The process for preparing MX$_2$ (M=Mo, W; X=Se, S) single crystal

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Abstract: The layered semiconductor compound, as transition metal dichalcogenide family MX$_2$ (M=Mo, W, X=S, Se) had stirred common interesting in solar energy conversion for its special photoelectronic properties. The synthesizing of its single crystal free of surface defects is a pressing matter of the moment. In this paper, the key points in preparing such single crystal are concluded, that is high vacuum, long time, and small $\Delta T$, sometimes the transport agents have to be used to help the matter diffusion. And the proper quantities of these parameters are detailed in this paper too.

1. Introduction

As to the particular electrical and optoelectronic properties of MX$_2$ (M=Mo, W; X=S, Se, Te), this kind of Lamellar transition metal dichalcogenides are well known as an interesting and competitive materials of semiconducting [1-7]. Also the layered semiconductor compound, as transition metal dichalcogenide family MX$_2$ (M=Mo, W, X=S, Se), own great potentialities for solar energy conversion. And this kind of special photoelectronic property makes it used to be photoelectrochemical (PEC) solar cells with MX$_2$ photoelectrodes. But the experiments have shown that the defects on the surface of these MX$_2$ play an important role about the corrosion and photo corrosion of the material. Consequently, many surface treatments of these materials were going on. But the experiments showed that due to the prolonged illumination, the conversion process vanished.

Actually, MX$_2$ monolayer was attracted in exhibiting unique electrical, mechanical and optical properties [8-10]. A recently report [8, 11] showed that a CVD growth acid cleaning method form quartz tube and crucibles can completely make the residues in tube and crucibles cleaned. It is found that by combination of acid cleaning and high-temperature O$_2$ annealing treatment in the quartz tube and crucibles which finishing occurring multiple growth process, the CVD could generate big area monolayer crystals and films which is controllable and repeatably growed. But still the maximum size of a WS$_2$ single crystal just reaches 176 $\mu$m with uniform thickness. The other reported the largest domain size is about 18−20 $\mu$m by CVD method [12].

So, till now, mechanical cleavage or exfoliation in 3D parent compounds are main method of gaining these 2D crystals [13-17].

So, it is very important to synthetize large area MX$_2$ single crystal free of surface defects as much as possible. Here, the key process parameters reported are analyzed and concluded in this paper,
hoping this can-do help for further study in exploring new application and 2D properties of layered MX₂.

2. Parameters used in preparing process

2.1 Synthesis polycrystalline powder

Commonly, the pure single crystals of MX₂ are growing from its polycrystalline powder. In order to realize this, the purer starting polycrystalline powder should be made. To do this, usually raw powder are M=Mo,W, and X=Se,S, with purity of 3N-4N. These element powder were stoichiometrically blended or the X were excess, and then the mixture were sealed in a quartz tube which sometimes had been chemically and carefully cleaned and degreased with Ajax®, then etched by HF(10%) and dried before the reactants introducing into [13].

The quartz tube will be vacuumed before sealed and then slowly heated to 700-850°C in a step of 50°C or within 24-48hr and stayed at this temperature for several days, usually 2 days [18-20].

Sometimes, the gained polycrystalline powder would be take out from quartz tube to be milled to fine enough, and reintroduced in quartz tube to form a little bigger polycrystalline powder further more at higher temperature over 1000°C for 7days. And by this process, the homogeneous and well crystallized starting power will be prepared [21, 22].

For example, S.Y.Hu etc. [8, 23, 24] had prepared MoSe₂ single crystal by chemical vapor transport method, the elements (Mo, 99.99% pure; Nb, 99.99% pure; Se, 99.999%) were used as raw powder and using Br₂ as a transporting agent.

2.2 Long time growth for single crystal

In some reports, the element powder will be kept in such sealed quartz tube for 7-22days [18, 24-27], and the single crystal will be directly grown up. But at this kind of protocol, the formed crystals are very small in size and the shapes are complex. The typical morphology of these crystals is showed in Fig1. And it can be seen from figure 1, WS₂ tubular crystals grown as microtubes, micro ribbons, and micro ropes, the hollow micro tube with 2 mm in diameter (A); a twisted micro ribbon with a spiral period of 1 mm and 0.1 mm wide (B); and a rope composed of at least two nanotubes with 50 nm in diameter (C) [28].

![Fig. 1 Hollow WS2 microtube (A) 2 mm in diameter, twisted ribbon (B) 0.1 mm in width, and rope (C) composed of at least two nanotubes.](image)

Arrow shows single nanotube of WS₂ with a diameter less than 20 nm, grown on from the microtube surface [14]. Generally, the formed polycrystalline powder will further more be reintroduced to quartz tube for growth for single crystal by vapor transport. In this process, the two-zone furnace will be used. The temperature of the hot and cold zones for crystal growth was with an appropriate temperature gradient of 40-60°C. The sample will be kept for 5-10 days at such stage. And the gained crystals usually are in a size of millimeter scale [13, 19, 28]. And all single crystals are well developed, and have a strong metallic shine (Fig.2).
2.3 Transport agents usually used

Usually, chemical vapor transport technique use halogens (Cl, Br, and I) as agents. There are two advantages using these materials above as transporters. These materials not only introduce excess carriers into material but also transport desired compound; due to which, depending upon halogen used, crystals have p-type or n-type characters. So no further doping is required, it is an advantage. Generally, bromine or chlorine is used for growth of n-type crystals, while iodine is used in transportation for making p-type crystals. Usually, chlorine is taken in the form of TeCl₄.

It was also reported by Moussa Bougouma [1] et al. that the tungsten diselenide single crystals could be performed in two steps: firstly, preparation of polycrystalline WSe₂ from elemental tungsten and selenium, secondly, involving the chemical vapor transport of the polycrystalline powders in a temperature gradient by transport agent TeCl₄. And the largest single crystals, between 25 and 100 mm² [1].

The content of transport agents is between 10-25%.

But in some examples for preparing MX₂ single crystal, there are free of transport agents. A. J. Mathai et al. [29] had synthesized WSe₂ crystal without using agent, but using excess Se. and also Using these crystals, like Al-pWSe₂ Schottky barrier diodes in two different thicknesses of metal, 500 A and 1000 A were namely fabricated and their I-V characteristics were studied successfully.

2.4 High vacuums needed

As reported, the highly vacuum were needed in whole process. When preparing starting powder, as polycrystalline powder, the needed vacuums are usually 10⁻³-10⁻⁴pa [8, 13, 21, 24, 30, 31]. Such a secondary vacuum is mainly to avoid the pollution from the air. Also, the used quartz tube will also be cleaned absolutely.

Once the agent for transport has been successfully added to the polycrystalline powder, the transport tube is then jointed to high vacuum system immediately and sealed when secondary vacuum reaching 10⁻⁴pa.

3. Discussion

The key solution for crystal growth is nucleation, and the driving force for the nucleation is degree of supercooling (ΔT). The larger the ΔT, the easier the nucleation. But in order to avoid the unwanted nucleation sites, the ΔT should be proper, and then the number of nucleation sites will be a little, and the crystal will be grow bigger. So it can be seen from literature, that the chose ΔT are almost less than 50°C.

4. Conclusion

The main process parameters for preparing MX₂ single crystal were reviewed in this paper. It can be
concluded that such single crystal can be made at high vacuum, long time, and small $\Delta T$. Usually, the transport agents were used to help the matter diffusion.

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