was carried to the substrate surface by N_2 and reacts with the Mo layer on the heated substrate to form MoS_2. The diagram of CVD furnace body was shown in Figure 2. The chemical reaction in the furnace is as follows:

$$Mo(s) + S_2(g) \rightarrow MoS_2(s) \quad (1)$$

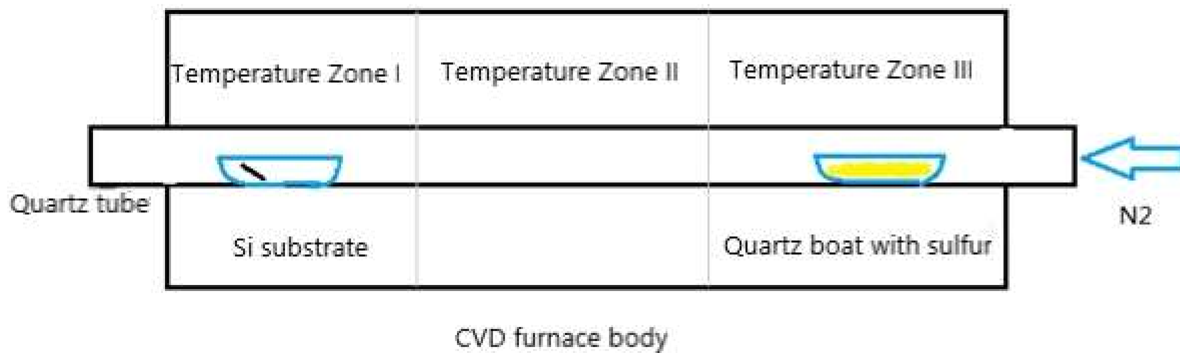

Figure 2. CVD furnace body diagram

2.3 Preparation of TEM Sample

TEM sample preparation must be completed before TEM characterization, the TEM Sample preparation procedure was as follows:

(1) Stick the sample on the slide with paraffin wax on the hot table, cut it into 2.5mm wide strips with a chainsaw, then remove the paraffin wax with acetone;

(2) Stick the cut sample strip and the foil piece (Si piece) with glue A, which should be noted that the sample side with film and the foil piece must be face to face. After sticking, place the strip on the hot table at 140℃ for 12 hours;

(3) Cut the bonded sample and the foil into 1mm×2.5mm pieces in the direction perpendicular to the bonding surface and the length of the sample strip;

(4) The sample to be thinned was fixed on the triangular grinding table with paraffin wax, so that the bonding surface was perpendicular to the grinding table, and the diamond sandpaper of 30um, 9um, 3um and 1um was successively used for mechanical polishing;

(5) Remove the polished sample from one side, glue the polished surface and the grinding table together again, and use diamond sandpaper of 30um, 15um, 9um, 6um, 3um and 1um successively for mechanical thinning. When the micro-transparent red light was observed under the transmission light of the optical microscope, it indicated that the sample thickness was less than 100um, then stop the mechanical thinning;

(6) Stick the molybdenum ring on the sample with glue B and stand for 24 hours;

(7) Soak the molybdenum ring with samples from the grinding table with acetone;

(8) Put the molybdenum ring with the sample into PIPSII for ion thinning at a voltage of 3.60keV, gas flow rate of 0.1 sccm, ion beam Angle of 4°, and thinning time of 100min.

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3. Results and Discussion

3.1 TEM

The sample after thinning was shown in Figure 3 and Figure 4. The samples were characterized by electron microscopy after preparation, and the following results were obtained. As can be seen from Figure 3 and Figure 4(a), this ion thinning resulted in holes in the adhesive layer which caused the film samples in the holes to be knocked off by ions. This was because the adhesive layer was too thick and the adhesive layer was particularly sensitive to ion beam, so it was easy to be knocked off. It can be seen from Figure 4(b) and Figure 4(c) that the film layer was about 30nm thick, and the integrity of the adhesive layer can ensure that the ion beam did not damage the film.

Figure 3. Sample after ion milling

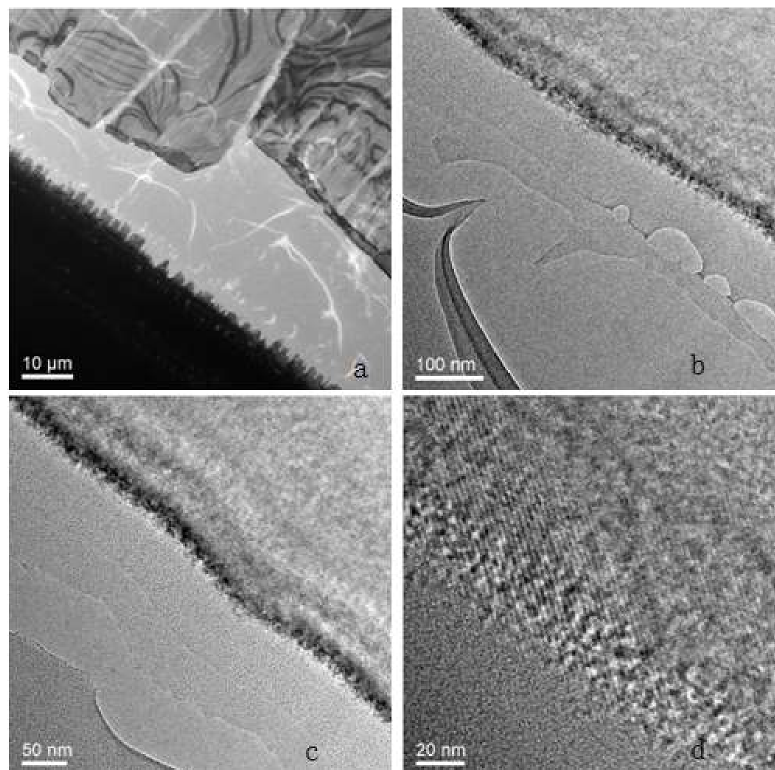

Figure 4. TEM images

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3.2 AFM

AFM is a simple and practical method to analyze the surface morphology of samples. AFM characterization was carried out after the Mo layer grown by magnetron sputtering of the sample. The working mode was contact mode, and the following results were obtained.

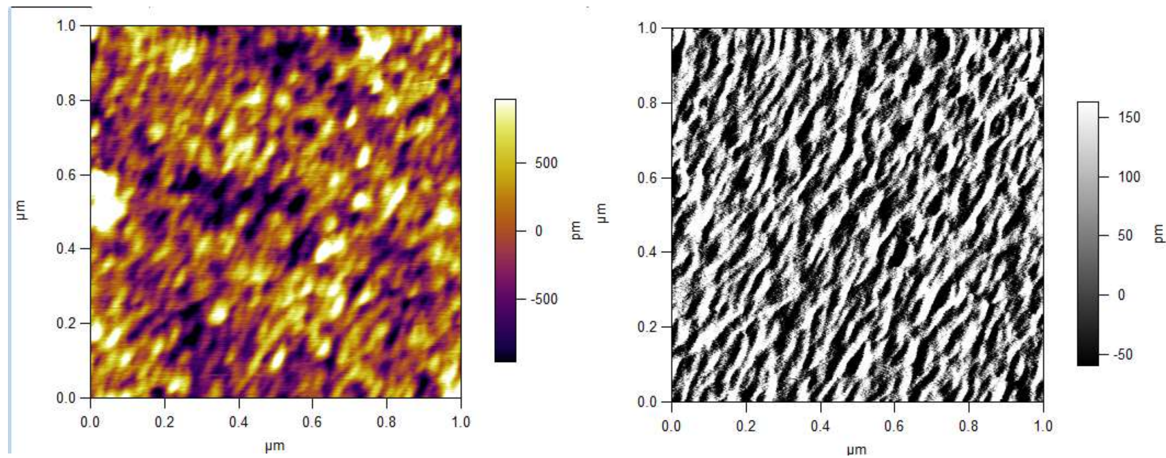

Figure 5. AFM image of Mo layer

In the Figure 5, we can see the dune like metal Mo, whose surface roughness RMS=479.334pm. After CVD growth, we performed AFM characterization on the samples again, the working mode was still contact mode and the results were shown in Figure 6. The scanning range of the left figure was 1um, the undulating MoS_2 can be observed above, its surface roughness RMS=1.356nm. The scanning range of the image on the right is 100nm, which can more clearly observe the surface fluctuation of MoS_2, the surface roughness RMS=448.409pm.

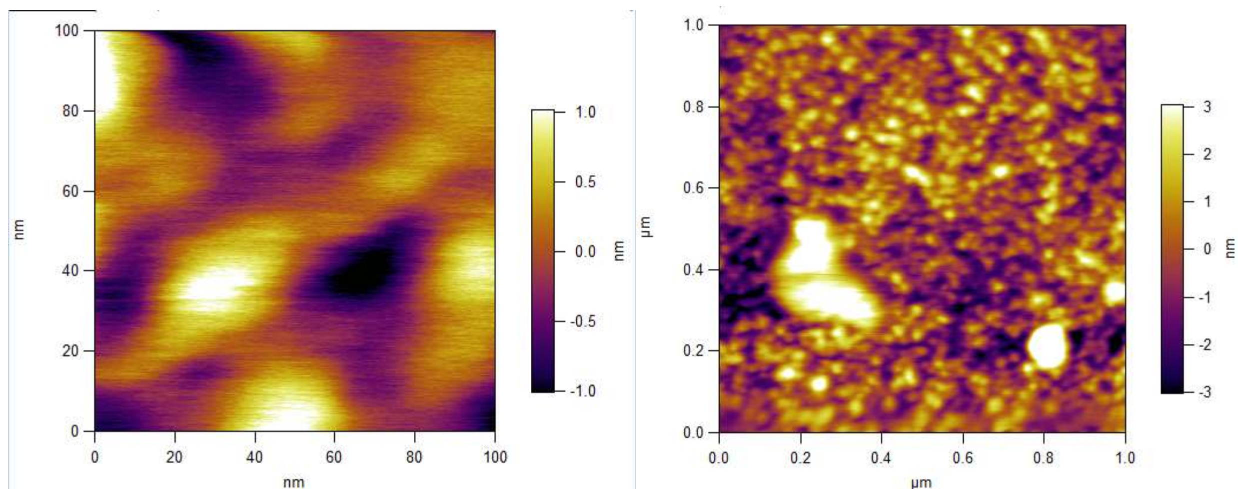

Figure 6. AFM image of MoS2

3.3 XRD

By analyzing the X-ray diffraction pattern of the sample, the composition of the material and the structure and morphology of the atoms or molecules inside the material could be obtained. The samples were tested by XRD, and the result was shown in Figure 7. In this test result, no peak position was found on Jade 6.5 software. But there was "steamed bun peak" at low angle, which was the XRD characteristic of amorphous indicating that the MoS_2 prepared by this sample was amorphous.

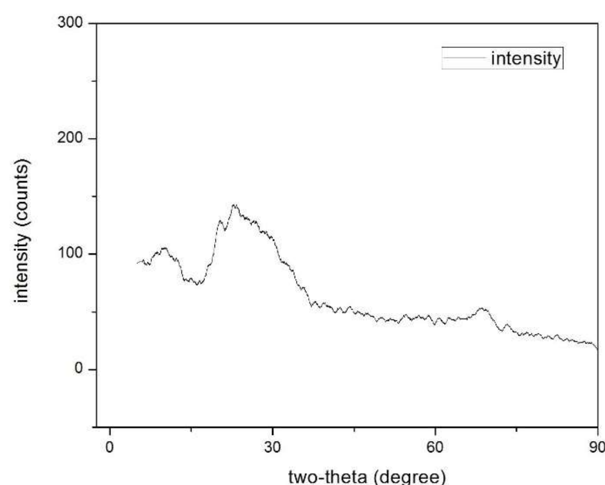

Figure 7. XRD result

4. Conclusion

In summary, low dimensional nano-thin film MoS2 was synthesized by a separated three-temperature zone CVD system. The magnetron-sputtered thin film Mo and sulfur powder were used as precursors at different temperature zones. X-ray diffraction characterization indicated that the synthesized nanoscaled MoS2 was amorphous. High resolution TEM characterization showed that the thickness of the as grown film on Si substrate was 30nm. The smooth surface morphology (rms=1.356nm) was reviewed by AFM. This sample was the first preparation after the assembly of CVD system equipment, and there were still some improvements to be made in the preparation and characterization process. Based on the feedback of this result, we will improve the process in the future experiments, and strive for better morphology after many times of preparation and characterization feedback.

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