High Pressure Sputtering of Mo targets in mixed $Ar/O_2/H_2$ atmospheres for hole selective contacts in photovoltaic cells

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***Abstract*—We have deposited thin films of MoO_x using high-pressure sputtering (HPS) and $Ar/O_2/H_2$ atmospheres aiming at the compositional and interface control. We found that H_2 impacts plasma composition, which in turn produces a reduction of the oxygen content and a change in the refractive index of the films. However, the presence of hydrogen in the plasma atmosphere enhances interfacial SiO_x regrowth, as FTIR shows. TEM measurements show that this regrowth is not critical for thin films. Also, increasing the hydrogen ratio produces a change from amorphous to an amorphous/polycrystalline mixture. Lifetime measurements show that these films are adequate for their integration into test HIT-like structures, but require more work to produce competitive *iVoc* values.**

Keywords—Photovoltaic cells, selective contact, molybdenum oxide, high-pressure sputtering

I. INTRODUCTION

In this work, we present characterization results of MoO_x films deposited on Si by an unconventional technique, high-pressure sputtering (HPS). This study aims to obtain structures that can act as hole-selective contacts (HSC) in heterojunction solar cells, using a low-cost low-damage technique such as HPS. The advantage is that the excited species that are sputtered from the target suffer many collisions before reaching the substrate (thermalization). Thus plasma damage by excited species bombardment is reduced[1]. However, sputtering in the mbar pressure range is difficult due to the reduced space charge zone, which imposes a careful system design to avoid power losses to the ground.

In order to produce HSC we have started by focusing on molybdenum oxide, which is the most promising candidate to be included as HSC in novel heterojunction cells [2]. Typically, given the insulating character of stoichiometric MoO_3, an O-to-Mo ratio (x) under 3 is desired (in other words, an oxygen-deficient film). We found previously that our films were very close to stoichiometry, even using our system's lowest attainable O_2 flux. Thus, we used a mixed $Ar/O_2/H_2$ sputtering atmosphere in these experiments, aiming at the composition control of the MoO_x film and SiO_x regrowth. In most published works MoO_x is not able to passivate the Si surface, and a PECVD a-Si:H film is needed [3]. We will also check if hydrogen presence in the plasma aids with passivation preservation.

II. EXPERIMENTAL

We sputtered pure metallic Mo targets on <100> n Si (300 µm thick, 1-5 Ωcm) using an $Ar/O_2/H_2$ plasma at room temperature. The wafer was cleaned with diluted HF for 1 min followed by a deionized water rinse just before loading to the HPS vacuum chamber. The plasma was excited using a rf power of 50 W, and a constant high pressure of 0.5 mbar. The O_2 to total flux ratio (R_{O2}) was fixed at 1% for all experiments. This ratio was the minimum oxygen ratio attainable by our

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system. In the case of the H_2 to total flux ratio (R_{H2}), in this set of experiments we varied it from 0% (no hydrogen in the atmosphere) to 4.8%.

The plasmas were characterized by glow discharge optical spectroscopy (GDOS). Moreover, some samples were analyzed with Fourier transform infrared spectroscopy (FTIR), X-ray Photoelectron Spectroscopy (XPS), and Transmission Electron Microscopy (TEM). We fabricated several batches. First a set deposited for a fixed time (3.5 h) for XPS, ellipsometry and FTIR measurements. Then, after measuring growth rate, we fabricated a second batch aiming at a MoO_x ~5nm thick. These samples were measured by TEM.

Finally, an a-Si:H/Si/a-Si:H/MoO_x stack was fabricated, and the minority carrier lifetime was measured by the quasi-steady-state photoconductance method (QSSPC).

III. Results and Discussion

GDOS showed that, as expected, introducing H_2 to the atmosphere produced an important decrease in oxygen emission in the plasma (Fig. 1). We found that the emission at 777.5 nm, which is related to atomic oxygen, almost vanishes. At the same time, two sharp emissions appear: at 486 and 656.3 nm, due to atomic hydrogen [4]. Finally, two broad bands in the 250-350 nm range also are noticeable. These are due to molecular OH^- emission [5]. The reason for these changes is that hydrogen mixes with oxygen in the plasma. Atomic oxygen mixes with hydrogen, and thus intense OH^- emissions are detected. This can affect the Si substrate re-oxidation and also film composition since less oxygen is available during growth.

This change of deposition atmosphere also impacts the film bonding arrangement: XPS shows (Fig. 2) that the 3d Mo(+6) binding energy shifts from 233 eV (R_{H2}=0%) to 234.5 eV (R_{H2} = 4.8%, not shown). Also, the increased intensity of Mo(+5) indicates that the films are sub-stoichiometric. From the fit of these 3d emissions, we found that x decreases from 2.97 to 2.94 (Fig. 3). Also, the refractive index increases with increasing R_{H2}, as fig. 3 also shows. Literature on MoO_x indicates that n increases with decreasing oxygen content [6]. Thus, these results indicate that, to some extent, MoO_x oxygen content can be tuned by hydrogen addition to the plasma.

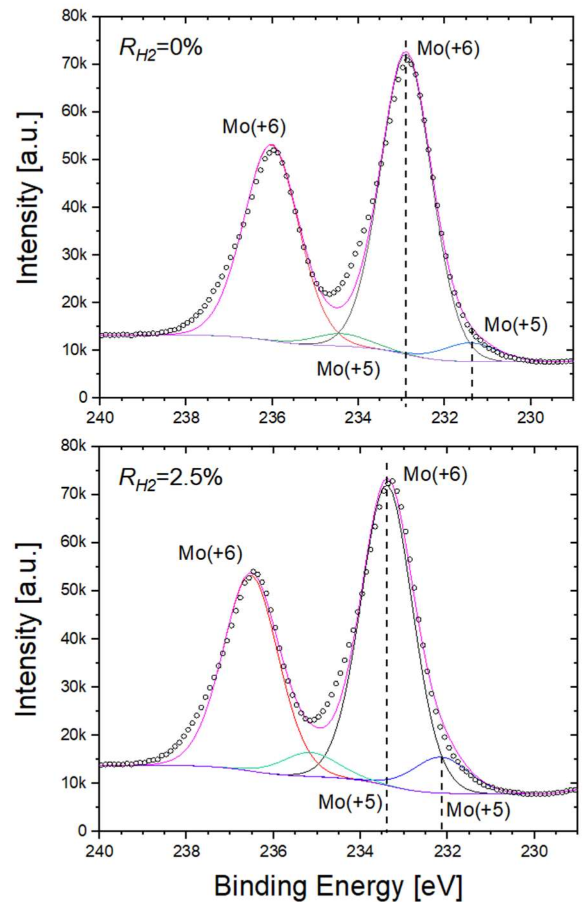

Fig. 2. XPS surface scan of the Mo 3d region of MoO_x sputtered without H_2 (top) and with an R_{H2} = 2.5% (bottom).

FTIR provides semi-quantitative information on the bonding configuration of the films. All spectra shown in Fig. 4 present a broad Mo-O band between 600 and 900 cm^{-1} [7].[8]This band is similar for all films indicating that there are no big differences in the thicknesses of the MoO_x films (ellipsometry indicated that all films were around 25 nm thick).

Also, several Si-related bands are present in the spectra: Si-O stretching at 1050 cm^{-1}, Si-H_2 stretching at 2090 cm^{-1},

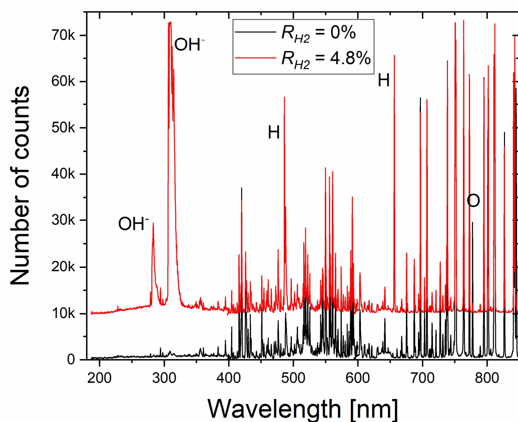

Fig. 1. GDOS spectra of two representative plasmas sputtered in Ar/O_2 (black) and Ar/O_2/H_2 (red). The main differences are highlighted.

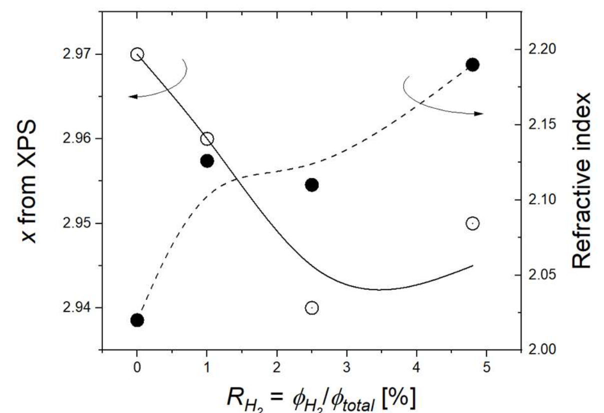

Fig. 3. MoO_x:H composition as calculated from the fit of the 3d Mo peaks measured by XPS (open symbols). Refractive index of the films measured at 632 nm (solid symbols). The lines are drawn as a guide to the eye.

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and Si-H wagging at 650 cm^{-1} [9]. These three absorptions are observed due to the interaction of the plasma with the Si substrate.

The Si-H related peaks are present only for the films with $R_{H2} > 0\%$, as expected. The intensity of these absorptions grows with R_{H2}. This result indicates that hydrogen is reacting with the Si substrate, and the interface is being affected. This can even be beneficial: this interface could produce Si substrate passivation, or in the case of the deposition of these films on a-Si:H, they may effectively inhibit hydrogen effusion or passivate bonds.

The Si-O stretching is present in all samples, but its area grows with hydrogen content in the plasma. When there is no H_2 introduction to the chamber this absorption is very low, and it enhances as R_{H2} grows.

The most likely interpretation of these FTIR results is that a SiO_xH_y interfacial film is growing between at the Si/MoO_x interface. This film grows thicker and more H_2-rich as the H_2 presence in the plasma grows.

To confirm these results and to quantify the interfacial thickness we deposited a batch of samples aiming at cell-relevant thickness (around 5 nm). We fabricated TEM lamellas for R_{H2} in the 0-2.5% range. Fig. 5 shows the transmission microscopy results.

In those images we notice some interesting results: as expected, the films have a bilayer structure. We find an SiO_x layer between the Si substrate and the MoO_x film. The thickness of this interface lies in the 4-5 nm range for the three samples measured, irrespective of H_2 ratio. This interfacial regrowth is typical of oxides in contact with Si [10], [11]. The fact that the SiO_x thickness is similar in all three samples is in apparent contradiction with the FTIR results, which clearly showed that higher hydrogen meant thicker SiO_x. However, FTIR results were obtained with films deposited for a long fixed time, while in this batch the deposition was shorter, aiming at a fixed MoO_x thickness. These results can only be matched if the hydrogen present in the plasma is enhancing Si oxidation during the process. Typically, this oxidation takes place at the first stages of deposition and then saturates. If this was the case here, the Si-O thickness would be similar for all samples, and the FTIR Si-O peak and SiO_x TEM thickness would be similar for all samples. However, FTIR suggests that when there is H in the atmosphere the oxidation process does not saturate. This means that H atoms diffuse to the interface and have a catalytic effect on substrate oxidation.

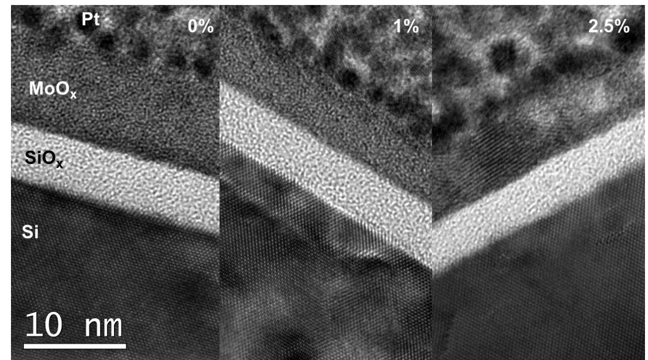

Fig. 5. TEM images of MoO_x deposited on Si with several R_{H2} values (the H_2 ratio for each image is included in the image).

Also we can observe that, while MoO_x films deposited at $R_{H2} \leq 1\%$ are amorphous, the sample deposited at 2.5% is an amorphous/polycrystalline mixture. Amorphous films can be excellent insulators, while comparatively polycrystalline films tend to exhibit comparatively inferior insulator characteristics due to conduction by grain boundaries. For PV cell application higher conductivity would be beneficial, since the MoO_x film is in the carrier path, thus impacting cell series resistance. Thus, so far all these results combined point that $R_{H2} = 2.5\%$ is the most promising condition for cell applications.

Thus, using those same conditions ($R_{H2} = 2.5\%$) we deposited a thin MoO_x film on a Si substrate passivated by thin PECVD a-Si:H on both sides. The goal was to study the HPS effect on minority carrier lifetime using HIT-like structures. The results are shown in Fig.6.

The sample measured just after MoO_x deposition shows a reduced lifetime, which is an indication that the sputtering plasma has produced interfacial defects. If those defects are due to UV radiation, they can be healed by moderate temperature annealing [12]. In the figure we observe that annealing at 200ºC is not enough to improve lifetime, but at

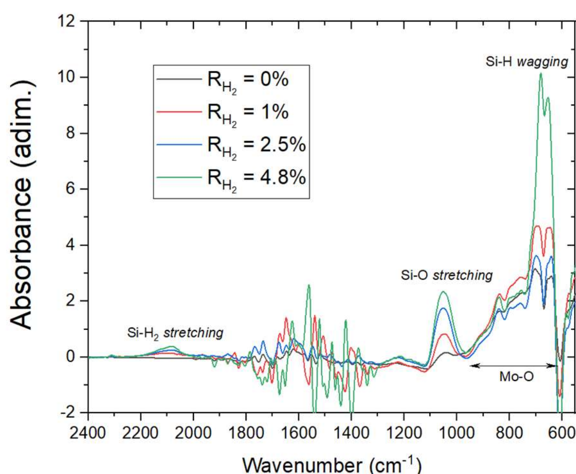

Fig. 4. FTIR spectra of the films deposited with different hydrogen ratios. The most relevant vibrations are shown in the spectra.

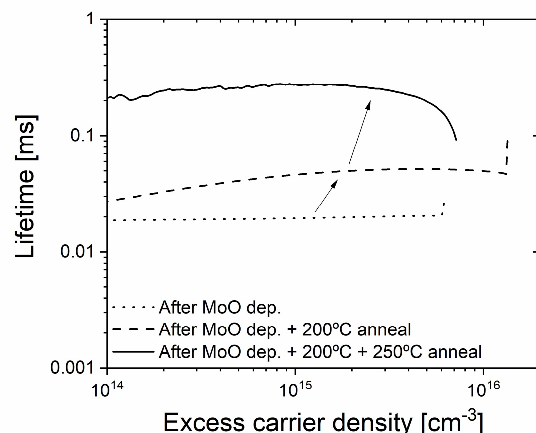

Fig. 6. Minority carrier lifetime of a MoOx/a-Si:H/Si/a-Si:H sample. The R_{H2} ratio used was 2.5%. The sample was measured also after two consecutive 10 min hot plate annealings at 200ºC and 250ºC.

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250ºC there is a strong lifetime recovery. The maximum lifetime is 277 µs. The iV_{oc} is 0.641 eV, which is still moderately low for a HIT cell, but encourages us to optimize deposition conditions.

IV. Conclusions

The results found show that H_2 addition is a useful knob to tune HPS MoO_x properties aiming at its integration in HIT-like solar cells. We found that the oxygen-to-molybdenum ratio decreases with R_{H2}, and also film structure is affected since the more oxygen-deficient films are an amorphous-polycrystal mixture. Hydrogen diffusion through the growing film impacts SiO_x regrowth. This can be problematic if thick MoO_x films are desired, but usually that is not the case in the photovoltaic field. Finally, the lifetime of passivated samples is reduced after MoO_x deposition but can be greatly recovered after a mild hot plate anneal.

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References

[1] D. Caudevilla et al., “Indium tin oxide obtained by high pressure sputtering for emerging selective contacts in photovoltaic cells,” Mater Sci Semicond Process, vol. 137, p. 106189, Jan. 2022, doi: 10.1016/J.MSSP.2021.106189.

[2] S. Acharyya et al., “Dopant-free materials for carrier-selective passivating contact solar cells: A review,” Surfaces and Interfaces, vol. 28, p. 101687, Feb. 2022, doi: 10.1016/J.SURFIN.2021.101687.

[3] J. Bullock et al., “Stable Dopant-Free Asymmetric Heterocontact Silicon Solar Cells with Efficiencies above 20%,” ACS Energy Lett, vol. 3, no. 3, pp. 508–513, Mar. 2018, doi: 10.1021/acsenergylett.7b01279.

[4] J. E. Sansonetti and W. C. Martin, “Handbook of basic atomic spectroscopic data,” J Phys Chem Ref Data, vol. 34, no. 4, pp. 1559–2259, 2005, doi: 10.1063/1.1800011.

[5] Gaydon A. G., The Identification of Molecular Spectra . Springer Netherlands, 1976. Accessed: Jul. 09, 2020. [Online]. Available: https://www.springer.com/gp/book/9789400957602

[6] B. Aissa, A. Zekri, Y. Zakaria, A. Samara, and C. Broussillou, “Tuning the Structural and Optoelectronic Properties of Sub-stoichiometric Molybdenum Trioxide (MoOx, x < 3) Thin Films through the Oxygen Flow During the Reactive Magnetron Sputtering Deposition,” 2021 IEEE 48th Photovoltaic Specialists Conference (PVSC), pp. 0068–0070, Jun. 2021, doi: 10.1109/PVSC43889.2021.9518553.

[7] J. Shi et al., “MoOx modified ITO/a-Si:H(p) contact for silicon heterojunction solar cell application,” Mater Res Bull, 2018, doi: 10.1016/j.materresbull.2017.09.005.

[8] E. San Andrés, A. Del Prado, I. Mártil, G. González-Díaz, D. Bravo, and F. J. López, “Thermally induced modifications on bonding configuration and density of defects of plasma deposited SiOx:H films,” J Appl Phys, vol. 92, no. 4, 2002, doi: 10.1063/1.1495068.

[9] E. San Andrés et al., “Bonding configuration and density of defects of SiOxHy thin films deposited by the electron cyclotron resonance plasma method,” J Appl Phys, vol. 94, no. 12, 2003, doi: 10.1063/1.1626798.

[10] M. Toledano-Luque et al., “Hafnium oxide thin films deposited by high pressure reactive sputtering in atmosphere formed with different Ar/O2 ratios,” Mater Sci Semicond Process, vol. 9, no. 6, 2006, doi: 10.1016/j.mssp.2006.10.018.

[11] E. San Andrés et al., “Physical properties of high pressure reactively sputtered TiO2,” Journal of Vacuum Science and Technology A: Vacuum, Surfaces and Films, vol. 23, no. 6, 2005, doi: 10.1116/1.2056554.

[12] B. Demaurex, S. De Wolf, A. Descoeudres, Z. Charles Holman, and C. Ballif, “Damage at hydrogenated amorphous/crystalline silicon interfaces by indium tin oxide overlayer sputtering,” Appl Phys Lett, vol. 101, no. 17, p. 171604, Oct. 2012, doi: 10.1063/1.4764529/24881.

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