Video Article

Niobium Oxide Films Deposited by Reactive Sputtering: Effect of Oxygen Flow Rate

Silvia L. Fernandes[1], Lucas J. Affonço[2], Roberto A. R. Junior[2], José H. D. da Silva[2], Elson Longo[1], Carlos F. de O. Graeff[2]

[1]Chemistry Department, Federal University of São Carlos (UFSCAR)
[2]Physics Department, School of Sciences, São Paulo State University (UNESP)

Correspondence to: Silvia L. Fernandes at sy.fernandes@hotmail.com

URL: https://www.jove.com/video/59929
DOI: doi:10.3791/59929

Keywords: Chemistry, Issue 151, niobium oxide film, reactive sputtering, compact films, electron transport layer, conductivity, perovskite solar cell

Date Published: 9/28/2019

Citation: Fernandes, S.L., Affonço, L.J., Junior, R.A., da Silva, J.H., Longo, E., Graeff, C.F. Niobium Oxide Films Deposited by Reactive Sputtering: Effect of Oxygen Flow Rate. *J. Vis. Exp.* (151), e59929, doi:10.3791/59929 (2019).

Abstract

Reactive sputtering is a versatile technique used to form compact films with excellent homogeneity. In addition, it allows easy control over deposition parameters such as gas flow rate that results in changes on composition and thus in the film required properties. In this report, reactive sputtering is used to deposit niobium oxide films. A niobium target is used as metal source and different oxygen flow rates to deposit niobium oxide films. The oxygen flow rate was changed from 3 to 10 sccm. The films deposited under low oxygen flow rates show higher electrical conductivity and provide better perovskite solar cells when used as electron transport layer.

Video Link

The video component of this article can be found at https://www.jove.com/video/59929/

Introduction

The sputtering technique is widely used to deposit high-quality films. Its main application is in the semiconductor industry, although it is also used in surface coating for improvement in mechanical properties, and reflective layers[1]. The main advantage of sputtering is the possibility to deposit different materials over different substrates; the good reproducibility and control over the deposition parameters. The sputtering technique allows deposition of homogeneous films, with good adhesion over large areas and at low-cost when compared with other deposition methods like chemical vapor deposition (CVD), molecular beam epitaxy (MBE) and atomic layer deposition (ALD)[1,2]. Commonly, semiconductor films deposited by sputtering are amorphous or polycrystalline, however, there are some reports on epitaxial growth by sputtering[3,4]. Nevertheless, the sputtering process is highly complex and the range of the parameter is wide[5], so in order to achieve high-quality films, a good comprehension of the process and parameter optimization is necessary for each material.

There are several articles reporting on the deposition of niobium oxide films by sputtering, as well as niobium nitride[6] and niobium carbide[7]. Among Nb-oxides, niobium pentoxide (Nb_2O_5) is a transparent, air-stable and water-insoluble material that exhibits extensive polymorphism. It is an n-type semiconductor with band gap values ranging from 3.1 to 5.3 eV, giving these oxides a wide range of applications[8,9,10,11,12,13,14,15,16,17,18,19]. Nb_2O_5 has attracted considerable attention as a promising material to be used in perovskite solar cells due to its comparable electron injection efficiency and better chemical stability compared to titanium dioxide (TiO_2). In addition, the band gap of Nb_2O_5 could improve the open-circuit voltage (V_{oc}) of the cells[14].

In this work, Nb_2O_5 was deposited by reactive sputtering under different oxygen flow rates. At low oxygen flow rates, the conductivity of the films were increased without making use of doping, which introduces impurities on the system. These films were used as electron transport layer in perovskite solar cells improving the performance of these cells. It was found that decreasing the amount of oxygen induces the formation of oxygen vacancies, which increases the conductivity of the films leading to solar cells with better efficiency.

Protocol

1. Etching and cleaning the substrate

1. Using a glass cutting system, form 2.5 x 2.5 cm substrates of fluoride thin oxide (FTO).
2. Protect part of the substrate surface with a thermal tape leaving 0.5 cm of one side exposed.
3. Deposit a small amount of zinc powder (enough to cover the area to be etched) on the top of the exposed FTO and drop concentrated hydrochloric acid (HCl) on the zinc powder slowly until all zinc powder is consumed by the reaction. Immediately after, rinse the substrate with deionized (DI) water.
   CAUTION: Hydrogen gas in abundance is generated from zinc and HCl reaction.

4. Remove the tape and wash with DI water and soap using a small brush.
   NOTE: The brush helps to remove some residual glue from the tape.
5. Leave the etched substrate in a soap solution (50% in water) and keep it for 15 min in an ultrasonicate bath. Then, sonicate for 15 min in DI water (2 times), followed by 10 more min in acetone and finally 10 min in isopropyl alcohol. Dry the substrate with nitrogen gas.

2. Deposition of niobium oxide films

1. Fix the substrate through a shadow mask protecting 0.5 cm of both sides.
   NOTE: On the side where the FTO was etched, it is important to certify that the FTO is covered in order to prevent short circuits when building the cell.
2. Introduce the substrate into the sputtering chamber and seal the chamber.
3. Start the mechanic pump. In the first 10 min, change the 3-way valve into roughing position to heat its oil and release water to improve the pumping. The primary pump works alone until the pressure is 6 x 10^{-2} Torr.
4. Change the 3-way valve to backing position, and turn the turbo molecular pump on. Once the molecular pump is started, open the gate valve at the vacuum pump entry. Deposition starts when the pressure reaches 3 x 10^{-6} torr.
   NOTE: Before starting the molecular pump, the primary vacuum should be better than 6 x 10^{-2} torr, however, not higher than 5 x 10^{-2} torr in order to prevent contaminating the chamber with pump oil.
5. When the vacuum reaches 5 x 10^{-5} torr, open the water cooler system and turn on the substrate heating system. Set the temperature at 500 °C. Increase the temperature slowly, 100 °C every 5 min until it reaches the desired value.
6. Set the gases parameters to be used in the deposition: argon of 40 sccm and oxygen of 3 to 10 sccm.
   NOTE: The oxygen flow rate was varied in each deposition: 3, 3.5, 4 and 10 sccm. Oxygen reacts with niobium forming niobium oxide.
7. Introduce argon onto the chamber, and set the pressure to 5 x 10^{-3} torr and the radio frequency (RF) to 120 W. Turn the RF on and tune using the impedance matching box. In case the plasma does not start, increase the pressure slowly until it reaches 2 x 10^{-2} Torr. In this pressure, the plasma should start. Set the pressure using a gate valve that can be opened or closed to change the pumping rate.
8. Keep the plasma at 120 W for 10 min to clean the niobium target removing any oxide layer present in its surface.
   NOTE: While cleaning the target, the substrate shutter is kept closed to protect the substrate from any material deposition.
9. Introduce oxygen into the chamber, after stabilization, set the radio frequency power to 240 W and open the substrate shutter. Deposition starts. Set the deposition time to have a final thickness of 100 nm based on previous studies that determined the deposition rate. For each deposition condition a different deposition rate is expected, so the deposition time does also differ.
10. Once the deposition time is completed, close the shutter immediately, turn the RF off, the close the gases and decrease the substrate temperature to room temperature.
11. As the substrate temperature reaches room temperature, introduce air to reestablish the ambient pressure and open the chamber..
    NOTE: Generally, the system takes 4 h to reach a temperature of 40 °C.

3. Constructing the solar cells

1. Preparing the solutions used to construct the devices
   1. TiO_2 paste solution: Mix 150 mg of TiO_2 paste in 1 mL of DI water. Stir it for 1 day before use.
      NOTE: Keep the suspension stirring even when you are not using it to be sure that the suspension is always homogeneous.
   2. Prepare the lead iodide solution (PbI_2) by mixing 420 mg of PbI_2 in 1 mL of anhydrous dimethylformamide. Use only anhydrous solvents.
   3. Prepare the methylammonium iodide (CH_3NH_3I) solution by adding 8 mg of CH_3NH_3I in 1 mL of isopropyl alcohol (IPA).
      NOTE: The water content in IPA must be less than 0.0005%.

2. Deposit TiO_2 mesoporous layer on top of the niobium oxide layer using a spin coater at 4,000 rpm for 30 s.
3. Put the substrate on the oven following the steps: 270 °C for 30 min; 370 °C for 30 min and 500 °C for 1 h. Wait until the oven reaches room temperature and remove the substrate.
   NOTE: The heat treatment decomposes the organic part of the paste leaving a porous layer over the film.
4. Deposit two layers of PbI_2 on top of the TiO_2 mesoporous using a spin coater at 6,000 rpm for 90 s and after each deposition put the substrate in a hot plate at 70 °C for 10 min.
   NOTE: The PbI_2 deposition must be inside a glove box filled with pure nitrogen or argon and with controlled atmosphere (water and oxygen < 0.1 ppm).
5. Deposit the CH_3NH_3I solution. Drop 0.3 mL of CH_3NH_3I solution onto PbI_2, wait 20 s and then spin at 4,000 rpm for 30 s. Put the substrate on a hot plate at 100 °C for 10 min.
   NOTE: The CH_3NH_3I deposition must be inside a glove box. The total amount of CH_3NH_3I solution must be dropped quickly in only one step.
6. Deposit Spiro-OMeTAD solution on top of the perovskite layer by spin coating at 4,000 rpm for 30 s. Leave the substrate in an oxygen atmosphere overnight.
   NOTE: The Spiro-OMeTAD deposition must be inside of a glove box. After the deposition, it is important to leave the substrate overnight in an oxygen atmosphere in order to oxidize the Spiro- OMeTAD increasing its conductivity.
7. Evaporate 70 nm of gold contact using a shadow mask at a rate of 0.2 A/s until 5 nm is reached and then increase the rate to 1 A/s.
   NOTE: It is important to use a slow rate at the beginning to prevent gold diffusion through the cell.

Representative Results

In the sputtering system, the deposition rate is strongly influenced by the oxygen flow rate. The deposition rate decreases when the oxygen flow is increased. Considering the present conditions of the target area used and plasma power, it is observed that from 3 to 4 sccm there is an expressive decrease on the deposition rate, however, when the oxygen is increased from 4 to 10 sccm it becomes less pronounced. In the regime of 3 sccm the deposition rate is 1.1 nm/s, decreasing abruptly to 0.1 nm/s for 10 sccm as seen in **Figure 1**.

The niobium oxide phase formed is dependent on the oxygen flow rate. For flows less than 3 sccm, niobium dioxide (NbO_2) is the main phase formed. For flows higher than 3.5 sccm the oxygen amount is too high to originate NbO_2, instead, Nb_2O_5 is observed as the main phase (**Figure 2**). Electron microscopy images (**Figure 2**) show the nanometric spherical particles of the films deposited at 3.5, 4 and 10 sccm. In contrast, the film deposited at 3 sccm shows sheets shape particles.

The films deposited by reactive sputtering in different oxygen flow rates show different electrical properties. The conductivity of the films increases when less oxygen is used, 3 sccm or less. Increasing the oxygen flow rate to 3.5, 4 and 10 sccm, a decrease in the conductivity is observed (**Figure 3A,B**). This represents a simple and easy way to increase the conductivity of oxide films by adjusting the flux of oxygen during film deposition.

The niobium oxide films deposited by sputtering were used as electron transport layer (ETL) in perovskite solar cells. For these solar cells, the film deposited at 3 sccm was not used because transparency is essential for ETLs. The performance of the solar cells also depends on the niobium oxide used (**Figure 4**). The cell made with the films deposited at 3.5 sccm has the best performance with the highest short-circuit current, a clear influence of the ETL film's properties on the final performance of the cells.

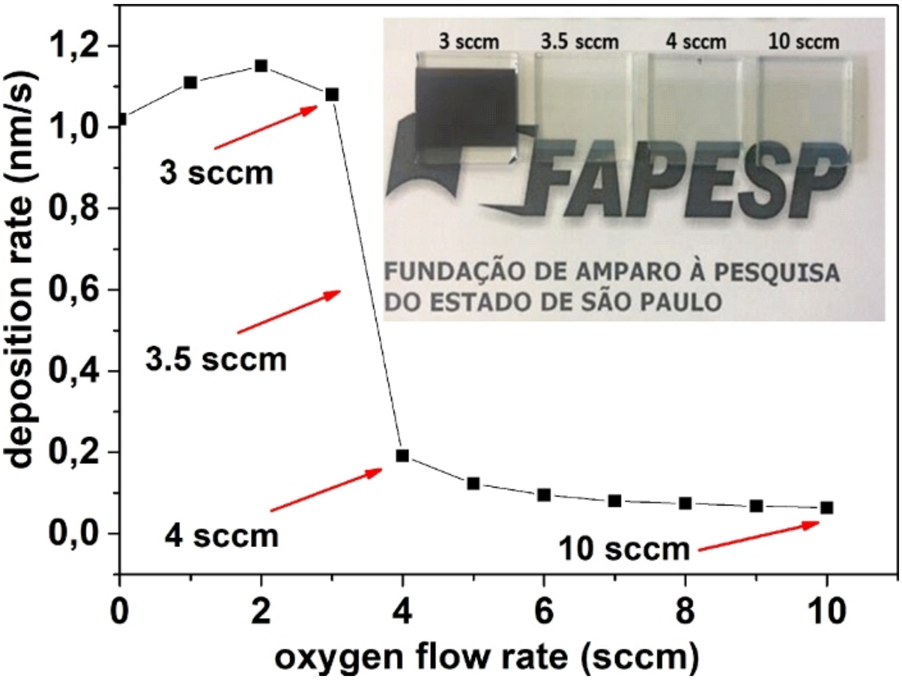

Figure 1: Deposition rate as a function of the oxygen flow rate during niobium oxide films deposition.
Images of the oxide films surfaces are shown as insets. This figure has been modified from Fernandes et al.[20]. Please click here to view a larger version of this figure.

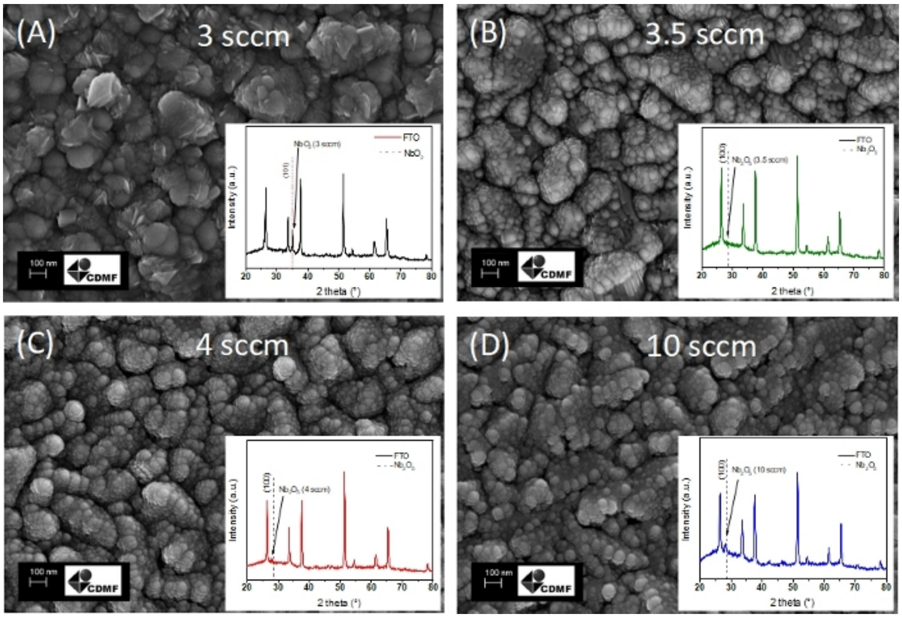

Figure 2: Electron microscopy images and X-ray difractograms of niobium oxide films deposited under different oxygens flow rates, 3 sccm (A), 3.5 sccm (B), 4 sccm (C) and 10 sccm (D).
The main NbO_2 (JCPDS #82-1142) and Nb_2O_5 (JCPDS #28-317) peaks are indicated. The other peaks are referred to FTO. This figure has been modified from Fernandes et al.[20]. Please click here to view a larger version of this figure.

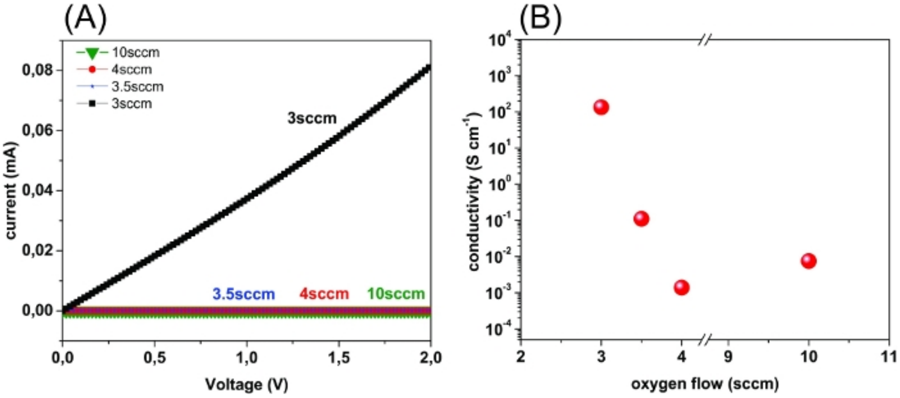

Figure 3: Current vs voltage of diferent niobium oxide films (A), and corresponding conductivity (B).
This figure has been modified from Fernandes et al.[20]. Please click here to view a larger version of this figure.

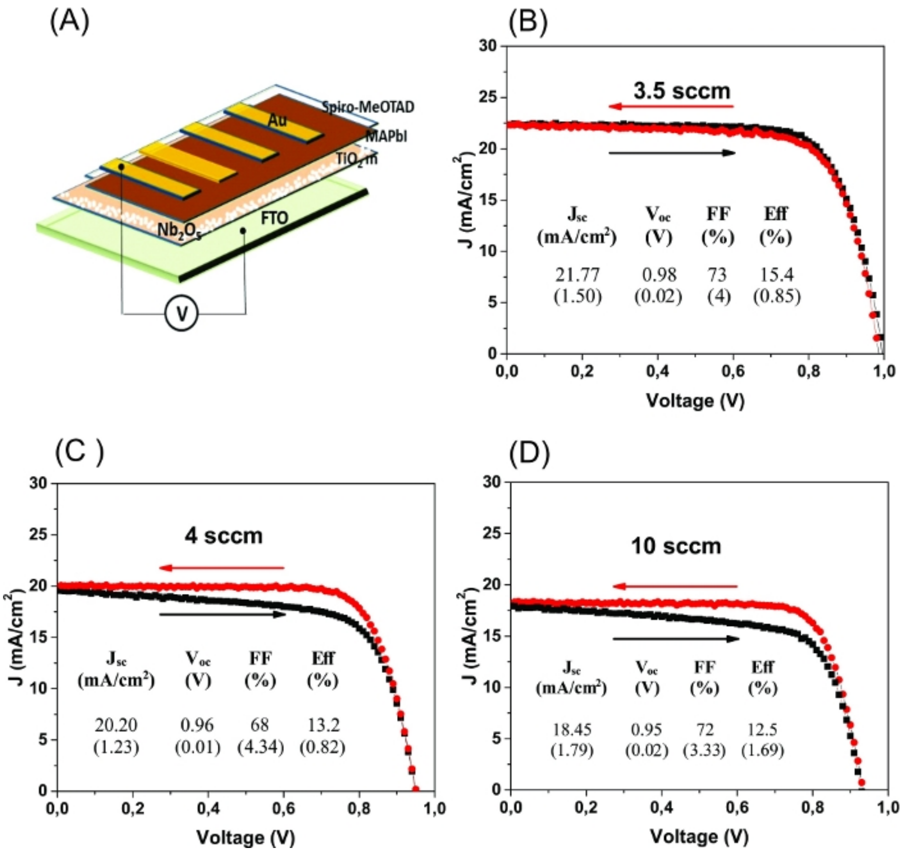

Figure 4: Schematic architecture of the solar cell devices (A), J-V curves of the perovskites solar cells using niobium oxide films deposited at different oxygen flow rate, 3.5 sccm (B), 4 sccm (C) and 10 sccm (D).
This figure has been modified from Fernandes et al.[20]. Please click here to view a larger version of this figure.

Discussion

The niobium oxide films prepared in this work was used as electron transport layer in perovskite solar cells. The most important characteristic required for an electron transport layer is to prevent recombination, blocking holes and transferring efficiently electrons.

In this respect the use of reactive sputtering technique is advantageous since it produces dense and compact films. Also, as already mentioned, compared to sol-gel, anodization, hydrothermal, and chemical vapor deposition synthesis methods[14,21,22], reactive sputtering is the most suitable to deposit large areas[1,2,14]. However, understanding the role of the deposition parameters on film properties is a challenge[5,15,20], especially in the case of niobium-oxide that can form many different stable crystal structures.

Nb can be found in tree oxidation state as II, IV and V, which are predominant in NbO, NbO_2, and Nb_2O_5 phase respectively[14]. Although niobium pentoxide (Nb_2O_5) is the most stable phase, controlling the amount of oxygen in the chamber during deposition can produce different phases. This is a critical and important step, requiring fine control. In our system oxygen flow of 3 sccm favors the formation of NbO_2. The use of oxygen flow rate higher than 3 sccm leads to the formation of Nb_2O_5.

An excess of oxygen in the chamber leads to oxygen contamination of the target. This results in a decrease in oxide film deposition rate and the formation of different phases as explained in a previous publication[20]. On the contrary, oxygen deficiency in the chamber significantly decreases film transparency. Besides the formation of different phases, changing the oxygen flow results in films with different density of oxygen vacancies. This leads to significant changes in film properties, for example its conductivity. NbO_2 shows high conductivity, while Nb_2O_5 is a more resistive phase. The lower electrical conductivity of Nb_2O_5 compared to NbO_2 films is explained by the chemical nature of the bond, Nb has a charge state of 5^+, with all of its 4d electrons bond to O 2p-orbital. For the Nb_2O_5 films (films deposited with 3.5, 4 and 10 sccm of oxygen flow), the highest conductivity is observed in films deposited with 3.5 sccm of oxygen flow, which is attributed to an increase in oxygen vacancies[20].

The cell made with a film deposited with 3.5 sccm of oxygen flow has the best performance with the highest short circuit current. This high performance is due to the better conductivity of the correspondent niobium oxide film. As the resistivity of the niobium oxide film increases, the devices show less efficiency.

Clearly, sputtering is a powerful deposition technique that allows a finer control of deposition parameters compared to other chemical deposition techniques. The major limitation of sputtering is the use of ultra-high vacuum required to avoid contaminants, which implies relatively long waiting times for pumping. The waiting time can be partially avoided in system equipped with a pre-chamber, or a differential pumping system. Nevertheless, this requirement allows the production of films of high purity.

In conclusion, the use of sputtering allows the formation of dense and compact films with controlled stoichiometry. In our case, good conductivity was achieved by adjusting the oxygen content in the chamber. Sputtering is a promissing technique to deposit film in large areas to produce efficient solar cells.

Disclosures

The authors have nothing to disclose.

Acknowledgments

The work was supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Centro de Desenvolvimento de Materiais Cerâmicos (CDMF- FAPESP Nº 2013/07296-2, 2017/11072-3, 2013/09963-6 and 2017/18916-2). Special thanks to Professor Máximo Siu Li for PL measurements.

References

1. Wasa, K., Kitabatake, M., Adachi, H. *Thin film materials technology : sputtering of compound materials.* William Andrew Pub. (2004).
2. Kelly, P. J., Arnell, R. D. Magnetron sputtering: A review of recent developments and applications. *Vacuum.* **56**, 159–172 (2000).
3. Chen, W.-C., Peng, C.Y., Chang, L. Heteroepitaxial growth of TiN film on MgO (100) by reactive magnetron sputtering. *Nanoscale Research Letters.* **9**, 551 (2014).
4. Guo, Q. X. *et al.* Heteroepitaxial growth of gallium nitride on (1 1 1) GaAs substrates by radio frequency magnetron sputtering. *Journal of Crystal Growth.* **239**, 1079–1083 (2002).
5. Berg, S., Nyberg, T. Fundamental understanding and modeling of reactive sputtering processes. *Thin Solid films.* **476**, 215-230 (2005).
6. Wong, M. S., Sproul, W. D., Chu, X., Barnett, S. A. Reactive magnetron sputter deposition of niobium nitride films. *Journal Vacuum Science & Technology A: Vacuum, Surfaces and Films.* **11**, 1528–1533 (2002).
7. Zoita, C. N., Braic, L., Kiss, A., Braic, M. Characterization of NbC coatings deposited by magnetron sputtering method. *Surface and Coatings Technology.* **204**, 2002–2005 (2010).
8. Nico, C., Monteiro, T., Graça, M. P. F. Niobium oxides and niobates physical properties: Review and prospects. *Progress in Materials Science.* **80**, 1–37 (2016).
9. Aegerter, M. A., Schmitt, M., Guo, Y. Sol-gel niobium pentoxide coatings: Applications to photovoltaic energy conversion and electrochromism. *International Journal of Photoenergy.* **4**, 1–10 (2002).
10. Fernandes, S. L. *et al.* Hysteresis dependence on $CH_3NH_3PbI_3$ deposition method in perovskite solar cells. *Proceedings of SPIE - International Society for Optics and Photonics* **9936**, 99360B (2016).
11. Fernandes, S. L. *et al.* Nb_2O_5 hole blocking layer for hysteresis-free perovskite solar cells. *Materials Letters.* **181**, 103–107 (2016).
12. Hamada, K., Murakami, N., Tsubota, T., Ohno, T. Solution-processed amorphous niobium oxide as a novel electron collection layer for inverted polymer solar cells. *Chemical Physics Letters.* **586**, 81–84 (2013).
13. Aegerter, M. a. Sol-gel niobium pentoxide: A promising material for electrochromic coatings, batteries, nanocrystalline solar cells and catalysis. *Solar Energy Materials and Solar Cells.* **68**, 401–422 (2001).
14. Rani, R. A., Zoolfakar, A. S., O'Mullane, A. P., Austin, M. W., Kalantar-Zadeh, K. Thin films and nanostructures of niobium pentoxide: fundamental properties, synthesis methods and applications. *Journal Materials Chemistry A.* **2**, 15683–15703 (2014).
15. Foroughi-Abari, A., Cadien, K. C. Growth, structure and properties of sputtered niobium oxide thin films. *Thin Solid Films.* **519**, 3068–3073 (2011).
16. Numata, Y. *et al.* Nb-doped amorphous titanium oxide compact layer for formamidinium-based high efficiency perovskite solar cells by low-temperature fabrication. *Journal Materials Chemistry A.* **6**, 9583–9591 (2018).
17. Graça, M. P. F., Meireles, A., Nico, C., Valente, M. A. Nb_2O_5 nanosize powders prepared by sol–gel – Structure, morphology and dielectric properties. *Journal of Alloys and Compounds.* **553**, 177–182 (2013).
18. Kogo, A., Numata, Y., Ikegami, M., Miyasaka, T. Nb_2O_5 Blocking Layer for High Open-circuit Voltage Perovskite Solar Cells. *Chemistry Letters.* **44**, 829–830 (2015).
19. Ueno, S., Fujihara, S. Effect of an Nb_2O_5 nanolayer coating on ZnO electrodes in dye-sensitized solar cells. *Electrochimica Acta.* **56**, 2906–2913 (2011).
20. Fernandes, S. L. *et al.* Exploring the Properties of Niobium Oxide Films for Electron Transport Layers in Perovskite Solar Cells. *Frontiers in Chemistry.* **7**, 1–9 (2019).
21. Shirani, A. *et al.* Tribologically enhanced self-healing of niobium oxide surfaces. *Surface and Coatings Technology.* **364**, 273–278 (2014).
22. Yan, J. *et al.* Nb_2O_5/TiO_2 heterojunctions: Synthesis strategy and photocatalytic activity. *Applied Catalysis B: Environmental.* **152–153 (1)**, 280–288 (2014).