Optimization of CVD growth conditions of atomically thin $MoSe_2$ as photoresponsive material

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Abstract

In this work, the optimization of an atmospheric pressure chemical vapour deposition system was carried out in order to grow atomically-thin $MoSe_2$, a prominent semiconductor belonging to the family of two-dimensional transition metal dichalcogenides. The growth was carried out using a so-called "two-powder route", where the two precursors (the transition-metal and the chalcogen) are supplied in powder form. Several deposition parameters where probed, and an extensive characterization (Raman spectroscopy, photoluminescence, scanning electron microscopy, x-ray diffraction, x-ray photoelectron spectroscopy and atomic force microscopy) of the produced samples was conducted. As a final result, a reliable experimental procedure has been established which leads to the growth of atomically-thin $MoSe_2$ films with a lateral size of 1 cm^2. Furthermore, the grown samples were used as photoactive material in test photodetectors. Such devices were designed with a suitable architecture and fabricated in clean room with state-of-the-art equipment. The electrical characterization provided insights into the optical properties of 2D $MoSe_2$ in terms of photoresponse and photoconductivity.

Keywords: transition metal dichalcogenides, $MoSe_2$, chemical vapor deposition, 2D materials, photodetectors.

Introduction

Two-dimensional transition metal dichalcogenides (TMDCs) are a prominently group of semiconductor materials within de 2D materials class that may be useful in this regard. Atomically thin molybdenum diselenide ($MoSe_2$) in particular is a prominent semiconductor from the TMDC family with a direct bandgap of 1.5 eV, which makes it useful for applications such as photovoltaic cells and photodetectors. However, this versatile and interesting material still lacks a reliable synthesis method which can produce high quality, large area, and standardized samples of this material has yet to surface. In this thesis, relying on the well-established technique of chemical vapor deposition, the goal of growing and characterizing monolayers of this material was pursued. Thin $MoSe_2$ films were synthesized using atmospheric pressure CVD (APCVD) system.

TMDC Properties

TMDCs are a class of materials that, like graphene, are natural occurring [1]. They are defined by their MX_2 structure, where the M stands for transition metals (TMs) such as Mo, W, etc, and X for a chalcogen – group 16 elements such as sulphur, selenium or tellurium [2].

TMDCs exhibit a layered structure with consecutive layers being bonded by van der Waals forces and ionic-covalent bonds as intra-layer bonds [3]. The weaker forces at the inter-layer gap dictate the preferential cleaving direction for bulk TMDC crystals. Each individual layer is around 6-8 Å thick (0.6 - 0.7 nm). The transition-metal atom in a TMDC compound can be found in one of two coordinations with the surrounding chalcogen atoms: trigonal prismatic and octahedral, also called trigonal-antiprismatic, consequence of its d-electron count. This in turn will give rise to different phases or polytypes, with different lattice arrangements (Figure 1): trigonal anti-prismatic coordination gives rise to

the 1T phase, while trigonal prismatic gives rise to the 2H and 3R and are the most common polytypes for these materials.

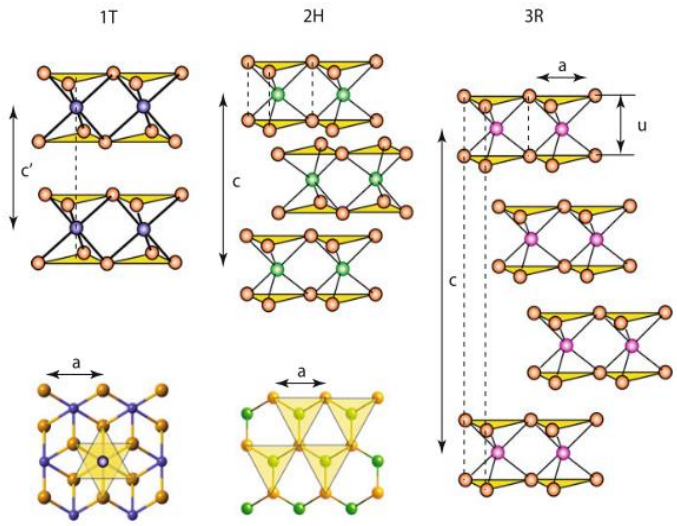

Figure 1 - 1T, 2H and 3R polymorphs

Applications

Given the wide variety of properties shown in the above section, it comes as no surprise that the materials from the TMDC family have a wide range of applications. MoS_2 and $MoSe_2$ have traditionally used as solid-state lubricants[4,5], catalysts[6,7] and electrodes[8]. Recently, with the exploration of materials at 2D thickness, it has been uncovered that a single monolayer of $MoSe_2$ has a bandgap of ~1.5 eV[9], while MoS_2 has a broader ~1.8 eV[10]. The narrower bandgap of $MoSe_2$ makes it more interesting for harvesting solar energy in single junction solar cells[11,12] by covering both the visible and IR parts of the solar spectrum. In fact, its use on photoelectrochemical[12], CIGS[13,14] and dye sensitized solar cells[15] has been reported. Not only are the optical properties of MoSe2 interesting for solar cells, but they make it an interesting material to be used for photodetectors[9,16,17,18], [9,12,18–20]. These are usually fabricated through metal contact on a film surface using lithography as depicted in Figure 2.

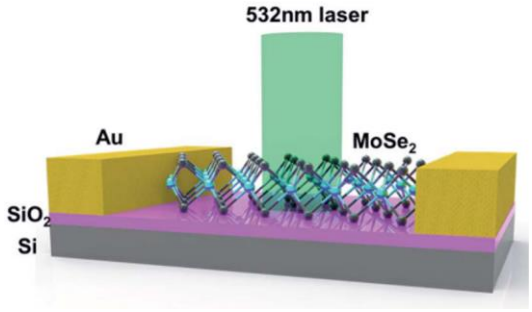

Figure 2 - Schematic of a $MoSe_2$-based photodetector with gold contacts [9].

In relation to MoS_2, $MoSe_2$ has a higher carrier mobility and narrower bandgap[21]. Additionally, photocurrent measurements have shown response times ~1ms [22]. Semiconductor TMDCs can be used to build field effect transistors (FETs)[723242526272829], including applications chemical sensing devices, such as gas sensors for pollutant concentration monitoring[30]. The fabrication of a $MoSe_2$ FET will be the ultimate goal of this thesis work, which shows that the grown material can be successfully used as a semiconductor layer. In addition to this, it is worth mention other interesting and promising applications outside the scope of this work, such as hydrogen evolution reaction (HER) [3132], computer memory applications[33], the possibility of incorporating these materials in space bound devices[34] and the rising fields spintronics[35,36], valleytronics[37] and polaritronics[38]. For these materials to be used in future technological applications, their production methods must be optimized and scaled to industrial level. This thesis focus will be put on $MoSe_2$, an interesting semiconducting material from the TMDC family, and its adequacy as an active layer in test photodetectors evaluated.

MX_2 production methods

2D TMDCs can be synthesized by either one of two radically different approaches: top-down or bottom-up[2].Top-down approaches yield 2D layers of material by taking the bulk materials and thinning them down to atomically thin layers by taking advantage of the weak binding forces at the inter-layer gap.

Mechanical exfoliation

The approach by which graphene was firstly isolated: by using an adhesive Scotch tape, researchers were able to peel of single graphene layers from graphite. The mechanical

action will preferentially break down the weaker van der Waals bonds, thus resulting in the separation of thinner layers of material. The thinner flakes will then stay adhered to the tape and can be transferred to a target substrate, in a process regarded as deterministic. This became known as the Scotch tape method and is currently one of the most efficient ways to obtain highly crystalline and atomically-thin TMDC layers[2], allowing their study. However, mechanical exfoliation acts solely on the principle of exploiting the weaker inter-layer bonds, and thus is not limited to the usage of the scotch tape. Other approaches have been used that act on this principle as well, such as coating a TMDC sample with a Ni layer and peeling with tape, which can then be transferred to a target substrate[39]. The single layers that result from exfoliation are stabilized by the development of a ripple structure, similarly to what happens in graphene[40]. Despite its simplicity and good results, this method is not adequate for large scale production due to the non-controllable size and thickness of the flakes, as well as lack of scalability.

Chemical vapor deposition of MoX_2

Chemical vapor deposition (CVD) is a technique for depositing films based on the chemical reaction between vapor phase reactants. Most materials used in the semiconductor industry can be obtained through CVD[41], including $MoSe_2$. This is the production method that will be explored in this thesis work. In particular, the so-called "two-powder route" was selected as the CVD growth method. In this approach the M and X components are supplied in powder for in two zones of the furnace held at different temperatures.

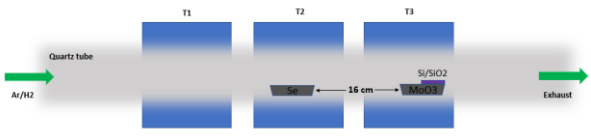

Figure 3 - CVD system schematic and crucible position example. In this image the crucibles are spaced

Notable examples of this approach to synthesize $MoSe_2$ are the works of Fremes et al.[42] and Campbell et al.[43], having achieved 0.5 mm singles crystals and a polycrystalline film of a few square millimetres, respectively. Give the current status of the methodology concerning the CVD growth of $MoSe_2$, several CVD parameters need to be optimized to produce atomically thin $MoSe_2$ with the desired properties. The main challenges in this context are two-fold: the suppression of vertical growth (by thermodynamic favouring of horizontal crystal growth[44]) that gives rise to multilayer samples, and the control over the nucleation density as to grow monocrystalline samples, which would have better electrical properties than to polycrystalline ones due to the absence of grain boundaries[45].

Experimental Procedure

The growth experiments in this work were carried out in a CVD setup featuring a 1 m quartz tube furnace with 60 mm of internal diameter. The furnace has 3 separate heating zones. Powder Se (99,99%, Alfa Aesar) and powder MoO_3 (99,99%, Alfa Aesar) were used as precursors. In each run ~300 mg of Se and ~20 mg of MoO_3 were placed in alumina crucibles with a depth of 70 mm. While the placement of the Se crucible is variable, the MoO_3 is placed always in the third zone. The Si/SiO_2 substrates were placed on the MoO_3 crucible with the polished side facing the powder. The growth zone was set to 750ºC with a heating ramp of 50ºC/min. Se evaporates at ~220ºC, while MoO3 sublimates at 550ºC, contributing to the vapor phase. Upon reaching 750ºC, the temperature was kept for 12 minutes, and then the heating was turned off and a flow of 220 sccm of Ar was set. The cool-down step (to a temperature below 70ºC) took around 30 minutes.

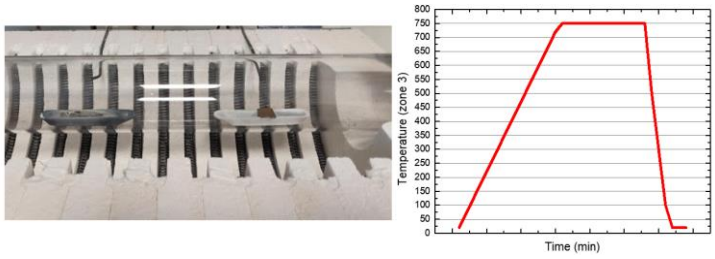

Figure 4 - Precursor boat and substrate configuration (left) and temperature profile during procedure (right)

The growth experiments in this thesis used Ar and H_2 gases in different proportions. A mass flow controller with connection to Ar, H2, Ar/H_2 mix and N_2 lines, was used to control the gas flow inside the tube during all operations. The control over the gas flow during the process was crucial and strongly influenced the final quality of the deposits.

Results

It was possible through optimization of the CVD parameters to establish a reliable experimental procedure to grown atomically thin $MoSe_2$.

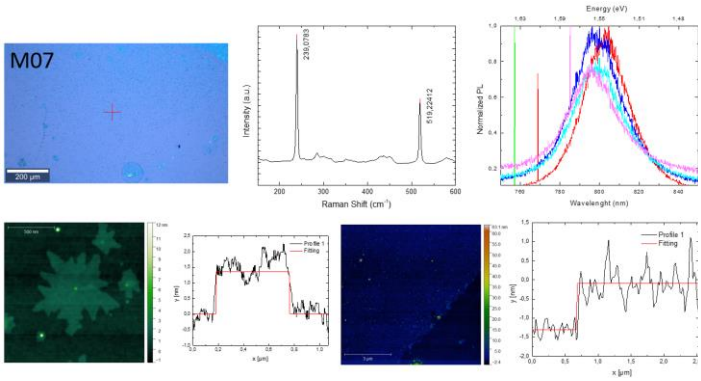

Figure 5 - Sample M07, grown with 0/10Ar/H_2 sccm

Sample M07 was grown using solely a H_2 flow without the use of Ar as a carrier gas. Observations in the optical microscope show a continuous deposit with some clusters of material. The Raman peaks of this deposit are located at 239 cm^{-1}, which agrees with the literature in regard to the position the A_{1g} peak in $MoSe_2$ monolayers. PL emission measurements place its bandgap at 1.55 eV. AFM measurements on a single flake located on the edge of the substrate shown revealed a height 1.34 nm, with an associated error of 0.42 nm, while the measurements performed on the edge of the continuous film reveal a height of 0.5448 nm with an error of 0.31 nm, placing the film thickness in the monolayer range.

The quality of the two-powder-route-grown $MoSe_2$ was assessed through the presence of defects peak in the Raman spectra (250 cm^{-1}) and XPS. These samples show no signs of degradation after more than 3 months from the growth (aside from scratches resulting from sample manipulation). Lorentzian fittings of the Raman spectra show no signs of the 250 cm^{-1} peak, and the XPS analysis performed on sample M07 revealed that the atomic percentage of the Mo and Se elements is nearly 1:2, as expected in stoichiometric $MoSe_2$, as well as no signs of oxidation (Figure 6).

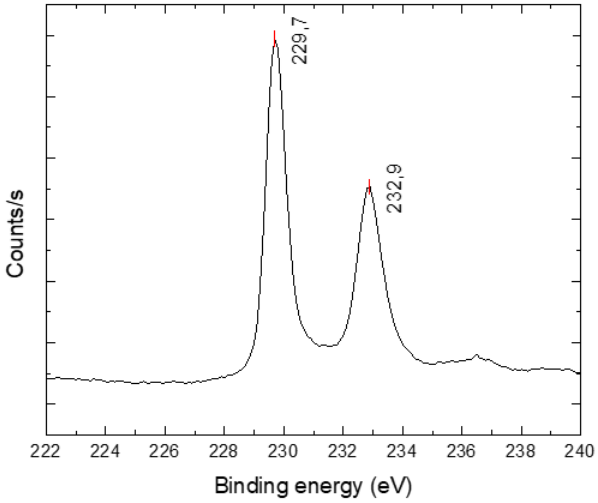

Figure 6 - XPS measurements performed on sample M07, 4 months after production

Fabrication and electrical characterization of CVD-MoSe2-based photodetectors

CVD-grown $MoSe_2$ samples were used as substrates to deposit metallic contacts with the intention of measuring photocurrent. Figure 7shows generically the fabrication steps in the fabrication of the devices in the cleanroom.

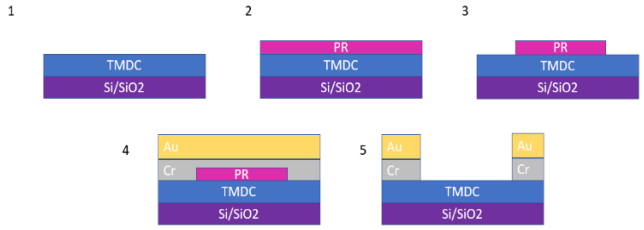

Figure 7 - Schematics for the cleanroom fabrication steps: 1. CVD grown $MoSe_2$ on Si/SiO2 2. Photoresist spin coating 3. Photoresist patterning through direct write laser 4. Metal contact deposition. The metal contact is a stack consisting on 20 nm of gold stack on 3 nm Cr, for adhesion

After fabrication, the devices were electrically tested in a 2-probe setup under a white LED, revealing an increase in current when under illumination.

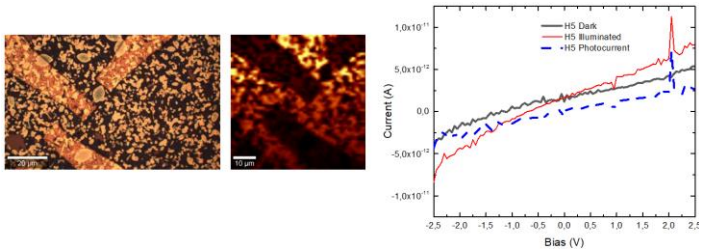

Figure 8 - Device H5 exhibits photocurrent when illuminated with a white LED. The quality of the film in between the contacts was investigated under Raman

Additionally, the optical bandgap of the material was measured.

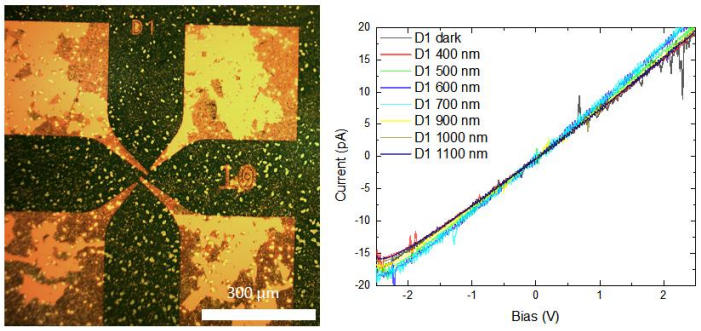

Figure 9 - Optical bandgap of the sample measured on device D1 using a light source coupled with a monochromator

Optical bandgap measurements agree with the results of the PL emission measurements from samples with similar characteristics, which placed the bandgap of the films at ~1.5 eV. Back gating measurements were performed on the same region, on device E1 between the probes of the bottom row.

Outlook

Following the conclusion of this thesis, future steps concerning the thesis can be envisaged.

Firstly, experimentation with growth configuration needs to go forwards in order to achieve the goal of wafer-area coverage (up to several inches).

Regarding the CVD setup, a more accurate pressure measurement system could be implemented in order to control the partial vapour pressure from each of the precursors along the process, allowing greater control over the available amount of reactant. As for the choice of substrate, c-plane sapphire substrates could be considered in order to promote an epitaxial growth (i.e. crystal alignment through minimization of lattice mismatch between grown material and substrate). Direct growth on supported graphene could also be explored, in order to fabricate heterostructures without the need of a transfer step.

In general, however, the transfer step needs to be considered: one of the proposed applications of 2D materials was specifically in flexible electronics. However, both a direct growth on flexible substrate (usually a polymer) and a post-growth transfer process imply the use of high temperatures, which are detrimental to those substrates.

Further, the optimization of the transfer process to place CVD-grown $MoSe_2$ onto transmission electron microscopy (TEM) grids is an interesting research task in order to characterize the material in terms of its lattice structure at atomic resolution. Some methods have been proposed such as coating the TMDC films with a metallic layer, which is then peeled off and transferred to a target substrate, such as reported in reference[39], but so far no consensus has been reached on the optimal approach. Lastly, the fabrication steps required for the fabrication of optoelectronic devices based on 2D TMDCs need further consideration, as these steps were found to deeply affect the device performance, often shadowing the advantages of using such an innovative material

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