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Production And Characterization Of Moo_3 Films For Photocatalytic Application In The Visible Region Of The Solar Spectrum

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RESUMO: A produção de hidrogênio por fotólise da água é uma boa alternativa para substituir o uso de combustível fóssil e atender a demanda energética global. Esse trabalho teve por objetivo obter filmes de MoO3 com capacidade de realizar a fotólise da água sob luz visível. O efeito da fração de oxigênio na mistura gasosa (O_2/Ar+O_2) sobre as fases formadas foi investigado. Os resultados de difração de raios x mostraram que os filmes depositados com 5% de O_2 eram majoritariamente monoclínicos, enquanto que os filmes depositados com fração de oxigênio a partir de 20% eram majoritariamente ortorrômicos. A análise de transmitância desses filmes mostrou um deslocamento no patamar de absorção fundamental, de 400 nm para 750 nm, com o decréscimo da fração de oxigênio, e um consequente decréscimo da banda proibida, de 3,20 eV para 1,51 eV, permitindo a absorção de luz na região visível do espectro solar. Além disso, as imagens de microscopia de força atômica mostraram que a rugosidade e a área superficial aumentaram com o decréscimo da fração de oxigênio. Esses resultados indicam que a fração de oxigênio na mistura gasosa pode ser usada como parâmetro controlador das propriedades óticas, microestruturais e de superfície do material.

PALAVRAS-CHAVE: trióxido de molibdênio, propriedades óticas, microestrutura, fotólise, pulverização catódica.

ABSTRACT: Hydrogen production from photocatalytic water splitting is a clean and renewable alternative to replace fossil fuels and meet the global demand for energy. Currently. The objective of this work is to obtain thin films of MoO3 for dissociating water under visible light. The effect of the oxygen fraction in the gas mixture (O2/Ar+O2) on the crystalline phases was investigated. X-ray diffraction results showed that films with 5%O2 were mostly monoclinic, while films deposited with oxygen fractions above 20% were mostly orthorhombic. Transmittance analyzes showed a change in the fundamental absorption edge, from 400 nm to 750 nm, as the oxygen fraction decreased. The band gap decreased from 3.20 eV to 1.51 eV, favoring visible light absorption. Atomic force microscopy images showed that the roughness and surface area increased as the oxygen fraction decreased. These results indicate that the fraction of oxygen can be used as a control parameter for the microstructural, optical and surface properties of the material.

KEYWORDS: molybdenum trioxide, optical properties, microstructure, photolysis, sputtering.

1. Introduction

One of the biggest technological challenges in the near future is to meet the energy demand, because with the continuous increase in the global population there is an increase in energy consumption. This increase in consumption linked to fossil fuel energy sources accelerated global warming. A renewable and clean alternative to replace fossil fuels is hydrogen, since it can be produced from the separation of water using also renewable energy, such as solar [1].

The photocatalysis of water for the production of hydrogen can occur from the use of semiconductors. Several semiconductors such as titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten trioxide (WO_3), cadmium sulfide (CdS), among others, have already been tested as photocatalysts, and so far the most accepted is TiO_2, as it is a low-cost, non-toxic and water-stable material

However, due to the high bandgap value (3.2 eV), this material absorbs in the ultraviolet region of the light spectrum, therefore, it is not possible to use it to separate water in the visible region of the spectrum.

Furthermore, the rate of recombination of electron/hole pairs is very high in this material, which limits its application as a photocatalyst. [2]

According to the literature, semiconductor oxides of transition metals, such as molybdenum oxides (Mo_xO_y), have shown promise in different applications, such as: gas sensors, catalysis, lithium batteries, organic light emitting diodes, organic solar cells and electrochromic devices. [3, 4] This diversity of applications is possible due to the possibility of stoichiometry variation, the optical and electrical properties and the high stability in aqueous media. [5]

MoO_3 can be fabricated as an n-type or insulating semiconductor and exhibits polymorphism and may be orthorhombic (α-MoO_3), monoclinic (β-MoO_3) or hexagonal (h-MoO_3). In addition, the oxide can also present sub-stoichiometries with different Mo oxidation states and crystalline structures [6, 7], such as: MoO_2 (tetragonal, monoclinic and hexagonal), Mo_4O_{11} (monoclinic and orthorhombic), Mo_5O_{14} (tetragonal), Mo_8O_{23} (monoclinic) and Mo_9O_{26} (monoclinic and triclinic).

Due to the different oxidation states of molybdenum, the Mo_xO_y has a wide range of bandgap values ranging from 0.92 to 3.2 eV. Thus, MoO_2 presents a bandgap of 0.92 eV [8], while MoO_3 has a band that varies between 2.8 and 3.2 eV [3, 4, 9], which gives it high transmittance in the visible spectrum.

Oxygen deficiency can be caused by defects in the material, such as vacancies, dislocations, stacking faults, and grain boundaries, which affect local oxygen binding. [3, 4] In addition, oxygen deficiency also controls the electrical properties of the oxide.

Thin films of molybdenum oxides can be prepared by several techniques, such as: thermal evaporation, sputtering, pulsed laser deposition, among others. [4, 10, 11] The sputtering technique allows the production of films at low temperatures and the control of the oxygen concentration in the thin film, varying the deposition parameters. [12]

The crystalline phases of the molybdenum oxide films deposited by sputtering depend on the deposition parameters, including the composition of the gaseous mixture ($Ar+O_2$), in case the deposition is reactive.

The control of the phases present in Mo_xO_y films is important for application as a photocatalytic semiconductor. A semiconductor to be used in the photolysis of water needs to have the energy of the lowest unoccupied molecular orbital (LUMO) greater than the reduction potential of water and the energy of the highest occupied molecular orbital (HOMO) less than the potential of oxidation.

However, not all semiconductors, specifically materials with a response in the visible light region, meet this requirement, that is, they do not have the gap band and the HOMO and LUMO necessary for the dissociation of water molecules. For this reason, a photocatalytic system based on photosynthesis known as the Z scheme has attracted considerable attention. This scheme consists of combining two semiconductors, one that will absorb light in the visible region of the solar spectrum and another that will meet the requirement for the dissociation of water molecules. [13-15]

Thus, the purpose of this work is to optimize the processing of MoO_3 thin films obtained by reactive sputtering, in order to obtain the appropriate phases for photocatalysis of water in the visible region. The effect of the composition of the gas mixture ($Ar+O_2$) in the formed phases and, consequently, in the optical, microstructural and morphological properties of the films will be analyzed.

2. Materials And Methods

The MoO_3 films were deposited on soda lime glass substrates using the reactive sputtering technique with radiofrequency (RF) and magnets, in equipment designed at the Thin Films Laboratory of the Instituto Militar de Engenharia. A 3" diameter molybdenum target from AJA International was used. Substrate temperature and deposition pressure were maintained at 350 °C and 5x10-3 Torr, respectively. The fraction of oxygen in the gaseous mixture ($O_2/Ar+O_2$) varied between 5 and 70%.

This ratio was controlled by oxygen and argon fluxes. The working power was 165 W, except in the sample deposited with 5%, in which it was 125 W, as it

was found that at higher powers the deposited material was metallic molybdenum. These values were adopted based on results obtained in previous studies [16]. The thickness of the films was maintained at around 500 nm.

The microstructural characterization was carried out in an x-ray diffractometer, model D8 Discover by Bruker, with a copper source, voltage of 40 kV and current of 40 mA, with the Bragg-Brentano geometry. The surface characterization was carried out in an atomic force microscope model N-TEGRA Spectra from MT-MDT and the optical characterization was carried out in a spectrophotometer, model Cary 5000 from Varian, in the range of 200 – 800 nm.

3. Results And Discussion

The transmittance spectra of MoO_3 films deposited in different fractions of oxygen in the gas mixture can be seen in **figure 1**. It is observed that films grown with larger amounts of O_2 present a fundamental absorption plateau between 400 and 500 nm and, therefore, do not absorb most of the visible spectrum. The films deposited with the smallest fraction of O_2 (5%) present a fundamental absorption level close to 750 nm, which allows them to absorb a large part of the visible light.

The change in the absorption region as a function of the amount of oxygen in the gaseous mixture is related to the crystalline structure of the films and suggests that films deposited with O_2 above 5% are formed by the α-MoO_3 orthorhombic phase. This hypothesis is supported by data from the literature [16,17] which show that, for films deposited by reactive sputtering above 350 ºC and with O_2 fractions above 10%, the α-MoO_3 orthorhombic phase is preferably formed, presenting an absorption plateau around 400 nm.

The forbidden band of the films was determined from a Tauc graph, considering indirect transition. [16] The bandgap values varied between 1.5 eV and 3.2 eV, as shown in **table 1,** being within the range reported in the literature for the α-MoO_3 crystalline phases (eg., 3,3 eV [19]) and for the mixture of sub-stoichiometric oxides MoO_{3-x} and MoO_2 (eg.,1,5 eV [3,4,18]).

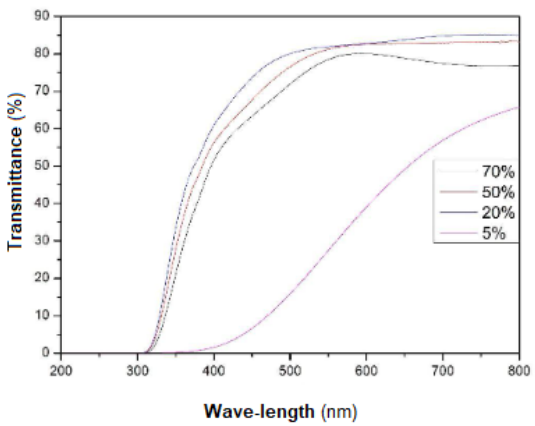
There is a considerable increase in the gap band of the films deposited with higher fractions of O_2 in relation to that deposited with 5% of O_2. This behavior, already identified in **figure 1**, is related to the formation of the α-MoO_3 orthorhombic phase in higher oxygen fractions. In addition to the growth temperature, the formation of phases, α-MoO_3 or β-MoO_3, also depends on the fraction of oxygen present in the MoO_3 growth process [19].

The β-MoO_3 phase has a greater capacity to stabilize oxygen defects and, therefore, would be preferentially formed in processes with small fractions of oxygen. The α-MoO_3 phase is preferentially formed in higher fractions of oxygen because a higher oxygen pressure will increase the probability of "curing" the β and, consequently, will increase the probability of formation of the phase α. Furthermore, it is expected that the films deposited in higher fractions of oxygen have a composition closer to the stoichiometric one.

The gap band variation can also be attributed to the variation in the concentration of oxygen vacancies [3]. These vacancies are created during the deposition of MoO_3 films, which create fault states and narrow the bandgap. [3] These defects are responsible for the formation of localized states. When the atmosphere is rich in oxygen, these vacancies disappear and there is a clear deviation from the bandgap towards regions of higher energies.

Therefore, there is the ability to obtain a shift in the fundamental absorption level, from the ultraviolet region to the visible region, varying the fraction of oxygen, enabling the production of the "Z scheme" junction with a film that will absorb in the visible and another, with the largest bandgap, that will perform the water breakdown. [20, 21] .

Fig. 1 – Transmittance of MoO3 films deposited by sputtering with different fractions of oxygen in the gas mixture



Tab. 1 – Gap band of MoO3 films deposited by sputtering with different fractions of oxygen in the gas mixture.

O_2 PRESSURE	Eg (eV)
5%	1,51
20%	3,20
50%	2,96
70%	2,96

The effect of the oxygen fraction on the phases formed in the deposited films can be seen in the x-ray diffractograms in **figure 2**. The diffractograms show that, regardless of the oxygen fraction, all films are crystalline.

The diffractogram of MoO_3 films manufactured with 5% O2 shows films mostly in the β-MoO_3 monoclinic phase, with the presence of small amounts of sub-stoichiometric oxides, while the samples produced above this percentage of oxygen are almost exclusively formed by the α-MoO_3 orthorhombic phase. The forms used for identification were PDF 85-2405, for the β phase, and PDF 35-0609, for the α phase. It is observed that the increase in the oxygen fraction favored the growth of the α-MoO_3 stable phase, as reported in the literature. [3, 4, 16, 19]

Small amounts of molybdenum oxides with formula Mo_yO_x were identified with x/y ≈ 2.80. These oxides were identified by the EVA software as: Mo_4O_{11}, orthorhombic, Mo_5O_{14}, monoclinic; Mo_8O_{23}, monoclinic. Thus, for films formed with 5% oxygen, the presence of sub-stoichiometric molybdenum oxides is verified with the monoclinic structure, the same as the stable phase β-MoO_3, while for fractions of oxygen from 20%, it is observed, in a very small amount, the presence of the sub-stoichiometric oxide Mo_4O_{11} with the orthorhombic structure, the same as the α-MoO_3 stable phase.

It is reported in the literature that small fractions of oxygen favor the formation of sub-stoichiometric films [3,20], what was expected for the film deposited at 5%. However, films deposited with 70% O_2 still showed a small amount of the oxide Mo_4O_{11}, that is, this percentage of O_2 was not sufficient for the production of stoichiometric molybdenum oxide.

Therefore, the lowest fraction of oxygen (5%) was sufficient for the production of mostly monoclinic films, while higher fractions of oxygen were sufficient for the production of almost exclusively orthorhombic films.

These results show the possibility of manufacturing a "Z-scheme" semiconductor junction, β-MoO_3-x/α-MoO_3, it suffices to promote, during the deposition of the films, the phase transition at the same temperature and at the same working pressure, just varying the fraction of oxygen during the deposition.

In this scheme, the film deposited with the smallest fraction of oxygen would absorb light in the visible region of the solar spectrum, while the film deposited with 20% oxygen, which presented the largest bandgap, would be responsible for the dissociation reaction of water molecules. A cyclic voltammetry analysis will be able to inform the position of the HOMO and LUMO energy levels of each film and thus confirm if the film deposited with the highest band gap has the necessary requirement for photolysis.

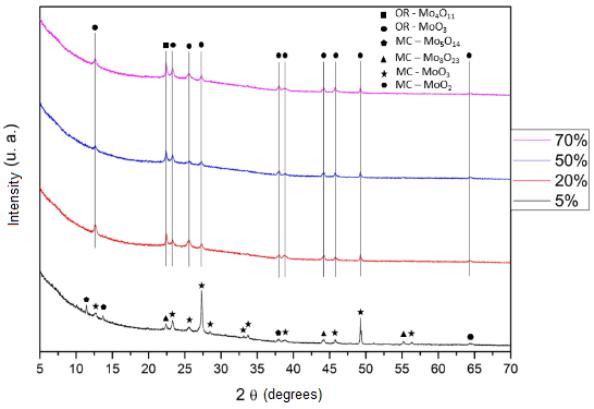


Fig. 2 – X-ray diffractogram of MoO3 films deposited by sputtering with different fractions of oxygen in the gas mixture.

The effect of the fraction of oxygen on the surface of the films can be seen in the atomic force microscopy (AFM) images in **figure 3**. The images show that there is a decrease in the roughness of the films with the increase in the oxygen fraction, as can be seen in **table 2**.

This behavior can be attributed to the deposition power. Image a) represents the film deposited with 5% oxygen, which was added at the lowest power (125 W),

while the others represent the films that were deposited at the highest power (165 W). In sputtering, the energy with which the atoms arrive at the substrate can be derived from the deposition power and the temperature of the substrate. So, for the film deposited at the lowest power, the atoms adsorbed on the surface of the substrate did not have enough energy to organize themselves in an orderly manner, resulting in disorderly and rough growth.

On the other hand, the adsorbed atoms from a higher deposition power have enough energy for an orderly growth, resulting in a smooth surface. Other authors reported similar growth on MoO_3 films deposited at 125 W power, resulting in a rough surface, as shown in **figura 3.a**) [16]

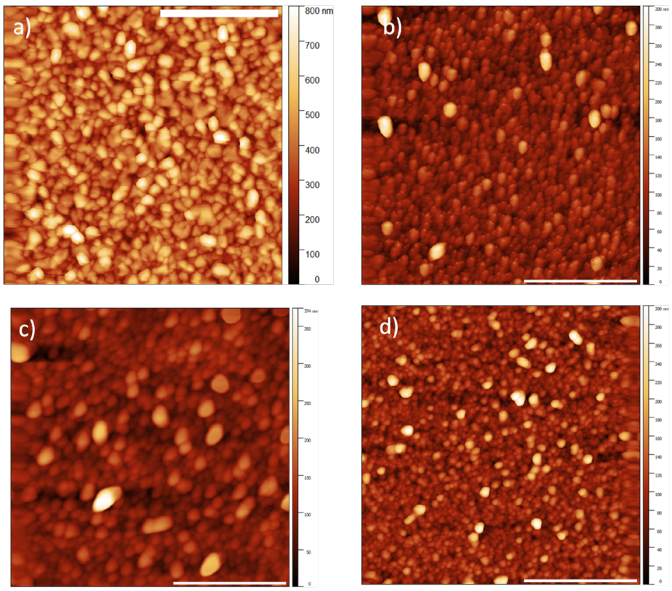
Mean square roughness values varied between 106.9 nm and 28.6 nm, as shown in **table 2**. The film deposited with 5% showed the highest roughness, 106.9 nm, a value higher than that reported in the literature for MoO_3 deposited by sputtering. [22, 23] Thus, the low transmittance shown in **figura 1** can be attributed to the greater roughness of the film deposited with 5% O_2.

Although this film is used only for the absorption of visible light, this high roughness can be detrimental to the production of the Z-scheme junction, as it can add points of recombination of charge carriers at the interface between the two films. Furthermore, roughness can serve as a center of light scattering, promoting diffuse reflection and multiple reflections on the surface. [22]

The films deposited from 20% showed a roughness within the range reported in the literature [22, 23] and the increase in the fraction of oxygen was not enough to increase the roughness of the film that will be responsible for breaking the water.

It is also interesting to note that the grains of the MoO_3 films deposited with 5% O_2 grew with a spherical morphology, which favors the increase in surface area.

Fig. 3 – AFM image of MoO3 films deposited by sputtering with different fractions of oxygen in the gas mixture: a) 5%; b) 20%; c) 50%; d) 70%



Tab. 2 – Root mean square roughness of MoO3 films deposited by sputtering with different fractions of oxygen in the gas mixture.

O_2 PRESSURE	Mean Square Roughness (nm)
5%	106,9
20%	28,6
50%	35,6
70%	33,6

From the AFM results it was possible to determine the surface area of the films, shown in **figure 4**. It can be noted that the film deposited with the lowest fraction of oxygen has the largest surface area, according to the values obtained for mean square roughness. This larger surface area can be attributed to the spherical morphology of the grains, as discussed earlier. The 5% film is the best in surface area, but as it will not break water, this area can be detrimental to the "Z-scheme" joint. On the other hand, the films deposited with 20% and 70% have a surface area around 110 μm^2, indicating that mostly orthorhombic films have a smaller surface area.

The water dissociation reaction is a reaction that occurs on the surface of the material and, therefore, one of the characteristics that optimize this reaction is the

surface area of the photocatalytic semiconductor. Because of this, materials that have a large surface area are sought, since the greater the surface area, the greater the interaction between the semiconductor and water. [24, 25] The films deposited with 20% and 70%, which presented the largest surface area, among the orthorhombic ones, will be investigated regarding the HOMO and LUMO energy levels, as well as the photocatalytic efficiency.

The presented results show that films deposited with 5% O_2 are promising for absorbing sunlight, while films deposited with 20% and 70% O_2 are promising for separating water. Additional analyzes, such as cyclic voltammetry and photocatalysis reaction rate, will be performed to confirm this hypothesis.

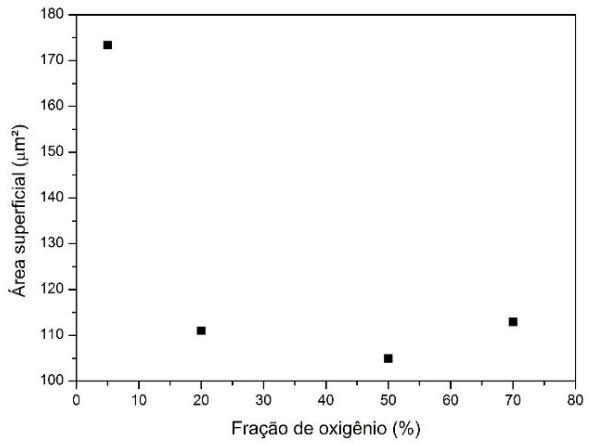


Fig. 4 – Surface area of MoO3 films deposited by sputtering with different fractions of oxygen in the gas mixture.

4. Conclusion

MoO3 films were deposited by RF-reactive sputtering in different oxygen fractions. The films deposited with 5% O_2 are mostly formed by the β-MoO_3 monoclinic phase with a gap of 1.51 eV. The α-MoO_3 orthorhombic phase was obtained for films deposited from 20% O_2, with bandgap ranging from 2.96 to 3.20 eV. There was also an increase in the roughness of the films and in the surface area with a decrease in the oxygen fraction.

The results showed that the oxygen fraction can be used as a parameter to control the crystalline structure of the films, the surface morphology and the level of optical absorption. In order to manufacture a Z-scheme heterojunction, the films deposited with 5%, which are ideal for absorbing visible radiation, and the films deposited with 20% and 70% O_2, which are promising for separating water, will be investigated for photocatalytic efficiency and location of HOMO and LUMO energy levels.

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