

PAPER

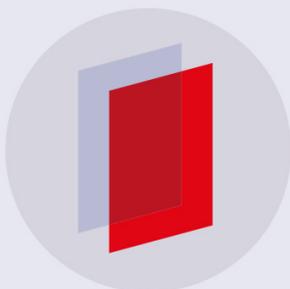
Accelerated ageing of molybdenum oxide

To cite this article: Marina Jorge *et al* 2017 *Mater. Res. Express* **4** 115502

View the [article online](#) for updates and enhancements.

Related content

- [Robust p-type doping of copper oxide using nitrogen implantation](#)
Marina Jorge, Stanislav M Polyakov, Simon Cooil *et al.*
- [Electronic structure of Fe \(0–5 at. percent\) doped MoO₂ thin films studied by resonant photoemission spectroscopy](#)
Ram Prakash, R J Choudhary and D M Phase
- [Irradiation-induced degradation of PTB7 investigated by valence band and S 2p photoelectron spectroscopy](#)
Erik Darlatt, Burhan Muhsin, Roland Roesch *et al.*



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.



PAPER

Accelerated ageing of molybdenum oxide

RECEIVED
20 September 2017REVISED
8 October 2017ACCEPTED FOR PUBLICATION
11 October 2017PUBLISHED
7 November 2017Marina Jorge¹, Simon Cooil¹, Mark T Edmonds², Lars Thomsen³, Mohammadreza Nematollahi^{4,5},
Federico Mazzola^{1,6} and Justin W Wells¹ ¹ Center for Quantum Spintronics, Department of Physics, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway² School of Physics and Astronomy, Monash Centre for Atomically Thin Materials, Clayton Victoria 3800, Australia³ The Australian Synchrotron, 800 Blackburn Road, Clayton, Victoria 3168, Australia⁴ Department of Physics, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, NorwayE-mail: quantum.wells@gmail.com**Keywords:** molybdenum oxide, photoemission spectroscopy, synchrotron radiation, surface scienceSupplementary material for this article is available [online](#)**Abstract**

The stability and lifetime of materials proposed for photovoltaic applications are important parameters, because such devices should offer long-term reliable performance whilst operating in a harsh environment. In this work, we present a powerful approach to accelerate and study the degradation mechanisms of molybdenum oxide, a material which has shown promise for next generation photovoltaics, and for enhanced hole extraction in organic photovoltaics. We use UV and soft x-rays to drive accelerated ageing, boosting the ageing time by a factor of up to 1000. Using this method, we find that molybdenum oxide does not offer reliable performance in environments in which heating or ionising radiation are present, because of its propensity to reduce, thus strongly modifying its electronic properties. We estimate that ≈ 100 d of unfiltered sunlight exposure would be sufficient to reduce this material into metallic MoO₂. We also show that a very similar degradation can be driven by thermally, and that in both cases, the creation of oxygen vacancies is responsible. A lack of robustness to harsh operating conditions (i.e. UV and/or heat) brings the suitability of unprotected molybdenum oxide in photovoltaic applications into question.

Introduction

Molybdenum trioxide (MoO₃) has attracted increasing interest for photovoltaic applications. For example, it has been proposed (together with NiO_x or CuI) as a hole extraction or transport layer [1–3] for organic photovoltaics (OPV) and as a potential active layer in intermediate band solar cells (IBSCs) [4, 5]. OPVs have attracted increasing attention due to their potential as low-cost alternatives to silicon-based solar cells, as well as promising reduced environmental impact. IBSCs are photovoltaic devices with an electronic band within the material band-gap [6–8]. The presence of such a band has been predicted to offer an improved efficiency limit of 63%, a much higher value than the 41% obtained for standard single-gap solar cells, under the same conditions [6].

In order to meet the prerequisites of high-efficiency, simple processing and low toxicity, several materials have been suggested as potential candidates for next generation photovoltaics [9, 10]. As well as a requirement for controlling the Fermi level position within the bulk bandgap—for which several doping strategies exist [11, 12]—it is important that candidate materials are suitably resilient to ageing processes. An ability to control and stabilise the electronic and structural properties of photovoltaics is important since these devices should be able to offer a reliable performance, often in harsh operating conditions, over many years.

In this work we demonstrate a powerful method based on photoemission spectroscopy to study *in situ* the ageing of molybdenum oxide caused by light exposure and heat. In particular, by a controlled choice of the radiation energy and exposure time, we are able to accelerate the ageing rate of the samples by several orders of magnitude. This approach allows us to study the time-scales associated with the sample deterioration and to understand the expected ageing mechanisms during sunlight exposure.

⁵ Present address: MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands⁶ Present Address: School of Physics and Astronomy, University of St Andrews, St Andrews, Fife KY16 9SS, United Kingdom

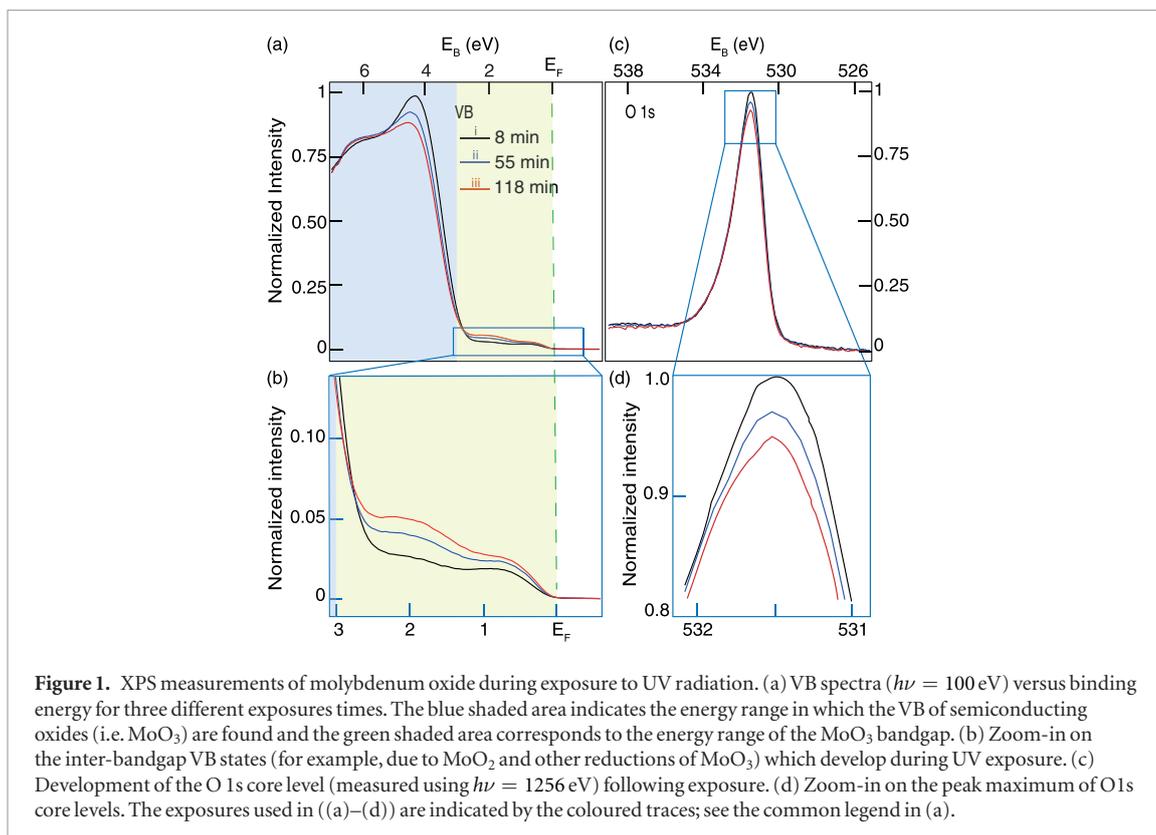


Figure 1. XPS measurements of molybdenum oxide during exposure to UV radiation. (a) VB spectra ($h\nu = 100$ eV) versus binding energy for three different exposures times. The blue shaded area indicates the energy range in which the VB of semiconducting oxides (i.e. MoO_3) are found and the green shaded area corresponds to the energy range of the MoO_3 bandgap. (b) Zoom-in on the inter-bandgap VB states (for example, due to MoO_2 and other reductions of MoO_3) which develop during UV exposure. (c) Development of the O 1s core level (measured using $h\nu = 1256$ eV) following exposure. (d) Zoom-in on the peak maximum of O1s core levels. The exposures used in ((a)–(d)) are indicated by the coloured traces; see the common legend in (a).

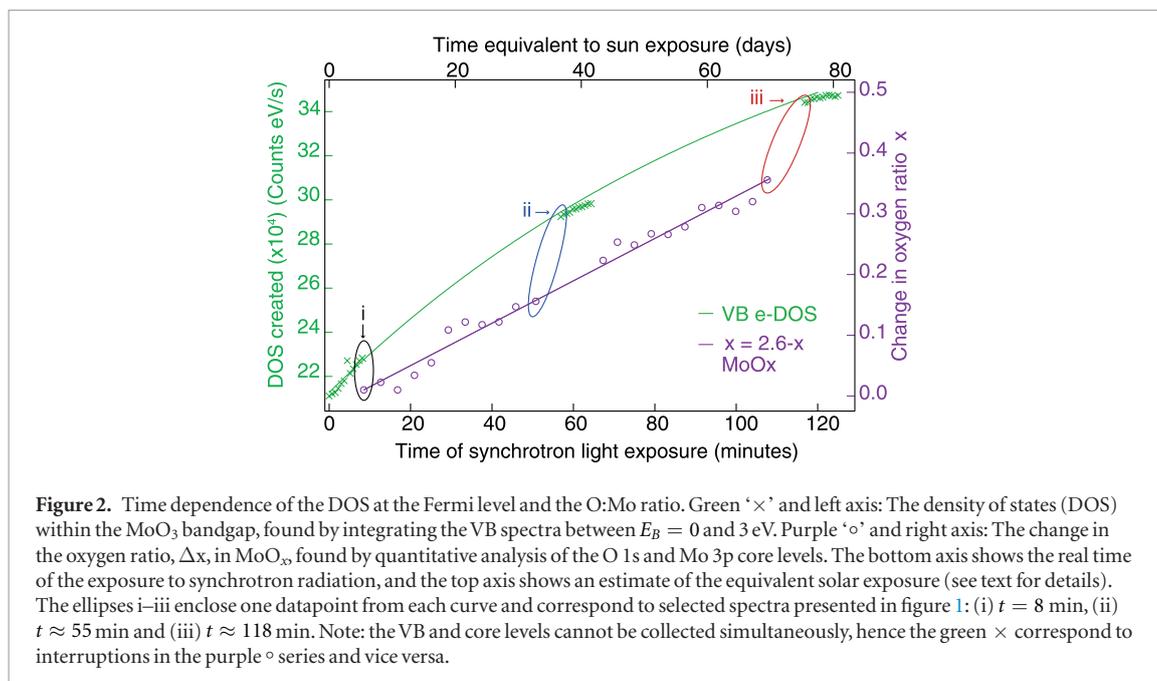
Molybdenum oxide was chosen because it attracts interest for both OPV and IBSC applications. It has a wide band gap [13], low cost and high carrier mobility [14]. In addition, it is environmentally friendly (i.e. low toxicity). On the other hand, electron-beam and UV induced damage of MoO_3 has previously been reported [15, 16], hence the potential stability under harsh operating conditions is an important and unaddressed question.

In order to observe and understand photon-induced damage to Molybdenum oxide, XPS measurements were performed following exposure to an increasing dose of monochromatic (synchrotron) light. High intensity synchrotron light is known to accelerate damage in a wide range of materials [17, 18], and may help to elucidate the mechanism responsible for ageing. Finally, XPS measurements were made as a function of sample temperature in order to (i) study the stability of molybdenum oxide in hot environments and (ii) to help understand the degradation mechanisms. Our study shows that the driving force behind sample degradation by both heat and light exposure is the removal of oxygen. Whilst we also demonstrate that exposure to light offers an easy method for controlling the density of oxygen vacancies (and therefore the electronic properties), we show that the propensity to damage precludes the use of molybdenum oxide in applications where stability against heat and ionising radiation are important.

Methods

Polycrystalline MoO_3 films were grown on Si(001) substrates by pulsed laser deposition. Prior the deposition, the substrates were cleaned with ethanol, acetone, and deionized water in an ultrasonic bath. A KrF excimer laser (248 nm, 20 ns) was operated at 10 Hz to ablate a (99.95%) MoO_3 target. Before each deposition, the target was pre-ablated by 3000 pulses to have a steady state condition. During deposition, the substrates were held at 500 to 570 °C in flowing O_2 gas (55–70 sccm, resulting in a corresponding background pressure of 2 to 4×10^{-2} mbar, respectively). The target to substrate distance was 4 cm for all films, and 18 000 pulses were used for the depositions (corresponding to a film thickness of 390 nm). XRD analysis indicates that the samples already have a small oxygen deficiency, and are in fact closer to $\text{MoO}_{2.75}$ [19].

Controlled sample irradiation was performed by using either ultraviolet (UV) radiation, from a helium discharge lamp, or monochromated synchrotron radiation. Experiments were performed at the soft x-ray (SXR) beamline of the Australian Synchrotron [20] (for synchrotron radiation exposure) and at our home photoemission laboratory using He I α radiation (with energy $h\nu = 21.2$ eV). Samples were studied using x-ray photoelectron spectroscopy (XPS), both before and after irradiation. The XPS measurements were collected in a very short time (typically ≈ 30 s), such that the irradiation during measurements was negligible compared to the irradiation dose used to test the sample stability (typically 30 min). The samples were sufficiently conductive such that no charging was observed during measurements, and the energy scale was calibrated relative to the Fermi energy of a gold foil in electrical contact with the sample.



Valence band and O 1s core levels measurements

In d-electron systems such as MoO₃, changes in the stoichiometry, oxidation states and crystal environment can be expected to prominently affect the valence band (VB) structure of the material, because the d-derived valence electrons are generally more susceptible to external stimuli than core electrons. This is especially important for photovoltaics since it is these VB states which dictate their photo-absorption properties.

In figure 1(a), the valence band of the molybdenum oxide sample is shown as a function of exposure time to synchrotron light. As expected, a large peak at binding energy $E_B \approx 4.4$ eV is seen; reminiscent of semiconducting MoO₃ [21] (blue region in figure 1(a)). This peak shows an intensity reduction with increasing photon dose. On the other hand, the opposite trend is observed within the range between $E_B \approx 3$ eV and $E_B = 0$ eV (green region in figures 1(a) and (b)), where states characteristic of reduced molybdenum oxides are detected (see zoom-in; figure 1(b)) [22, 23]. The initial intensity in this region is not zero, presumably because the unexposed sample contains MoO_{3- δ} . In particular, MoO_{2.75} contributes spectral intensity in the range $E_B = 0$ to 1 eV [21]. A slight intensity reduction with increasing light exposure is also observed in the O 1s core level in figures 1(c) and (d), indicating that the origin of the changes detected in the VB is correlated with the creation of oxygen vacancies.

Time dependence

Data similar to that presented in figure 1 has been collected throughout an incrementally prolonged irradiation series. Over an exposure period of ≈ 2 h, VB, Mo 3p and O 1s measurements were recorded. The density of states (DOS) within the MoO₃ bandgap, and the O:Mo ratio were extracted from the data acquisitions and are plotted versus exposure time in figure 2.

For each data acquisition, the DOS is extracted by integrating the area of the VB between $E_B = 3$ eV and the Fermi level (E_F). For MoO₃, this corresponds to the bulk bandgap, and hence the DOS should be 0 for a pure MoO₃ sample. However, if oxygen depletion is occurring, and MoO₃ \rightarrow MoO₂, then states due to MoO₂ (and other reductions of the trioxide) are expected to appear in this binding energy range [21]. As already shown in figure 1(a), the VB intensity in this region does indeed increase with prolonged photon exposure. The experimental data describing the VB DOS as a function of exposure time (green crosses in figure 2) find an extremely good agreement with a simple parabolic fit (green solid line in figure 2). Naïvely, we can expect that prolonging the time of exposure even further, we will reach a saturation condition, where a maximum number of oxygen sites will be vacated, turning the semiconducting MoO₃ into metallic MoO₂. By extrapolating the parabolic fit in figure 2, we find that such a saturation condition would be reached after $t \approx 3$ h of irradiation. According to our estimation (described below), this corresponds to ≈ 100 d of sunlight exposure.

Complementary information is given by monitoring the time evolution of the amount of oxygen relative to the amount of molybdenum (MoO_x, where x indicates the O:Mo ratio). From the experimental data, x can be found from a quantitative analysis of the O 1s and Mo 3p core levels, throughout the exposure. To this end, the core levels have been fitted with Voigt functions and their area extracted. The initial O to Mo concentration is found to be $x = 2.6$ instead of the ideal $x = 3$ expected for MoO₃. The observed initial oxygen deficit is prob-

Table 1. Flux of ionising radiation per unit area and time impinging on a sample, estimated for cosmic rays, the sun, a lab-based helium discharge lamp and for the synchrotron beamline (for a range of photon energies).

Source	Energy E (eV)	Flux (ionising) N ($\text{m}^{-2}\text{s}^{-1}$)
Cosmic rays	$\approx 10^9$ – 10^{13}	≈ 10 – 100
Sun	>6.6	1.2×10^{18}
He lamp	21.2	5.5×10^{18}
	100	9.8×10^{20}
	150	1.5×10^{21}
Synchrotron	200	3.6×10^{20}
	500	1.2×10^{21}
	550	1.3×10^{21}
	1256	1.4×10^{21}

ably due to a surface depletion of oxygen during growth. The results of our analysis shows that the O:Mo ratio changes with exposure time, see figure 2 (purple markers). Note that the change of the O:Mo ratio in figure 2 (Δx) is plotted relative to the initial value of $x = 2.6$. Δx is seen to increase with exposure time and by fitting it, we find that after 3 h (which is the time obtained for the VB DOS saturation), $\Delta x \rightarrow 0.6$. i.e. the O:Mo ratio $x \rightarrow 2$. This confirms that the process responsible for the sample damage is oxygen removal, which is gradually reducing the material to create metallic MoO_2 .

An important point in figure 2 is that it is possible to present the results of the VB DOS and of the oxygen loss during the radiation dose with two different time-scales. Whilst the bottom axis is the real experiment time, i.e. the time during which the samples have been actually exposed to synchrotron light, the top axis is the corresponding time that would have been needed if sunlight was used for the irradiation. The two scales are very different, for instance 1 h of exposure to synchrotron radiation is equivalent to ≈ 40 d of exposure to sunlight. Using synchrotron radiation is therefore a powerful approach to study the accelerated ageing of the samples caused by exposure to electromagnetic radiation. For MoO_3 , we found that 100 d of sunlight exposure would be enough to fully turn this material into a metal, thus compromising the efficiency of an hypothetical photovoltaic device based on MoO_3 , whose wide band gap is one of the most prized properties for its possible application in this field.

Acceleration of ageing

In order to estimate the acceleration of aging, we have used the following approach: We assume that the sample is only damaged by ionising radiation, and we estimate the number of photons (with sufficient energy to ionize) per unit area and unit time which impinge the material in both sunlight and synchrotron light exposure.

In the case of sunlight, excluding absorption from the earth atmosphere, the solar radiation can be approximated by a blackbody at temperature $T_{\text{sun}} = 5780$ K [24]. The total number of photons emitted by a blackbody can be readily calculated from Planck's law which describes the intensity (per unit area and time) emitted from a blackbody ($I(E, T)$), as a function of source temperature (T) and energy (E) of the emitted photons. Thus, we can calculate the total number of ionising photons N emitted from the black body as

$$N = \int_{E_i}^{\infty} \frac{I(E, T)}{E} dE, \quad (1)$$

where E_i is the minimum energy necessary to remove an electron from the sample surface, (i.e. the work-function), which is 6.6 eV for MoO_3 [25]. By using equation (1) we find out that in one second the number of photons with energy >6.6 eV impinging the surface is 1.24×10^{18} per m^2 , at a distance from the sun corresponding to that of the earth's orbit. Note that this estimation is valid outside of the earth's atmosphere, because atmospheric UV absorption is not taken into consideration.

Cosmic rays also have the potential to damage solar cell materials, however, it is worth noting that the flux is negligible in comparison to the solar UV flux: approximately 10–100 particles per m^2 per sec [26]. In addition, their attenuation length and interaction volume is very much larger [27], thus we assume that ageing due to cosmic rays is insignificant compared the UV ageing.

The flux density for a synchrotron beamline depends on the stored beam current in the synchrotron, as well as on the insertion device and beamline optics. Furthermore, this photon flux is energy dependent. In table 1, we show the flux of photons impinging a sample for different photon energies, and for the light sources we have used in the measurements presented above (i.e. the soft x-ray beamline at the Australian Synchrotron and a helium UV lamp).

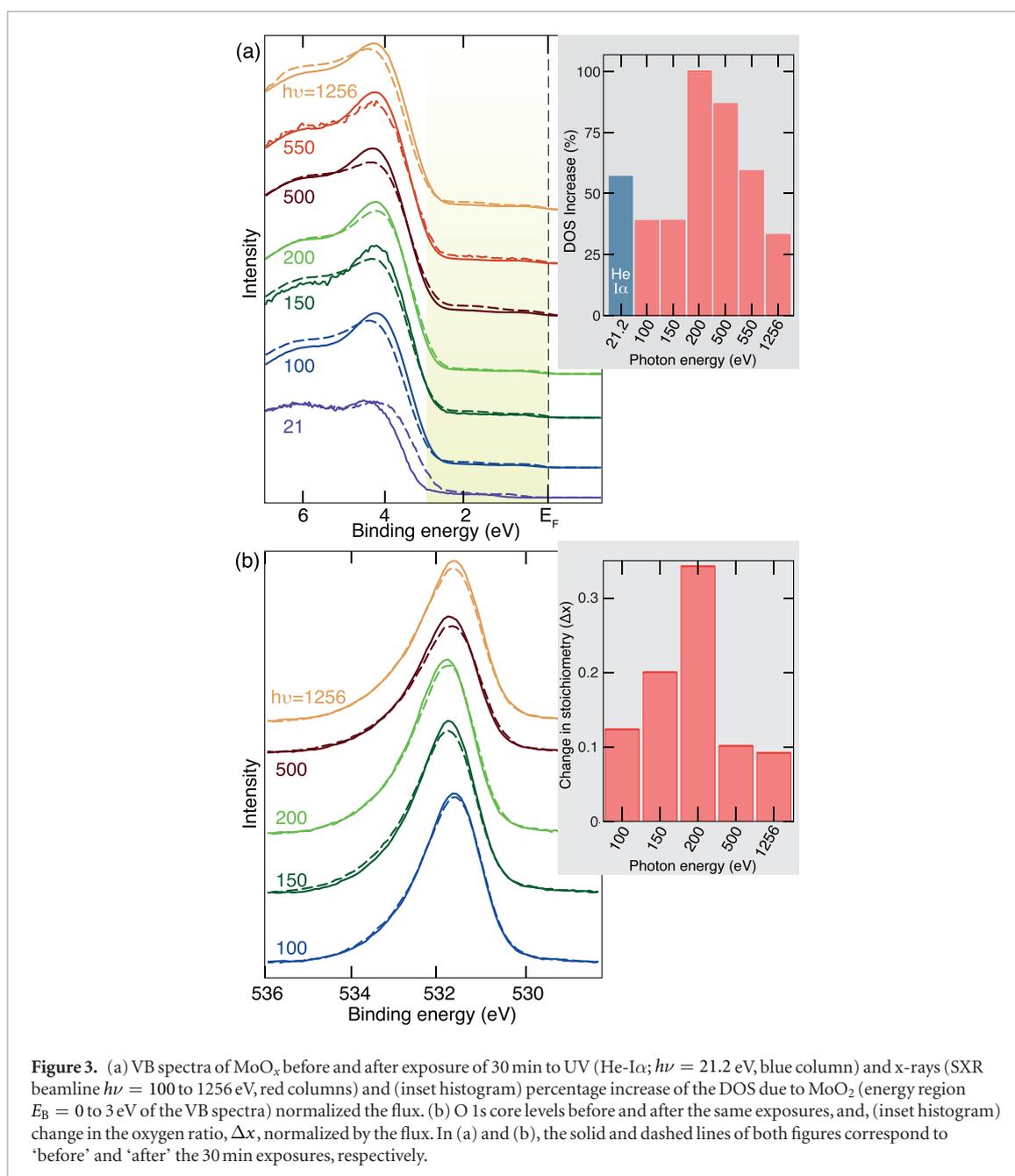


Figure 3. (a) VB spectra of MoO_x before and after exposure of 30 min to UV (He-I α ; $h\nu = 21.2$ eV, blue column) and x-rays (SXR beamline $h\nu = 100$ to 1256 eV, red columns) and (inset histogram) percentage increase of the DOS due to MoO_2 (energy region $E_B = 0$ to 3 eV of the VB spectra) normalized the flux. (b) O 1s core levels before and after the same exposures, and, (inset histogram) change in the oxygen ratio, Δx , normalized by the flux. In (a) and (b), the solid and dashed lines of both figures correspond to 'before' and 'after' the 30 min exposures, respectively.

As can be seen from table 1, the flux of photons with energy above the ionisation threshold is around 300–1000 times larger than from the sun. This means that 1 min of exposure to the synchrotron beam can be considered equivalent to 5–15 h of sunlight (depending on the photon energy of the synchrotron light). Using a lab-based He discharge lamp increases the flux of ionising radiation ≈ 4 times relative to sunlight. Although the flux of the synchrotron beamline is energy dependent, within the range of photon energies used, the flux varies by not more than a factor of 3 (see table 1). It is therefore reasonable to expect a comparable level of damage to the sample at all photon energies used. However, we also point out excitation volume is also energy dependent and hence the volume and rate of damage during exposure may also have a dependence on photon energy.

Photon energy dependence

The degradation *versus* photon energy has been presented as figure 3, demonstrating that the ageing of the sample shows a dependence on the energy used for the irradiation. Figure 3(a) shows the VB following exposure at different photon energies, varied between 21 eV and 1256 eV. Figure 3(b) shows the corresponding measurements of the O 1s core level. Dashed traces are used to indicate the measurements after 30 min of synchrotron light exposure, and solid traces are obtained before exposure and in a sufficiently short time for damage during the measurement to be considered negligible, thus offering reliable reference spectra of the undamaged sample. Between taking measurements for each energy, the sample was moved to a fresh (unexposed) region.

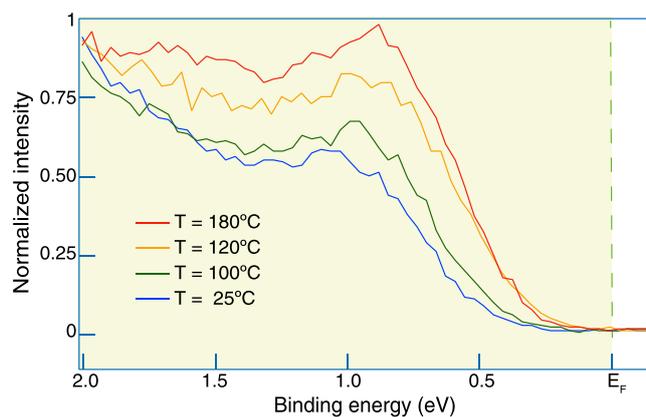


Figure 4. Thermal evolution of the states within the MoO₃ bulk band gap, measured using a He discharge lamp ($h\nu = 21.2$ eV).

By integrating the spectra of figure 3(a) in the range $E_B = 0$ to 3 eV (i.e. the shaded region in figure 3), we can extract the DOS within the MoO₃ bandgap. As described above, these states increase because of the photon-induced reduction, and hence their intensity is an indicator of the reduction of MoO₃. The relative change in this DOS is plotted as a function of photon energy in the histogram of figure 3(a). The intensities have been normalized by the beamline flux and presented (in %) relative to the maximum DOS change observed. As is clear from the histogram, the ageing of the sample caused by light irradiation is not independent of photon energies, indeed, it varies by a factor ≈ 3 , with medium energies (200 and 500 eV) being the most damaging. The flux of photons from the sun at these energies is extremely small; the majority of the ionizing solar radiation is concentrated at ≈ 6 to 8 eV (see supplementary information (stacks.iop.org/MRX/4/115502/mmedia)), thus the rate of damage due to solar exposure is likely to be less than the maximum observed using $h\nu = 200$ eV. On the other hand, the variation of rate with energy is not so strong; the rate varies by approximately $\times 4$ across the whole energy range studied (21 to 1256 eV). It is therefore possible to speculate that whilst the damage due to solar exposure may have a different rate, it is probably of the same order of magnitude.

Analysis of the O:Mo ratio, as extracted from the core level intensities, has also been performed (see histogram in figure 3(b)). Following exposure to monochromatic light, the O:Mo ratio reduces by an amount (Δx), which also depends on the photon energy during exposure, with 200 eV also being the most damaging.

Discussion

It is interesting to question the mechanism of degradation; Mo and O have x-ray absorption edges at around 228 and 532 eV, respectively, and hence this could contribute to the increased efficiency of the degradation at these energies. On the other hand, oxygen reduction (histogram inset of figure 3(b)) shows most efficient oxygen loss at 150 and 200 eV, which does not correlate with the main absorption features. More efficient oxygen removal at low energy may simply be due to the reduced interaction volume. In fact, given the large photon energy range studied, the rate of degradation does not vary strongly with photon energy, indicating that the degradation is not caused by high energy core-hole excitations and their subsequent decay, by mechanisms such as Auger loss. As elucidated previously, UV photons at any energy above the photoionisation threshold appear to create damage, suggesting that removal of electrons from low binding energy bonding orbitals leads to the creation of oxygen vacancies.

The analysis of the O 1s core level and the O:Mo ratio suggests that the main mechanism behind the ageing process is related to a loss of oxygen. To confirm this, we have also carried out temperature dependent measurements monitoring the evolution of the VB, since raising the temperature is a well known approach to create oxygen vacancies in metal oxides [28–30]. In figure 4, the VB spectra following a series of *in vacuo* annealing is reported. The states close to the Fermi level increase with annealing temperature, giving spectra qualitatively very similar to those presented in figure 1(b) caused by UV exposure. The strong similarities between annealing and UV exposure suggest that a common mechanism is driving the degradation observed in MoO_x.

Our annealing study is also important by itself because it sheds light onto another important aspect of the stability of photovoltaic devices: Such devices are expected to withstand a certain degree of heating during normal operation in sunlight. For example, considering the Stefan–Boltzmann law, applied to a surface in thermal equilibrium, the temperatures of solar cells operating outside the atmosphere (for example, on a satellite) are estimated to reach ≈ 120 °C. Thus, the annealing study presented in figure 4 constitutes a useful piece of information as it gives an estimate of modification of the electronic properties of MoO_x as a function of annealing

temperature and for a temperature range which is comparable to the conditions in which photovoltaics may be required to operate.

Finally, since the ageing is caused by the liberation of O from the solid material into the surrounding environment, it is reasonable to assume that granular films, with a larger surface area, will have a higher propensity to damage than, for example, epitaxial films. On the other hand, we speculate that the difference in rate is not large since we observed no significant difference with samples of varying crystal quality.

Summary and conclusions

We have presented a study of the accelerated ageing of molybdenum oxide. In particular, we show that MoO₃, which has been promoted as a potential candidate [1, 4, 31] for photovoltaics, is not a particularly suitable choice for applications in which it is exposed to ionising radiation, or elevated temperatures, because it quickly ages under such conditions. We estimate that after only ≈100 d of sunlight irradiation the material's electronic properties are strongly modified, and MoO_{3-δ} turns into MoO₂, with the release of oxygen.

Our interpretation is fully consistent with studies of other transition metal oxides, where the use of intense UV radiation allows the selective creation of oxygen vacancies in these materials, to turn on a metallic behavior defined by two dimensional electron gases/liquids at the material surface, from an initially insulating ground state [32–34].

In conclusion, we have presented an approach which could be exploited to study a large variety of materials for photovoltaic materials; to test their suitability for harsh operating environments. This method is general and allows us to monitor and study accelerated ageing of materials under exposure to x-rays and UV, giving a direct comparison to unprotected exposure to sunlight. Complementary *in situ* annealing allows also a further insight into the possible mechanisms involved in ageing processes and constitutes an additional suitability test for harsh working conditions.

Acknowledgments

This project was partially funded by the Research Council of Norway through project number 240466.

ORCID iDs

Justin W Wells  <https://orcid.org/0000-0001-6366-366X>

References

- [1] Wang G, Jiu T, Li P, Li J, Sun C, Lu F and Fang J 2014 *Solar Energy Mater. Solar Cells* **120** 603
- [2] Schulz P, Cowan S R, Guan Z-L, Garcia A, Olson D C and Kahn A 2014 *Adv. Funct. Mater.* **24** 701
- [3] Yoon S, Kim H, Shin E-Y, Bae I-G, Park B, Noh Y-Y and Hwang I 2016 *Org. Electron.* **32** 200
- [4] Kostis I, Vourdas N, Papadimitropoulos G, Douvas A, Vasilopoulou M, Boukos N and Davazoglou D 2013 *J. Phys. Chem. C* **117** 18013
- [5] Chen C, Li Y and Tang X 2016 *Phys. B: Condens. Matter* **481** 192
- [6] Luque A and Martí A 1997 *Phys. Rev. Lett.* **78** 5014
- [7] Luque A, Martí A and Stanley C 2012 *Nat. Photon.* **6** 146
- [8] Okada Y et al 2015 *Appl. Phys. Rev.* **2** 021302
- [9] Ramiro I, Martí A, Antolín E and Luque A 2014 *IEEE J. Photovolt.* **4** 736
- [10] Mazzola F, Nematollahi M, Li Z S, Cooil S, Yang X, Reenaas T W and Wells J W 2015 *Appl. Phys. Lett.* **107** 192104
- [11] Luque A, Martí A, López N, Antolín E, Cánovas E, Stanley C, Farmer C, Caballero L J, Cuadra L and Balenzategui J L 2005 *Appl. Phys. Lett.* **87** 083505
- [12] Klein A, Körber C, Wachau A, Säuberlich F, Gassenbauer Y, Harvey S P, Proffitt D E and Mason T O 2010 *Materials* **3** 4892
- [13] Hussain O, Rao K S, Madhuri K, Ramana C, Naidu B, Pai S, John J and Pinto R 2002 *Appl. Phys. A* **75** 417
- [14] Balendhran S et al 2013 *Adv. Mater.* **25** 109
- [15] Lin T T and Lichtman D 1978 *J. Vac. Sci. Technol.* **15** 1689
- [16] Fleish T and Mains G 1982 *J. Chem. Phys.* **76** 780
- [17] Cabailh G, Wells J W, McGovern I T, Vearey-Roberts A R, Bushell A and Evans D A 2004 *Appl. Surf. Sci.* **234** 144
- [18] Vinje J, Falck M, Mazzola F, Cooil S P, Koch H, Høyvik I-M and Wells J 2017 *Langmuir* just accepted (<https://doi.org/10.1021/acs.langmuir.7b02473>)
- [19] Inzani K, Nematollahi M, Vullum-Bruer F, Grande T, Reenaas T W and Selbach S M 2017 *Phys. Chem. Chem. Phys.* (<https://doi.org/10.1039/C7CP00644F>)
- [20] Cowie B C C, Tädich A and Thomsen L 2010 *AIP Conf. Proc.* **1234** 307
- [21] Tokarz-Sobieraj R, Hermann K, Witko M, Blume A, Mestl G and Schlögl R 2001 *Surf. Sci.* **489** 107
- [22] Greiner M T, Chai L, Helander M G, Tang W-M and Lu Z-H 2012 *Adv. Funct. Mater.* **22** 4557
- [23] Baltrusaitis J, Mendoza-Sanchez B, Fernandez V, Veenstra R, Dukstiene N, Roberts A and Fairley N 2015 *Appl. Surf. Sci.* **326** 151
- [24] Jones B W 2004 *Life in the Solar System and Beyond* (Berlin: Springer) ch 1, p 7
- [25] Guo Y and Robertson J 2014 *Appl. Phys. Lett.* **105** 222110
- [26] Kochanov A A, Sinegovskaya T S and Sinegovsky S I 2008 *Astropart. Phys.* **30** 219

- [27] Brown E T, Brook E J, Raisbeck G M, Yiou F and Kurz M D 1992 *Geophys. Res. Lett.* **19** 369
- [28] Picozzi S, Ma C, Yang Z, Bertacco R, Cantoni M, Cattoni A, Petti D, Brivio S and Ciccacci F 2007 *Phys. Rev. B* **75** 094418
- [29] Vanheusden K, Seager C H, Warren W L, Tallant D R and Voigt J A 1996 *Appl. Phys. Lett.* **68** 403
- [30] Monsen Å, Song F, Li Z, Boschker J, Tybell T, Wahlström E and Wells J 2012 *Sur. Sci.* **606** 1360
- [31] Zhao D W, Sun X W, Jiang C Y, Kyaw A K K, Lo G Q and Kwong D L 2008 *Appl. Phys. Lett.* **93** 083305
- [32] McKeown Walker S, de la Torre A, Bruno F Y, Tamai A, Kim T K, Hoesch M, Shi M, Bahramy M S, King P D C and Baumberger F 2014 *Phys. Rev. Lett.* **113** 177601
- [33] King P D C, Wei H I, Nie Y F, Uchida M, Adamo C, Zhu S, He X, Bozovic I, Schlom D G and Shen K M 2014 *Nat. Nano* **9** 443
- [34] Meevasana W, King P D C, He R H, Mo S-K, Hashimoto M, Tamai A, Songsiriritthigul P, Baumberger F and Shen Z-X 2011 *Nat. Mater.* **10** 114