

Survey of synthesis and application of Molybdenum Diselenide

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Abstract. The structure, properties and functions of molybdenum diselenide are described briefly. The present situation of the synthesis of molybdenum diselenide is surveyed on the basis of the introduction of chemical, restacking and physical methods. The application of molybdenum diselenide in solar cells, lubricating oil, field-effect transistor etc. is introduced in details. The advantages and disadvantages of various methods were evaluated, with the development tendency of preparation technique of nanoscaled molybdenum diselenide shown and it was emphasized that more attention should be paid on the combinations of preparation methods of nanocomposites.

0. Introduction

Transition metal dichalcogenide (TMDs) are characterized by a MX_2 formula, where M stands for a transition metal (Mo, W) and X stands for a chalcogen (Se, S, or Te).^[1-2] The layer type structure compounds transition metal dichalcogenides have been paid much attention in the last ten years because of their application in photo-voltaic, photoelectrocatalytic solar energy converters, electrocatalyst, solid lubricants, etc.^[3] Molybdenum diselenide ($MoSe_2$) is a member of transition metal dichalcogenides family. $MoSe_2$ not only has all the characteristics of transition metal dichalcogenides described above, while compared with other disulfide, $MoSe_2$ also has a back gate effect, solid lubrication properties etc. The superior performance of $MoSe_2$ draw much attention of researchers in these years.

1. Structure

$MoSe_2$ is grayish-black covalent compound with lamellar, close-packed hexagonal and layered structure that is similar to a sandwich. The atoms are held by covalent bounds while adjacent layers forming each other are Van der Waals forces.

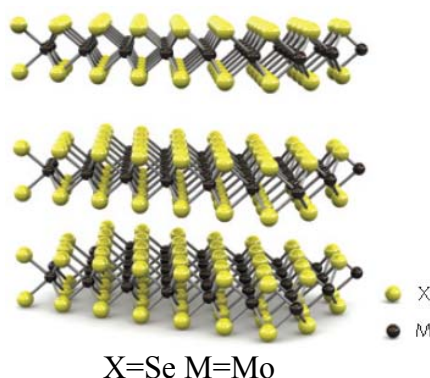


Figure 1. Structure of $MoSe_2$

2. preparation

Nowadays, there have been a lot of methods for preparing $MoSe_2$ at home and abroad. Generally, they can be divided into chemical method, physical method and restacking method.

2.1 chemical method

2.1.1 chemical bath deposition method

The substrate surface that is activated is immersed in the deposition solution without applied electric field and other energy. Thin films are deposited on the substrate surface through controlling complexation of reagents and chemical reaction at ordinary pressure and low temperature. Generally, the reaction processes in alkaline condition. D. J. Sathe^[4] prepared MoSe₂ with the precursor solution containing ammonium molybdate, sodium selenosulphite with hydrazine hydrate as a reducing agent. Optical properties indicate that the band gap energy of direct band gap is nearly 1.43 eV and specific electrical conductivity is in the order of $10^{-5} (\Omega\text{cm})^{-1}$. Huaqiang Shi et al.^[5] have reported a chemical reaction where di-(2,4,4-trimethylpentyl) dithiophosphinic acid extractant is used as reducing agent, home-made NaHSe is used as Se source, to synthesize flake-like MoSe₂ nanomaterials. The measurements of XRD, TEM, EDXS indicate that flake-like MoSe₂ with a diameter of about 70 nm was obtained.

2.1.2 Chemical vapor deposition method

So far, the chemical vapor deposition method is the most superior in so many methods for preparing transition metal dichalcogenides. Because the surface of samples may be damaged and the crystallinity of sample may be reduced, which is obtained by plasma, laser, or annealing process. Jonathan. Shaw^[6] used Se and MoO₃ as the chemical vapor supplement to prepare optically distinguishable single-layer and multi-layer nanosheets on the typically triangular shaped domains with edge lengths around 30 μm of 300 nm SiO₂/Si substrates.

2.1.3 chemical vapor transport (CVT) method

MoSe₂ polycrystalline powders obtained through chemical vapor transport have been studied for many years, which carbon assisted mass transport enhancement effect is used to obtain the target crystal. S. Y. Hu^[7] utilized CVT process with Br₂ as a transporting agent to grow large size MoSe₂ single crystals. The maximum size are about 10 mm \times 10 mm in surface area and 2 mm in thickness. Alberto Ubaldini^[8] used four different transport agents: I₂, NH₄Cl, NH₄Br and NH₄I for preparing single crystals of MoSe₂. A ratio between I₂ and Mo as high as 0.1 and 0.2 for other transport agents was used.

2.2 Restacking single layer of MoSe₂ method

Object substance of restacking method is a lot including Co²⁺, R₄N⁺^[9], 1,10-phenanthroline^[10], Fe(III)-porphyrin^[11], etc. in restacking method.

The properties of MoSe₂-IC show undergone tremendous change in optical, electrical, magnetic, catalytic, and other functions. W. Sienicki^[12] have reported that the intercalated MoSe₂ was obtained in the form of polycrystalline thin films M_{0.5}MoSe₂, where M stands for Ga, In or Tl.

2.3 physical method

Physical method is described that MoSe₂ is produced through mechanical grinding, high energy physics and other means to achieve the purpose. J. H. Zhan^[13] used a stoichiometric amount of elemental molybdenum and selenium in a sealed evacuated tube at a temperature of at least 900 °C for several days to synthesize crystalline molybdenum diselenide. Crystalline was yielded through a metathetical reaction between high-valent molybdenum halides and alkali-metal selenides. J. C. Bernede^[14] heated molybdenum powders and selenium powders under dynamic vacuum at 680 K for 24 h. Stoichiometric layers MoSe₂ have been obtained and are hexagonal structure through testing.

3. Application

3.1 Application for solar cells

The solar cell contains a first electrode layer and a second electrode layer. In the p-type semiconductor layer, a first region at the n-type semiconductor layer side and a second region at the first electrode layer side are different from each other. Semiconductor materials MoSe₂ meet all the requirements for electrode of solar cells. In addition, the prevention of electrolyte corrosion is main advantages of MoSe₂ because non-bonding d-d-orbitals of Mo atoms is involved in the phototransition. Kristl M^[15] make the product whose configuration of fabricated cell is n-MoSe₂ | NaI (2 M) + I₂ (1 M) | C. The fill factor and efficiency of the cell were found to be 34.22 and 1.01% respectively.

3.2 Application for lubricating oil

MoSe₂ have a crystal structure, which is similar to graphite and whose layers are held by van der Waals forces. MoSe₂ slip easily between the layers. Golub A S [16] use chemical vapor deposition method for preparing IF-MoSe₂ nano materials and the lamellar MoS₂. MoSe₂ and MoS₂ are dispersed by Span80 dispersion and then put in UMT-2 friction test machine for friction test. The results show that IF-MoSe₂ is a much better antiwear and friction-reducing additive in liquid paraffin than MoS₂. Powell A Vi [17] use X-ray diffraction, scanning electron microscopy and transmission electron microscopy to characterize MoSe₂. Friction test is operated to investigate the tribological properties of the 150nm lubricating oil added with MoSe₂ nanoflakes. The results indicate that the friction coefficient of the basic oil added with MoSe₂ is higher than the basic oil.

3.3 Application for field-effect transistor

Field-effect transistors having an extremely high input impedance, low noise, high limited frequency, low power consumption, simple manufacturing process, good temperature characteristics and other good characteristics, are widely used in various amplification circuits, digital circuits and microwave circuits. Nakagaki S [18] used ultra-thin, mechanically exfoliated MoSe₂ flakes to fabricate the back-gated field-effect transistors. The MoSe₂ field-effect transistors with On/Off ratios larger than 10⁶ are n-type and have a high gate modulation. A discovery explained by the presence of Schottky barriers at the metal contact/MoSe₂ interface indicates that FETs have asymmetric characteristics on swapping the source and drain. The intrinsic conductivity and mobility of MoSe₂ as a function of gate bias are measured through using four-point and back-gated devices. FETs having a room temperature mobility of ~50 cm²/V indicates that a strong temperature dependence, suggesting phonons are a dominant scattering mechanism.

4. Conclusion and prospect

In summary, the methods described above have advantages and disadvantages. MoSe₂ meet different functional requirements can be prepared by chemical methods. However, there are also disadvantages for chemical methods, such as the high requirement of raw materials, long process flow, and high production costs. The defects of chemical methods can be remedied by physical methods and the natural lattice of MoSe₂ will be not destroyed. But the machine requirement of physical methods is higher, the method is not flexible enough, and products obtained are singular. Thus the development direction of preparation of MoSe₂ diversify into a new process that the chemical method and physical method are combined each other.

Compared with the most common photo-catalytic materials TiO₂, the band gap of MoSe₂ is narrower, which is about 1.43 eV and make it absorb visible light and near-infrared light. This is a premise that MoSe₂ become photo-catalytic materials that is widely used.

Currently, the research of the preparation and application of MoSe₂ is still in the initial stage, which a large area of production and application can not be realized. Researchers at home and abroad should continue to work hard.

Acknowledgments

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References

- [1] Yoffe A D. Low-dimensional systems: quantum size effects and electronic properties of semiconductor microcrystallites (zero-dimensional systems) and some quasi-two-dimensional systems. [J]. Advances in Physics, 1993, 42(2): 173-262.
- [2] Ataca C, Ciraci S. Dissociation of H₂O at the vacancies of single-layer MoS₂. [J]. Physical Review B, 2012, 85(19): 195410.

- [3]Frindt R F, Yoffe A D. Physical properties of layer structures: optical properties and photoconductivity of thin crystals of molybdenum disulphide.[J]. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 1963, 273(1352): 69-83.
- [4]Sathe D J, Chate P A, Hankare P P, et al. A novel route for synthesis, characterization of molybdenum diselenide thin films and their photovoltaic applications[J]. Journal of Materials Science: Materials in Electronics, 2013, 24(2): 438-442.
- [5]Shi H, Zhou X, Lin Y, et al. Synthesis of MoSe₂ nano-flakes modified with dithiophosphinic acid extractant at low temperature[J]. Materials Letters, 2008, 62(21): 3649-3651.
- [6]Shaw J C, Zhou H, Chen Y, et al. Chemical vapor deposition growth of monolayer MoSe₂ nanosheets[J]. Nano Research, 2014, 7(4): 1-7.
- [7]Hu S Y, Liang C H, Tiong K K, et al. Effect of Re dopant on the electrical and optical properties of MoSe₂ single crystals[J]. Journal of alloys and compounds, 2007, 442(1): 249-251.
- [8]Ubalini A, Jacimovic J, Ubrig N, et al. Chloride-Driven Chemical Vapor Transport Method for Crystal Growth of Transition Metal Dichalcogenides[J]. Crystal Growth & Design, 2013, 13(10): 4453-4459.
- [9]Pol V G, Pol S V, George P P, et al. Combining MoS₂ or MoSe₂ nanoflakes with carbon by reacting Mo (CO)₆ with S or Se under their autogenic pressure at elevated temperature[J]. Journal of Materials Science, 2008, 43(6): 1966-1973.
- [10]Srivastava S K, Avasthi B N. Synthesis and characterization of indium intercalation compounds of molybdenum diselenide, In x MoSe₂ (0 ≤ x ≤ 1)[J]. Journal of Materials Science, 1989, 24(6): 1919-1924.
- [11]Xu H, Aylott J W, Kopelman R, et al. A real-time ratiometric method for the determination of molecular oxygen inside living cells using sol-gel-based spherical optical nanosensors with applications to rat C₆ glioma[J]. Analytical chemistry, 2001, 73(17): 4124-4133.
- [12]Agarwal M K, Patel P D, Gupta S K. Effect of doping MoSe₂ single crystals with rhenium[J]. Journal of crystal growth, 1993, 129(3): 559-562.
- [13]Zhan J H, Zhang Z D, Qian X F, et al. Synthesis of MoSe₂ nanocrystallites by a solvothermal conversion from MoO₃[J]. Materials research bulletin, 1999, 34(4): 497-501.
- [14]Bernede J C, Pouzet J, Alaoui Z K. Preparation and characterization of molybdenum diselenide thin films[J]. Applied Physics A, 1990, 51(2): 155-159.
- [15]Kristl M, Drofenik M. Synthesis of nanocrystalline MoSe₂ by sonochemical reaction of Se with Mo (CO)₆[J]. Inorganic chemistry communications, 2003, 6(1): 68-70.
- [16]Golub A S, Zaikovskii V I, Lenenko N D, et al. Intercalation of molybdenum disulfide with chlorobis (phenanthroline) copper (II)[J]. Russian chemical bulletin, 2005, 54(12): 2738-2745.
- [17]Powell A V, Kosidowski L, McDowall A. Novel intercalation compounds of MoS₂[J]. Molecular Crystals and Liquid Crystals, 2000, 341(2): 125-130.
- [18]Nakagaki S, Mangrich A S, Wypych F. A cationic iron (III) porphyrin encapsulated between the layered structure of MoS₂. A new approach to the synthesis of an Fe-Mo-S system[J]. Inorganica chimica acta, 1997, 254(2): 213-217.