Synthesis Methods of Two-Dimensional MoS2: A Brief Review

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Review

Synthesis Methods of Two-Dimensional MoS_2: A Brief Review

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Abstract: Molybdenum disulfide (MoS_2) is one of the most important two-dimensional materials after graphene. Monolayer MoS_2 has a direct bandgap (1.9 eV) and is potentially suitable for post-silicon electronics. Among all atomically thin semiconductors, MoS_2's synthesis techniques are more developed. Here, we review the recent developments in the synthesis of hexagonal MoS_2, where they are categorized into top-down and bottom-up approaches. Micromechanical exfoliation is convenient for beginners and basic research. Liquid phase exfoliation and solutions for chemical processes are cheap and suitable for large-scale production; yielding materials mostly in powders with different shapes, sizes and layer numbers. MoS_2 films on a substrate targeting high-end nanoelectronic applications can be produced by chemical vapor deposition, compatible with the semiconductor industry. Usually, metal catalysts are unnecessary. Unlike graphene, the transfer of atomic layers is omitted. We especially emphasize the recent advances in metalorganic chemical vapor deposition and atomic layer deposition, where gaseous precursors are used. These processes grow MoS_2 with the smallest building-blocks, naturally promising higher quality and controllability. Most likely, this will be an important direction in the field. Nevertheless, today none of those methods reproducibly produces MoS_2 with competitive quality. There is a long way to go for MoS_2 in real-life electronic device applications.

Keywords: Molybdenum disulfide; transition metal dichalcogenide; two-dimensional materials; micromechanical exfoliation; chemical vapor deposition.

1. Introduction

Recently, graphene has received considerable attention in scientific communities. It is recognized as a new wonder material (e.g., record carrier mobility, thermal conductivity, mechanical strength and flexibility), and applications in nanocomposites, paints, transparent electrodes, heat spreaders, etc. are being explored [1]. However, one should not forget that the original motivation for studying graphene was in its field effect [2], with a hope that it might play a key role in nanoelectronics, rather than serving as a passive element such as electrodes [3]. Nevertheless, at this stage, due to the difficulties in

opening an energy bandgap in graphene, it is not clear whether graphene will become a key material in electronics at all. Therefore, the search for other two-dimensional (2D) materials (materials with one or few atomic layers) with an inherent energy bandgap that is suitable to make transistors is essential. Black phosphorus [4], transition metal dichalcogenide (TMD) [5], gallium nitride [6], etc. are extensively explored. For any type of application, the material production is always the first experimental step. Among these 2D semiconductors, molybdenum disulfide (MoS_2) is relatively more mature in terms of its synthesis technologies. Hence, in this paper, we provide a short literature survey of recent progresses in the synthesis of MoS_2. The paper focuses only on the production techniques rather than serving as a complete review on MoS_2-related physics, materials and electronics. Also, we put special emphasis on the recent achievements in metalorganic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD), where gaseous precursors are used to grow MoS_2. It has a high potential for producing MoS_2 with better quality and controllability for nanoelectronic device applications.

2. Synthesis Methods of MoS_2

MoS_2 has several polymorphs, where the 2H MoS_2 has a layered hexagonal structure with lattice parameters of a = 0.316 nm and c = 1.229 nm [7], yielding an inter-layer spacing of 0.615 nm [8], as schematically shown in Figure 1. Bulk 2H MoS_2 is an indirect bandgap semiconductor (~1.29 eV). With decreasing thickness, the bandgap increases. When it comes to monolayer MoS_2, it becomes a direct bandgap material, and the energy gap can be as large as ~1.90 eV [9], suitable for fabricating most electronic devices. The synthesis methods of MoS_2 can be divided into top-down and bottom-up approaches. We hereby describe them in turn.

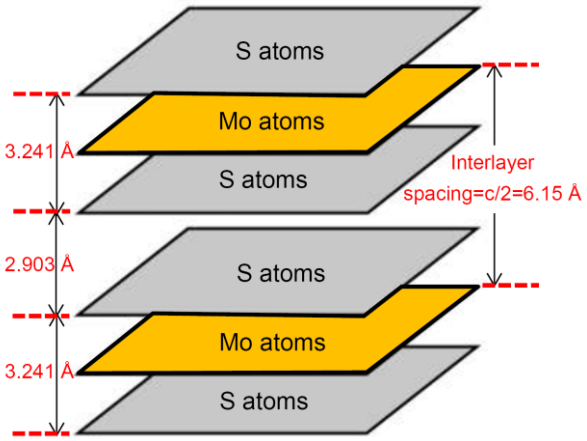

Figure 1. Distances between different layers in 2H MoS_2.

2.1. Top-down Approaches

2.1.1. Micromechanical Exfoliation

Similar to the micromechanical exfoliation of graphene (a vivid lab demonstration can be found in [10]), MoS_2 flakes can be produced on a substrate using sticky tapes. The starting material is bulk MoS_2, where some parts are peeled off with the tape and pressed into the substrate. Upon the release of the tape, some parts stay with the substrate rather than the tape due to the van der Waals force to the substrate. Repeating the process may produce flakes of MoS_2 with random shapes, sizes and numbers of layers. This method offers 2D materials of the highest quality, enabling to study the pristine properties and ultimate device performances. For example, Kis et al. have used micro-exfoliation to produce MoS_2 monolayers that are suitable for ultrasensitive photodetectors [11], analogue [12] and digital circuits [13], and observation of interesting physics such as mobility engineering and a

metal–insulator transition [14]. However, it was found that the van der Waals adhesion of many TMDs to SiO_2, a typical substrate, is much weaker than that of graphene. Therefore, the produced flakes are very small (typically <10 μm) in their lateral size [15]. These results notwithstanding, large area MoS_2 flakes can be exfoliated by slightly modifying the technique. Magda et al. obtained mono MoS_2 layers with lateral size of several hundreds of microns by improving the MoS_2-substrate adhesion, as shown in Figure 2 [15]. The mechanism is that sulfur atoms can bind more strongly to gold than to SiO_2. The drawback is that such as-exfoliated MoS_2 flakes have to be transferred to another new substrate, since in most applications the material is used on insulating substrates. In addition, like their graphene counterpart, the tape-assisted micromechanical exfoliation method offers very low yield, and it's not possible to scale up for large volume production, therefore MoS_2 synthesized by this method is limited to fundamental study at lab scale.

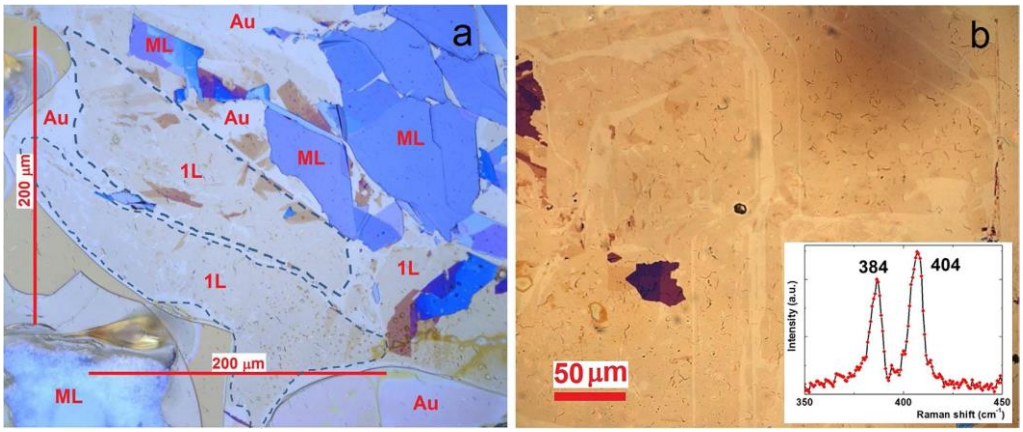

Figure 2. Large area MoS_2 flakes exfoliated with chemically enhanced adhesion to the substrate [15].

2.1.2. Liquid Phase Exfoliation

Liquid phase exfoliation also starts from bulk MoS_2, producing flakes with random shapes, sizes and number of layers. The quantities, however, are much larger, and the quality lower. Roughly, there are 2 routes to exfoliate MoS_2 in solution. The first is exfoliation by mechanical means such as sonication, shearing, stirring, grinding and bubbling [16–21]. The essence is purely physical, although some chemistry may still be involved [22–24]. For example, surfactants such as sodium deoxycholate (SDC) bile salt [22] and chitosan [23] may be added to the solution to prevent the exfoliated flakes from recombination. Electrolysis is employed to generate bubbles in some cases [24]. It is known that fine bubbles can squeeze into material interfaces and exfoliate them [25]. The yield of this method is dramatically improved from tape-assisted exfoliation, but the efficiency is still low for industrial applications. Therefore, a second route by atomic intercalation via solution chemistry [26] or electrochemistry [27] has been proposed. Lithium is typically used to intercalate between the MoS_2 layers and enlarge the interlayer spacing, easing the following exfoliation by mechanical treatment (e.g., sonication). Fan et al. developed a process to exfoliate MoS_2 nanosheets very efficiently using sonication assisted Li intercalation. They found that the complete Li intercalation with butylithium can be effected within 1.5 hours [28]. An example of the MoS_2 flakes synthesized by this method is shown in Figure 3. However, this method results in the loss of semiconducting properties due to the structural changes during Li intercalation. It is reported that above an annealing temperature of 300 °C, these MoS_2 flakes can be somewhat recovered [26].

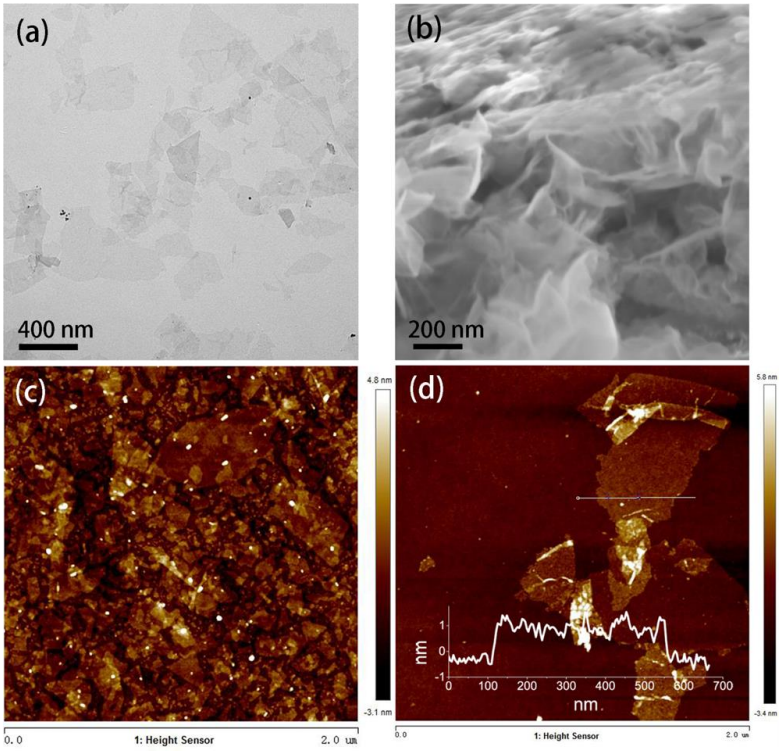

Figure 3. TEM, SEM and AFM images of MoS_2 flakes exfoliated by Li intercalation and sonication [28].

Liquid phase exfoliation is a simple technology with low cost, producing large quantity 2D nanosheets with relatively high quality. Therefore, it is regarded as the most suitable method for the large-scale industrial production of one- to few-layer 2D material flakes at low expense [29]. It is worth noting that liquid phase exfoliation can produce not only wet suspensions of flakes or dry powders, but macroscopically continuous thin films as well [30–32]. On substrates, through drop casting of the suspension and drying, MoS_2 thin films are prepared by Walia et al. [30–32], where optical and electrical properties can be studied.

2.2. Bottom-up Approaches

2.2.1. Physical Vapor Deposition

Although molecular beam epitaxy (MBE) is an advanced technology for growing single crystal semiconductor thin films, its application in producing 2D materials needs further development, and the grain size of the 2D material is not as high as expected [33]. In fact, even ordinary physical vapor deposition is rare. There is a report on growing MoS_2-Ti composite by vacuum sputtering, using Ti and MoS_2 as the targets [34]. However, the MoS_2 is an amorphous structure in this case.

2.2.2. Solution Chemical Process

There are various methods for producing MoS_2 by solution chemistry. Hydrothermal synthesis [35] and solvothermal synthesis [36] typically use molybdate to react with sulfide or just sulfur in a stainless steel autoclave, where a series of physicochemical reactions take place under relatively high temperature (e.g., 200 °C) and high pressure for several hours or longer. The resultant is MoS_2 powders of different shapes. The size of individual particles can be adjusted to some extent. Very frequently, the powders are high-temperature post-annealed, to improve their crystalline quality and purity. The only difference between hydrothermal and solvothermal synthesis is that the precursor solution in the latter case is usually not aqueous. Other solution chemical processes start at almost room temperature and atmospheric pressure, where post-annealing is often used anyway [37–41].

The products can be either a powder or thin film, depending on the preparation details. The most commonly-used precursor is $(NH_4)_2MoS_4$ (ammonium tetrathiomolybdate), or something similar. $(NH_4)_2MoS_4$ decomposes to form MoO_3 at 120–360 °C, which can be further converted into MoS_2. In some cases, electrochemical deposition [42–44] and photo-assisted deposition are used [45]. For instance, Li et al. fabricated MoS_2 nanowires and nanoribbons using MoO_x as the precursor [43]. The MoO_x precursor is then exposed to H_2S at high temperature (500–800 °C) to synthesize MoS_2. Depending on the temperature for processing, both 2H and 3R phase of MoS_2 can be synthesized. The MoS_2 nanoribbons can be 50 μm in length and are aligned in parallel arrays which are preferable for device fabrication, as shown in Figure 4.

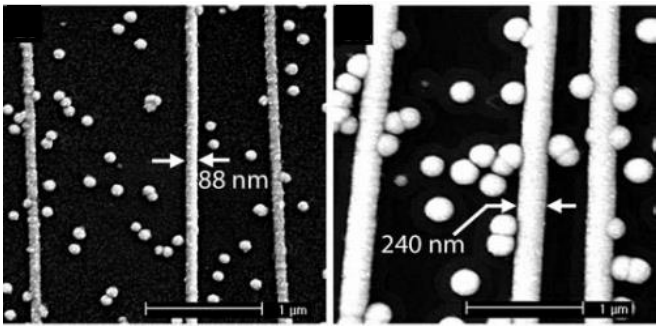

Figure 4. MoS_2 nanowires/nanoribbons synthesized from MoO_x precursor [43].

2.2.3. Chemical Vapor Deposition (CVD)

Among all the synthesis methods, CVD is the most compatible to existing semiconductor technology. Typically, it forms the film on a substrate, where chemical reactions are involved in the growth mechanism. The large-area growth of highly uniform MoS_2 will enable the batch fabrication of atomically thin devices and circuitry. Currently, most works start with solid state precursors of molybdenum, such as MoO_3 [46,47] or Mo [48]. If the Mo precursors are not vaporized in the process, often the technique is also called sulfurization [46–48]. Typical S precursors are H_2S gas [49] or vaporized S [46–48,50]. It is argued that using $MoCl_5$ precursors are easier to achieve monolayer MoS_2 over large area [50]. Earlier, the MoS_2 could be noncontinuous [47], which is not a big problem nowadays. The usual growth temperatures are 700–1000 °C, and the inclusion of a metal catalyst such as Au is favorable for the film quality [49]. Typical reactions taking place in the CVD are one of these:

$$MoO_3 + 2H_2S + H_2 = MoS_2 + 3H_2O \quad (1)$$

$$8MoO_3 + 24H_2S = 8MoS_2 + 24H_2O + S_8 \quad (2)$$

$$16MoO_3 + 7S_8 = 16MoS_2 + 24SO_2 \quad (3)$$

With plasma-enhanced chemical vapor deposition (PECVD), the growth temperature of MoS2 can be lowered to 150–300 °C, making it possible to directly deposit MoS_2 even on plastic substrates [51].

Metal-organic CVD is a special case of CVD where organometallic precursors are used. It is used in the modern semiconductor industry to produce single crystal expitaxial films. Recently, a few reports have appeared on the application of this method in the growth of MoS_2 thin films [49,52–54]. Kang et al. [52] have grown MoS_2 and WS_2 on 4-inch oxidized silicon wafers by MOCVD. The MoS_2 is grown with gaseous precursors of $Mo(CO)_6$ (boiling point 156 °C) and $(C_2H_5)_2S$. At 550 °C, monolayer MoS_2 with full coverage of the substrate (typically SiO_2/Si and fused silica) is deposited for t_0~26 h. Figure 5a shows scanning electron microscopy (SEM) images of the samples, demonstrating the effect of adding H_2 in the gas mixture. It is argued that H_2 enhances the decomposition of $(C_2H_5)_2S$ (increasing nucleation due to hydrogenolysis) and etches MoS_2 (preventing intergrain connection) [52]. It seems that a low H_2 rate is beneficial for growing continuous monolayer MoS_2. Nevertheless, H_2 is

necessary for removing the carbonaceous species generated during the MOCVD. Therefore, the H_2 flow should be optimized. To have successful growth, dehydrating the growth environment is also necessary. Figure 5b indicates that the growth mode is layer-by-layer under this specific condition. When $t < t_0$ there is almost no nucleation of the second MoS_2 layer, which takes place mainly at the grain boundaries of the first layer when $t > t_0$. Figure 5c shows a top gated (V_{TG}) MoS_2 transistor with a field-effect mobility of 29 cm^2 V^{-1} s^{-1} and transconductance 2 μSμm, determined from the transfer properties. The current saturation occurs at relatively low V_{SD} (see the inset). These features compete well with the-state-of-the-art MoS_2 transistors. Figure 5d–f demonstrates the optical absorption, Raman and photoluminescence spectra measured from the MOCVD grown MoS_2 (and WS_2) films, respectively, where the features agree well with the characteristics of exfoliated monolayer counterparts (denoted by diamonds).

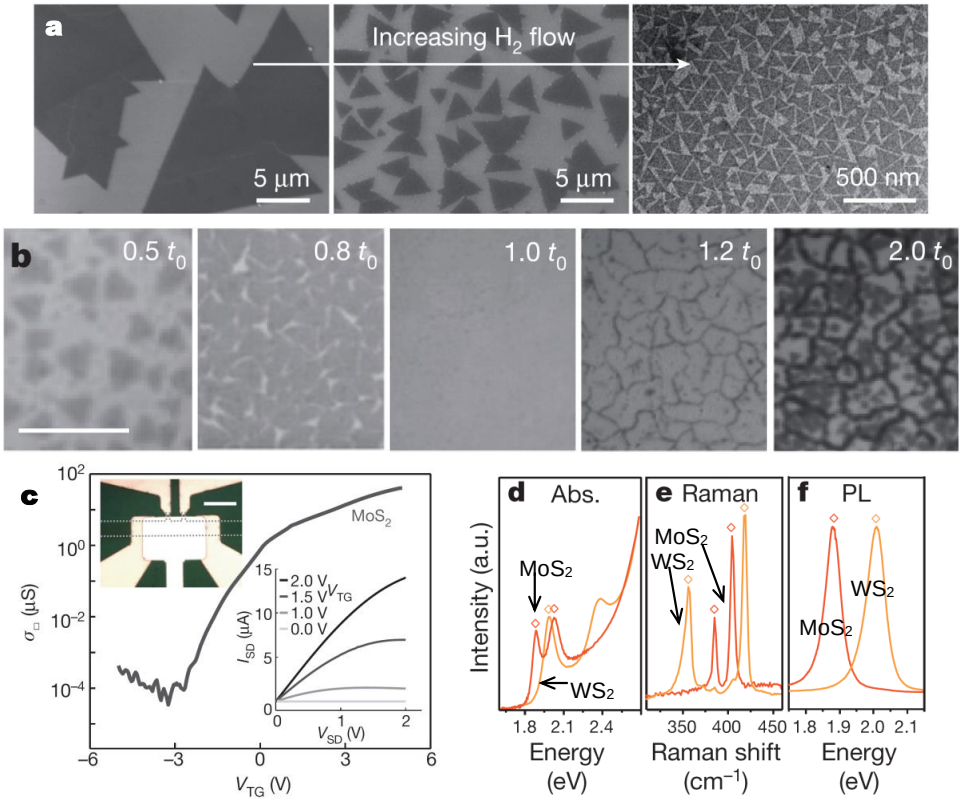

Figure 5. (**a**) Grain size evolution of monolayer MoS_2 as a function of H_2 flow. From left to right, 5, 20 and 200 sccm H_2. (**b**) Optical images of MoS_2 films as a function of growth time. t_0 is the optimal time for full monolayer coverage (~26 h). (**c**) Transfer and output properties of the field-effect transistor fabricated in the MOCVD grown MoS_2 with top gate configuration. $\sigma_{\square}$ denotes sheet conductance. Scale bar: 10 μm. (**d**–**f**) Optical absorption, Raman and normalized photoluminescence spectra of as-grown monolayer MoS_2 (red) and WS_2 (orange) films. The peak positions in (**d**–**f**) are consistent with exfoliated flakes (denoted by diamonds) [52].

At this stage, the material quality in [53] is still too low to be competitive. The large-area deposition of monolayer MoS_2 as well as other TMDs with spatial homogeneity and high performance is still challenging. MoS_2 films today are polycrystalline with the grain size typically ranging from 1 to 10 micrometers. This notwithstanding, the MOCVD synthesis of 2D semiconductors indeed opens a pathway towards future exciting nanoelectronic materials. The most important reason for this is that, in MOCVD, ultrapure gaseous precursors are injected into the reactor and finely dosed to deposit a very thin layer of atoms onto the substrate. Even if a solid or liquid precursor is used, it will be vaporized in situ in the chamber [53]. Unlike solid and liquid precursors, here the building-blocks for

growing the film are much finer, naturally leading to better quality and controllability. The heated metalorganic precursor molecules decompose via pyrolysis, leaving the atoms on the substrate. The atoms bond to the surface, and an ultrathin MoS_2 layer is grown.

Based on this argument, one can easily think of another promising synthesis method: ALD [55], which can be seen as a subclass of CVD. In ALD, the film is grown by exposing the substrate surface to alternating gas precursors. In contrast to ordinary CVD, the precursors are never simultaneously present in the chamber. Instead, they are introduced as sequential and non-overlapping pulses, separated by purges in between. In each pulse, molecules react with the surface in a self-limiting way. Hence, it is possible to grow materials with high-thickness precision (layer by layer). Indeed, very recently, people have used ALD to grow MoS_2, such as in [56]. Using $MoCl_5$ (vaporized) and H_2S precursors, monolayer to few-layer MoS_2 on large SiO_2/Si or quartz substrates is obtained [56]. In the photos of two 150 mm quartz wafers before and after the ALD, the substrate changes to dark yellow uniformly (~2 layers of MoS_2) [56]. It is found that photoresist residues on the surface lead to more nucleation sites for MoS_2, but this mechanism remains to be confirmed. Figure 6a plots Raman signals for 50 cycle ALD MoS_2, where the E^1_{2g} and A_{1g} characteristic peaks are sharper and higher for 475 °C deposition temperature, indicating its higher material quality. After the ALD, some samples are annealed in a sulfur environment (H_2S or S atmosphere). Figure 6b shows that after sulfur annealing at increasingly high temperature, the characteristic peaks get narrower, stronger and more symmetric. After annealing at 920 °C, the full width at half maximum of the E^1_{2g} peak is close to that of exfoliated MoS_2 monolayer (4.2 cm^{-1} vs. 3.7 cm^{-1}). By analyzing the separation Δ between E^1_{2g} and A_{1g} peaks, one can tentatively determine the number of layers in MoS_2 films [56]. In Figure 6c, the sample grown at 475 °C and annealed at 920 °C seems to be 1–2 monolayers. Future electronic measurements are needed to further examine the film quality.

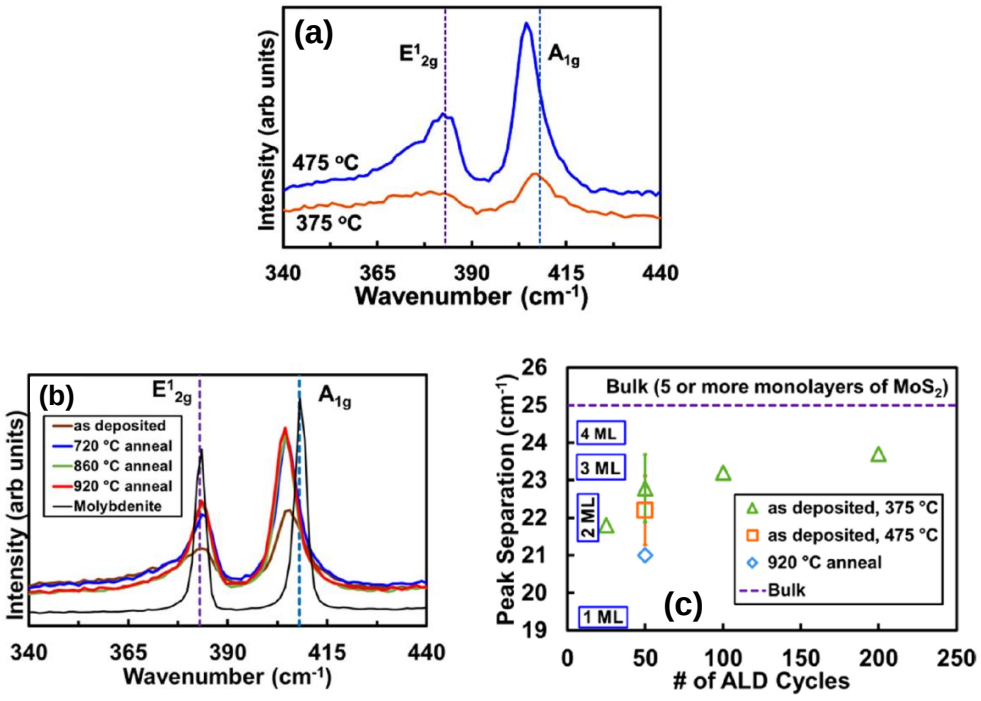

Figure 6. (**a**) Raman spectroscopy measurements of ALD MoS_2 at 375 or 475 °C, where the latter shows higher quality. (**b**) Raman spectra of 475 °C deposited MoS_2 films (some are post annealed in sulfur environment), where 920 °C annealing leads to the best quality. The curve for bulk MoS_2 is for reference. (**c**) E^1_{2g} to A_{1g} peak separation Δ plotted against the cycle number in ALD. Δ~19 cm^{-1} tentatively indicates MoS_2 monolayer, whereas bulk (>5 layers) material has Δ~25 cm^{-1} [56].

3. Conclusions

In this paper, we have reviewed the synthesis methods of MoS_2 in terms of top-down and bottom-up approaches. Micromechanical exfoliation offers the highest material quality but is limited by the yield so it is mainly for basic research, whereas liquid phase exfoliation and solution chemical process are of low cost, with decent material quality and suitable for large-scale industrial production. MoS_2 thin films aiming for high-end electronic applications are produced by CVD. In this review, we have put a special emphasis on the MOCVD and ALD methods, because they are more sophisticated technology with gas phase precursors and will most likely be the dominant techniques in producing MoS_2 films oriented towards real electronic device applications in the future. In most cases the MoS_2 films are transfer-free, which is vital for industrial applications that require a high process controllability and reproducibility [57]. At the moment, production of MoS_2 as a high quality electronic material is still challenging. This notwithstanding, most of the reviewed processes can be extended to other 2D materials (with some modification), and with future technological advances, the successful production of advanced 2D nanoelectronic materials can be envisioned.

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