

Desenvolvimento de um sistema robusto para preparação de substrato e crescimento de filmes finos de MoS₂, pela técnica de CVD

Development of a robust system for substrate preparation and growth of MoS₂ thin films by CVD technique

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Resumo: O primeiro material bidimensional descoberto foi o grafeno em 2004. A partir de então, estudos foram desenvolvidos com outros materiais e, um dos primeiros semicondutores a ser isolado foi o dissulfeto de molibdênio, o MoS₂. Ao contrário do grafeno, o MoS₂ tem gap de energia, e na forma de monocamada o gap passa de indireto para direto. Essa mudança resulta em uma fotoluminescência de alto brilho. Devido ao alto desempenho elétrico e óptico, o MoS₂ (2D) tem grande potencial de aplicação nos dispositivos eletrônicos e campos fotoeletrônicos. Existem diversas técnicas para produzir este material, e uma delas é através do método de Deposição Química de Vapor (CVD) que consiste na formação de cristais no substrato, pela deposição atômica ou molecular, sendo o sólido oriundo de uma reação química onde os precursores estão na fase de vapor. O objetivo deste trabalho será sintetizar e caracterizar o MoS₂ pelo método de CVD, a partir de um sistema de equipamento robusto construídos no laboratório. Para preparar os substratos foram submetidos a um tratamento de ultravioleta para permitir que os materiais depositados resistam ao desgaste por contato. Então construiu-se uma câmara para tratamento por radiação UV/ozônio, e, após a preparação, os substratos foram colocados em um forno com temperatura controlada e com atmosfera inerte. Este forno tubular também foi construído com o intuito da produção do MoS₂. Após os ensaios foi possível obter a formação de MoS₂ com a caracterização pelo MEV, EDS e DRX para análise e identificação dos materiais formados no substrato.

Palavras-chave: semicondutor bidimensional, filme fino, dissulfeto de molibdênio (MoS₂), deposição química de vapor (CVD).

Abstract: The first two-dimensional material discovered was graphene in 2004. From then on, studies were developed with other materials and one of the first semiconductors to be isolated was molybdenum disulfide, MoS₂. Unlike graphene, MoS₂ has an energy gap, and in monolayer form the gap goes from indirect to direct. This change results in high-brightness photoluminescence. Due to its high electrical and optical performance, MoS₂ (2D) has great potential for application in electronic devices and photoelectronic fields. There are several techniques to produce this material, and one of them is through the Chemical Vapor Deposition (CVD) method, which consists of the formation of crystals on the substrate, through atomic or molecular deposition, with the solid originating from a chemical reaction where the precursors are in the vapor phase. The objective of this work will be to synthesize and characterize MoS₂ using the CVD method, using a robust equipment system built in the laboratory. They were subjected to an ultraviolet treatment to prepare the substrates to allow the deposited materials to resist contact wear. A chamber was then built for UV/ozone radiation treatment, and, after preparation, the substrates were placed in a temperature-controlled oven with an inert atmosphere. This tubular furnace was also built with the aim of producing MoS₂. After the tests, it was possible to obtain the formation of MoS₂ with characterization by SEM, EDS and XRD for analysis and identification of the materials formed on the substrate.

Keywords: two-dimensional semiconductor, thin film, molybdenum disulfide (MoS₂), chemical vapor deposition (CVD).

Introduction

MoS₂ has excellent electronic behavior and mechanical properties. Research shows that it is a photothermal material with higher absorbance in the IR region than graphene oxide and gold nanorods (Zhu, 2018). Thus, it is possible to design suitable applications in biomedical, such as cancer therapy or drug delivery.

There are several methods of preparing the MoS₂ film. Common preparation methods include micromechanical exfoliation, lithium-ion intercalation, liquid-phase ultrasonography, and the chemical vapor deposition (CVD) method (Wu, 2013).

Among the different types of preparation, there is the CVD technique, which allows the growth of a thin film of nanostructured material on a relatively small substrate, in the order of centimeters, in addition to not having external contamination during deposition and there is the ease of cleaning of the materials used (Song, 2012).

The CVD technique is widely used for a variety of purposes. In industries, it is used from the coating of parts to replace human joints that are coated with a thin film making them biocompatible, to the coating of parts for engines (Pedersen, 2014). In the area of electronics, advances are as significant as in the construction of rechargeable batteries,

transistors, and solar cells, where thin films must be uniform (Ohring, 2002).

Due to MoS₂ being a promising two-dimensional semiconductor, this work is devoted to describing the construction of a CVD furnace and a UV chamber for substrate treatment and MoS₂ film growth aiming at the application of thermogenerators. Both the construction of the chamber and the oven aim at successful low-cost sample growth and at the production of a higher-performing semiconductor.

Material and Methods

Fused quartz glass discs with 99.99% level purity were chosen as a substrate. For the disk cleaning process, a digital ultrasound device was used for the substrate cleaning process. First, the discs were immersed in acetone and placed in the ultrasound tank. Through the sonication process, the substrates were left for 15 minutes to remove dirt such as dust. In sequence, they passed through an isopropyl bath and finally in deionized water. After this step, the substrates were dried with a high-purity nitrogen jet, thus properly sanitized for the next step.

To produce high quality thin film MoS₂ by the CVD technique is necessary good adhesion. For that, a surface treatment that leaves open or dangling bonds is necessary allowing the materials to resist wear due to

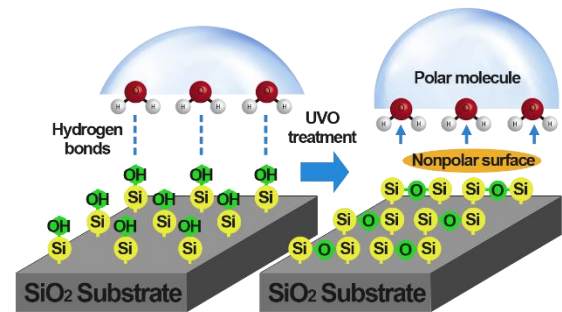
contact (LI, 2014). This research is carried out by exposing fused quartz glass discs to UV/Ozone rays (Uvo).

UVO treatment has been used to effectively remove surface contaminants from various materials (Kohli, 2019). Compared to other methods such as hydrofluoric solution and high velocity air blasts, UVO treatment generates little toxic or noxious gases and no residual liquid during the cleaning process. It can even produce nearly atomically clean surfaces. In addition to surface cleaning, UVO can also be used to modify the surface and improve the adhesion of the material to be deposited (Wang, 2017; Kimura, 2018; Wu, 2019).

The surface of quartz glass is mainly composed of silanol groups (-SiOH), which can oxidize in the presence of an ozone-rich atmosphere and form siloxane groups (-Si-O-Si-). The oxidation reaction can be seen in

Figure 1. Exposing quartz glass to UV rays can cause the breaking of some chemical bonds on the surface, resulting in the formation of free radical groups. These free radicals can then combine and form additional siloxane groups on the surface, increasing its density. These siloxane groups are naturally hydrophobic and contribute to quartz's low surface energy and therefore to its hydrophobicity (Zhuravlev, 2006; Owen, 2012; Ozçam, 2014; Schrader, 2018).

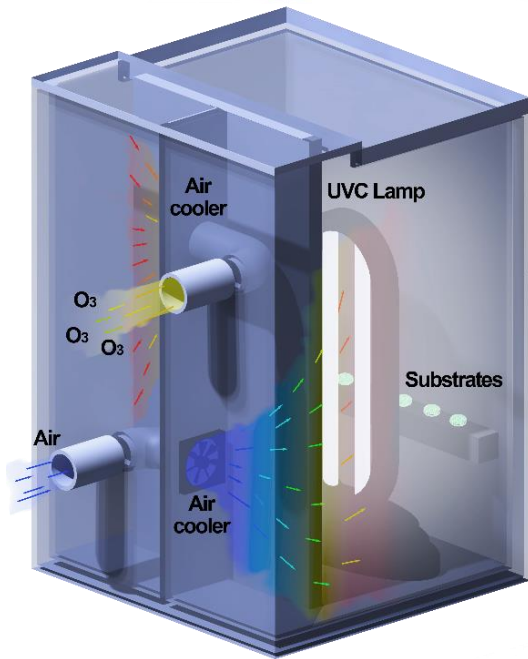
Figure 1 - Oxidation of substrate surface through UVO treatment.



UV radiation/ozone treatment is often used to improve the surface properties of quartz glass. During this process, ozone acts as a strong oxidant, accelerating the oxidation of silanol groups and the formation of siloxane groups on the surface. This contributes even more to the increase in hydrophobicity and can directly interfere with the surface quality of the sample (Zhuravlev, 2006; Owen, 2012; Ozçam, 2014; Schrader, 2018).

For the treatment of the substrates, a UVO chamber was manufactured (Figure 2) to block the rays emitted by the light source, adapted with an air cooler for air circulation, guaranteeing the elimination of the ozone formed during exposure to UV rays.

Figure 2 - UVO chamber for UV radiation treatment of substrates.

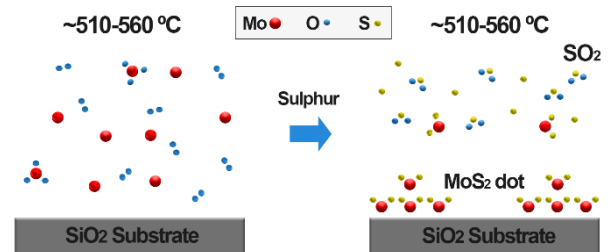


After surface treatment, the substrates are immediately inserted into the CVD oven for MoS₂ deposition. This oven is a tubular chemical vapor deposition furnace adapted for use as a CVD oven for the growth of MoS₂ thin films.

Basically, the chemical reactions that occur in the CVD oven use MoO₃ and sulfur are the precursor. They are placed at a specific position corresponding to temperature zones that vaporize them prior to combination and chemical reaction and subsequent drift towards the substrate by an inert gas. For this, the oven temperature is increased to 800 °C, first, the MoO₃ vapor is partially transferred by the high purity nitrogen carrier gas and the MoO₃ molecules are reduced to metallic Mo prior to binding to the substrate. In sequence, the sulfur is also vaporized and part of it reacts with oxygen, and part reaches the substrates and reacts with metallic Mo. So, the result is the

formation of MoS₂. The diagram of the MoS₂ growth mechanism can be seen in Figure 3.

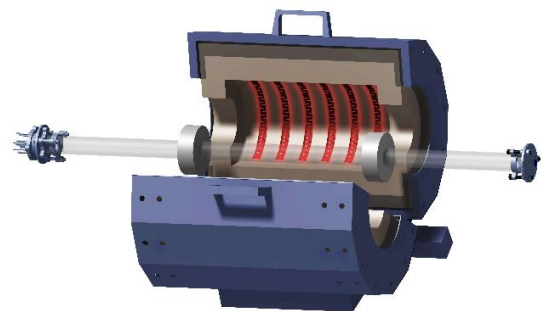
Figure 3 - Illustration of the MoS₂ growth mechanism on the substrate.



The oven reaction chamber is made up of a quartz glass tube inside, supported by a polygonal shape of stainless steel, see

Figure 4.

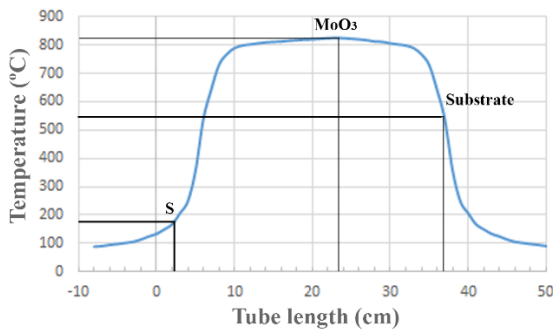
Figure 4 - Tubular oven used to prepare the MoS₂ growth.



Heating is done by metallic resistances mounted on the inner walls of the oven, supported by refractory molds. The tube is held in the oven by a fiberglass thermal tape. At each end of the tube, stainless steel rings were produced with openings for gas inlet and outlet and 3 perforations to accommodate the thermocouples. With these, it was possible to map and define temperature variations in relation to the length of the tube, see

Figure 5. The software used to control the ramp and temperature level was the same as used for the unmodified oven, i.e. Flycon by Flyeve.

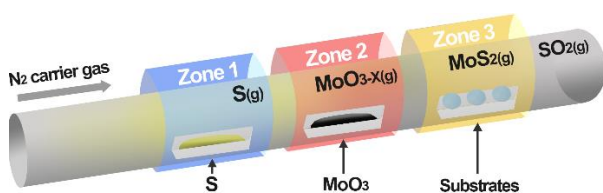
Figure 5 - Mapping of oven temperature and position distributions of each element.



In the experiment, the sulfur powder was placed in the low temperature zone on the left side of the tube furnace tube, the MoO_3 powder was placed in the high temperature zone in the middle of the tube, and the substrate on the right side of the tube. This scheme is represented by

Figure 6. The sulfur source, in the low temperature zone, was around 25 cm away from the molybdenum source in the high temperature zone, and the molybdenum source was 15 cm away from the substrate. Pure nitrogen gas flows from left to right in this scheme.

Figure 6 - Sketch of MoS_2 preparation by chemical vapor deposition (CVD).



Immediately after evacuating the tube with a mechanical pump, it is filled with high-purity nitrogen gas and allowed to flow at a constant rate for 5 min. The evacuation-fill processes are repeated three times to vent air and impurities from the tube furnace prior to allowing the flowing. After that, high purity nitrogen gas is introduced into the tube furnace, and when the pressure reaches 1.2 atm, the exhaust valve is opened and adjusted to make the pressure in the furnace greater than 1.0 atm. Then the oven is heated to a set temperature and held for a certain time. In the heating process, nitrogen gas is continuously introduced into the furnace. As an inert to the process gas, nitrogen gas is also the carrier medium for both sulfur vapor from the low zone to the high temperature zone and then to the substrate. At high temperatures, the molybdenum oxide vapor is reduced by the sulfur vapor. The produced gas compound reacted with the sulfur vapor to generate MoS_2 , which is deposited on the substrate to form MoS_2 nanocrystals. As the volume of gas in the tube shrinks with decreasing temperature during the cooling process, nitrogen gas needs to be supplied continuously until the temperature is completely reduced to room temperature to prevent outside air from entering the tube oven.

Results and Discussion

The effect of UVO exposure time on substrate surface performance was investigated by

detecting hydrophobicity and surface topography. Next, the film deposition condition was investigated and optimized for the control of parameters necessary for the formation of high-quality MoS₂ on the surface.

To investigate the hydrophobicity after the UVO treatments, the contact angles of water on the substrates were measured. Figure 7 shows the drops of water corresponding to the different exposure times and in Figure 8 the curves of the contact angles as a function of the treatment time. The contact angle is measured from the moment the drop remains constant. The contact angle increased from 4° to 27° when the UVO treatment time was up to 75 min. It is then observed that the hydrophobicity is increased through the chemical modification of the surface. It is believed that the siloxane groups induced by UVO treatments are hydrophobic, which increases the surface tension of the dispersion of pure water droplets.

Figure 7 - Drops of pure water deposited onto substrates treated by UVO on substrates for (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, and (f) 75 min.

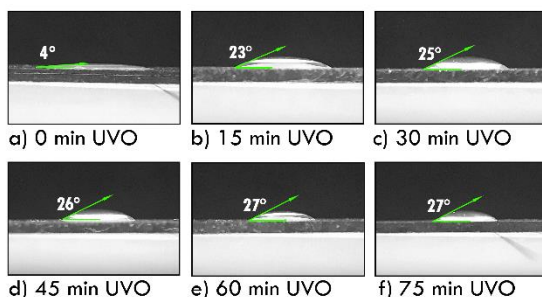
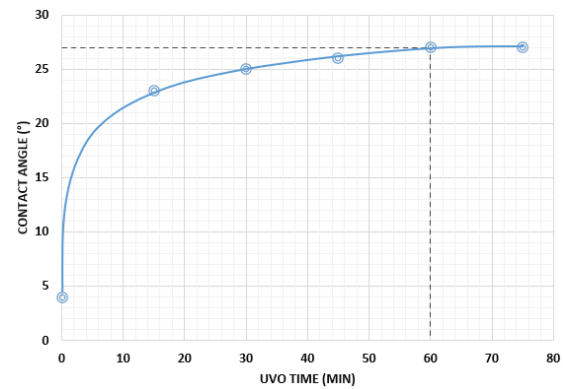


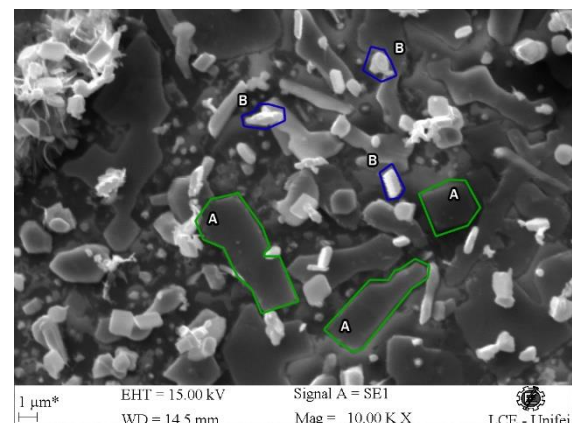
Figure 8 - Drop contact angles as a function of UVO treatment time.



Since the contact angle stops to increase, reaching 27° with the surface after an exposure time of 60 minutes, it was adopted for the treatment of the substrates. From this treatment, OH groups were created, forming a chemically active layer on the surface of the substrate, favoring the adhesion of subsequently deposited material.

Then, with the treatment finished, the substrates were allocated in the tubular furnace to allow a deposition of material on the surface for the formation of MoS₂. After manufacturing the compound, Scanning Electron Microscopy (SEM) analysis was performed and the micrograph of Figure 9 was obtained.

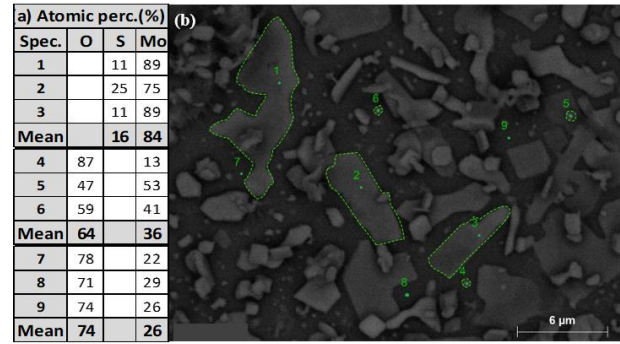
Figure 9 - Micrograph of MoS₂ obtained by SEM.



From Scanning Electron Microscope (SEM) micrographs it is observed that different types of structures are formed: by the letter A in the form of plates in the part close to the substrate with a dark tone, and by the letter B, on top of smaller dispersed particles with a lighter tone. To obtain the details of each type of particle identified, the Energy Dispersive X-ray Spectroscopy (EDS) analysis was carried out allows identification of the chemical elements present in the deposited samples. The technique consists of analyzing the modified wavelength emitted after the interaction between the electromagnetic radiation emitted by the equipment and the atomic structure of the elements.

In Figure 10, it is observed in (b) the micrograph of the MoS₂ sample, that it was possible to identify some plaques and small particles above the substrate. Then the selection of chosen points was subdivided into 3 groups: from 1 to 3 on top of the plates, from 4 to 6 on top of small particles, and from 7 to 9 on top of the substrate. It is observed in (a) the results of the identification of chemical elements in atomic percentage.

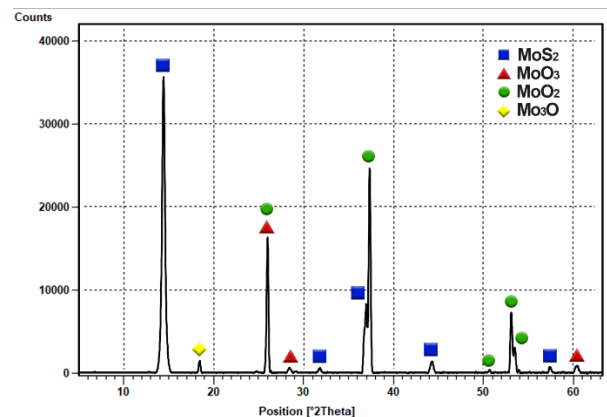
Figure 10 - Analysis of EDS obtained by SEM. In (a) the atomic percentage table of each identified element and in (b) the micrograph of the sample.



From the results obtained by EDS, for groups 1 to 3, it is observed that the compound formed has an atomic percentage equivalent to 5 parts of molybdenum to 1 of sulfur (Mo_{5x}S_x). For groups 4 to 6, an atomic percentage of approximately 1 part of molybdenum to 2 of oxygen (Mo_xO_{2x}). For the group from 7 to 9, it is observed that it presents an atomic percentage of approximately 1 part of molybdenum for 3 of oxygen (Mo_xO_{3x}).

Then, X-ray diffraction analysis (DRX) was performed to identify the deposited material. From the sets of peaks formed by the diffraction of the beams, the diffractogram of the analyzed material is obtained, Figure 11.

Figure 11 - X-ray diffractogram of the sample.



With the XRD results, it was possible to determine the presence of 4 types of materials. With the main component we have MoS₂, in

addition to identifying the oxides: MoO_3 , MoO_2 and Mo_3O .

Compared with the work of (Alves, 2022), who also used the CVD method, it generated many intermediate compounds, resulting in the formation of other types of materials: MoO_2 and MoOS_2 . Then, they had to carry out another resulfurization route to obtain the first fine flakes of MoS_2 , but at a low density on the substrate.

The formation of MoO_2 occurs at temperatures below 564°C . Despite introducing the substrates after this temperature to avoid the formation of this oxide, the presence of this compound in the sample was observed, although in small quantities. It is known that the decomposition of excess $\text{MoO}_3(\text{g})$ can form $\text{MoO}_2(\text{s})$. Therefore, the presence of MoO_2 may have occurred due to the high concentration of $\text{MoO}_3(\text{g})$ in the substrate region.

The presence of MoO_3 is also observed, which may have formed due to the concentration of precursor gases not being stoichiometrically balanced during the chemical reaction in the substrate region. If the evaporation rate of MoO_3 is much higher than that of S_2 , $\text{MoO}_3(\text{g})$ may not be completely reduced by $\text{S}_2(\text{g})$ in time, favoring the formation of MoO_3 on the substrate.

Conclusions

The construction of the entire robust system, even though it was built with laboratory equipment and recycled castings, enabled the growth of MoS_2 using the Chemical Vapor Deposition (CVD) method. This method proved to be quite complex, as it is necessary to have control of the various parameters that influence the process.

The sample was characterized by SEM to verify the different types and formats of deposited substances. Qualitatively, the sample underwent XRD analysis to identify the materials present in the substrate. It was noted that they generated many intermediate compounds. However, MoS_2 was found by XRD to be one of the main components formed.

So, the results were expected, with the formation of promising MoS_2 thin films that could be applied to the construction of new devices, such as thermogenerators.

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