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Electronic materials



Transparent electrodes based on molybdenum– titanium–oxide with increased water stability for use as hole-transport/hole-injection components

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ABSTRACT

Recently, dielectric/metal/dielectric (DMD) transparent electrodes based on MoO_3 have been applied in solar cells and organic light emitting diodes, by virtue of the favourable properties of MoO₃ as hole-transport/hole-injection material. However, amorphous MoO₃ layers are easily dissolved in water, thus inhibiting device processing with water-based solutions. To improve the stability in water, the present study introduces DMD electrodes based on mixed molybdenum-titanium-oxide (MTO), fabricated by DC magnetron sputtering from a conductive oxide target. It is demonstrated that the addition of Ti strongly increases the stability in water, while the desirable electronic properties of MoO_3 , specifically the high work function and wide bandgap, are maintained. The DMD electrodes, with Ag as metal layer, were fabricated on both rigid and flexible substrates, namely glass and polyethylene terephthalate (PET). The obtained electrodes have low sheet resistance around 5 Ω /sq and high average visible transmittance well above 0.7 (including the substrate). As a result of the MTO stability, processing with water-based solutions takes place without electrode degradation. To demonstrate the process compatibility for large-scale, industrial production, the DMDs were sputter-deposited by a roll-to-roll process on a 300 mm-wide PET foil, achieving similar electrode properties with the laboratory-scale samples.

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GRAPHICAL ABSTRACT



Introduction

The application of molybdenum oxide layers in electronic devices like solar cells and organic light emitting diodes (LEDs) has expanded considerably. Due to its high work function (> 5 eV), MoO_x with $x \approx 3$ is widely used as hole-transport/hole-injection layer between the photon absorber/emitter layer and the electrode, thus enhancing the device efficiencies [1–6]. In a further step, MoO₃ is already employed in dielectric/metal/dielectric (DMD) structures which could simultaneously serve as hole-transport/hole-injection layer and transparent electrode [7–9].

However, it was reported that poorly textured or amorphous MoO_3 layers are extremely instable when exposed to ambient humidity and liquid water. Moreover, water exposure has strong influence on important material properties, such as the electron energy levels [10–12], due to surface hydration or hydroxylation [13]. Over long exposure periods, humid air leads to the gradual degradation of thin MoO_3 layers. Further, the contact with liquid water leads to the complete and rapid dissolution of the amorphous MoO_3 layer [14], making processing with water-based solutions impossible.

One possibility to stabilize the MoO_3 in water is by crystallization of the layers, since crystalline layers are less prone to hydrolysis and subsequent dissolution [13, 15, 16]. However, crystalline layers are mostly achieved by annealing at high temperatures (300 °C and higher), which is not compatible with flexible substrates like polyethylene terephthalate (PET). These substrates are widely used in industrial manufacturing (also for roll-to-roll production) and low-cost flexible devices, but are instable at temperatures higher than ~ 120 °C.

The current study aims to increase the water stability of sputtered, amorphous MoO_3 layers without applying high temperatures, but by alloying with another refractory metal oxide to reduce hydrolysis and dissolution, while maintaining the essential electronic properties (i.e. wide band gap and high work function) of MoO_3 . To this end, titanium oxide is introduced to form a mixed molybdenum–titanium–oxide compound material. TiO₂ is known to be stable in water and in a wide pH range of aqueous solutions [17]. Additionally, TiO₂ is also composed of octahedral TiO₆ building blocks, analogous to the building blocks of MoO_3 [2], which gives both oxides a *d*-band dominated electronic band structure [18].

So far, composites of molybdenum and titanium oxide are reported in the form of crystalline nanomaterials, for different applications.

In the field of water electrolysis, Kim et al. [19] reported on oxide composites as support for Ir catalyst for the oxygen evolution reaction, using varying Mo content (0–36 at.% Mo) to enhance the electrical conductivity of TiO₂. Similarly, Chen et al. [20] studied Mo-doped TiO₂ nanoparticles to support Pt catalysts for the hydrogen evolution reaction and improve the performance, as well as the durability of the catalyst. In both studies, the added Mo yields stronger interaction with the metal catalyst and, thus, reduces corrosion.



TiO₂-MoO₃ composites have been also investigated in the field of photoactive components and photovoltaic devices. Khan et al. [21] presented TiO₂-MoO₃ nanocomposites (with max. 9% MoO₃) prepared by laser ablation in water to adapt the properties of TiO₂ for more efficient photodegradation processes for photocatalysis and for photovoltaic devices, through the lowering of the band gap and the reduction of carrier recombination. Khlyustova et al. [22] also reported on MoO_x -decorated TiO_x and TiO_x -decorated MoO_x materials synthesized by underwater plasma discharges and their beneficial influence on the photocurrent when used as electron transport layers in dye-sensitized solar cells. Liu et al. [23] elaborated on the photocatalytic activity of the composite heterostructures, synthesized from precursor suspensions, while Li et al. [24] observed promising photochromic properties of hydrothersynthesized mally TiO₂-MoO₃ core-shell nanomaterials.

 TiO_2 -MoO₃ composites, in the form of solutionprocessed core/shell nanowires, nanoparticles or nanofibers, have been also applied as components in Li-ion battery research, with the reported effects of the composite being high capacity, lithium storage efficiency and battery lifetime and stability [25–27].

In contrast to the aforementioned reports, the present work introduces for the first time compact, amorphous thin films, deposited by sputtering from a mixed molybdenum-titanium-oxide (MTO) compound target. The sub-oxidic composition of the sputter target allows fast deposition in direct current (DC) magnetron mode, achieving high sputtering rates that are relevant for industrial applications. The sputtered MTO layers are investigated in terms of their optical and electronic properties and, most interestingly, show significantly increased water stability as compared to amorphous MoO₃ layers, while maintaining the favourable energy band structure characteristics of MoO₃. This enables the exploitation of MTO as hole-transport/hole-injection layer, especially in devices where processing with water-based solutions is required. Furthermore, the paper introduces the use of MTO layers for the design and realization of transparent dielectric/ metal/dielectric (DMD) electrodes on glass and PET substrates. Finally, the compatibility of the MTObased DMD electrode concept with roll-to-roll industrial production is demonstrated.

Experimental section

Glass $(2.5 \times 2.5 \text{ cm}^2 \text{ Menzel Gläser}^{\text{®}})$ and PET (Melinex 504[®] foil, cut in $2.5 \times 2.5 \text{ cm}^2$) substrates were cleaned in a Hellmanex[®] III water solution under sonication, followed by sonication in DI-water and finally in isopropanol, each for 15 min. The substrates were then dry-blown in a nitrogen stream.

Sputter deposition was performed in a Leybold Univex sputter system with a base pressure of 1×10^{-7} mbar. MTO films were sputtered in DC magnetron mode from a 4-inch in diameter molybdenum-titanium-oxide target (from Plansee, Austria) at a process pressure of 10 μ bar in Ar or mixed Ar/O₂ atmosphere. Ag films were sputtered from a 4-inch target, at a process pressure of 2 µbar, in Ar atmosphere. The sputter power was set to 40 W, yielding a deposition rate of 0.6 nm/s. The sputter deposition rates were determined by a surface profilometer (KLA-Tencor, Alpha-Step IQ), measuring the step height. Surface characterization was performed by atomic force microscopy (AFM, Molecular Imaging, Pico Plus) in tapping mode using SSS-NCHR cantilevers (from Nanosensors) and by scanning electron microscopy (SEM, Zeiss Ultra 40) with an acceleration voltage of 5 kV and an in-lens detector. The SEM is additionally equipped with an EDAX Octane Elect Plus detector (from AMETEK) to perform energydispersive X-ray spectrometry (EDX). For EDX measurements, the acceleration voltage is increased to 20 kV and the APEX software (from AMETEK) is used for spectrum analysis and elemental quantification. Optical spectra were obtained by a Fourier transform spectrometer (Bruker Vertex 70) equipped with a visible, unpolarized light source. Direct transmittance is measured at normal incidence in reference to air and reflectance is measured at an incidence angle of 13° in reference to a calibrated mirror (STAN-SSH-NIST, Ocean Optics). Unless stated otherwise, the beam entered from the substrate side. Two detectors were used to cover the visible range: a GaP detector (300-550 nm) and a Si detector (500–1200 nm). Optical simulations were performed using a transfer matrix method (TMM) algorithm, as described by Ebner et al. [28] and Bauch et al. [29]. The sheet resistance was determined using an in-line four-point probe (Nagy SD-600) and the resistivity measured by a linear 4-point set-up (using an Agilent 4156C semiconductor parameter analyzer) after sputtering Au contacts (~ 100 nm thick) onto 100-nm-thick samples. For structural characterization, grazing incidence X-ray diffractometry (GI-XRD) was performed using Cu-K α (λ = 1.5419 Å) radiation (Thermo Fisher Scientific ARL Equinox 100). X-ray photoemission spectroscopy (XPS) was conducted (in a JEOL JPS-9030) using a monochromatic Al-Ka (1486 eV) excitation source. Ultraviolet photoelectron spectroscopy (UPS) spectra were obtained using the same system employing H Lyman-a lamp (Excitech) for photoexcitation. To measure the secondary electron cut-off (i.e. the work function), 5 V bias was applied between the sample and the analyser. The dissolution experiments were conducted by inductively coupled mass spectrometry (Agilent Technologies, 7900 ICP-MS, operated by MassHunter Software) using a specially designed flow-cell attachment, where ultrapure water (Milli- Q^{\otimes} , with resistivity 18.2 M Ω cm) is directed over the solid sample surface of approx. 7 mm² (sealed by a 3 mm diameter O-ring) and finally transferred to the ICP-MS. The laminar flow was monitored by an inline pressure sensor and by tracking the waste electrolyte exiting the instrument over time. External calibration was done for different pressure values with multielement standard solutions (from Agilent).

Results and discussion

Target fabrication and DC magnetron sputtering

The sputtering target is made from MoO_x and TiO_x powders, resulting in a Mo/Ti ratio of 1:1, while the oxygen target content is 71 at.%. Due to the sufficiently high electrical conductivity of the target, it is possible to sputter in DC magnetron mode, which generally allows for higher deposition rates, as compared to RF mode. First, the sputter power was set to 164 W (2 W/cm^2) to obtain a significant deposition rate, compatible with industrial production, without jeopardizing the lifetime of the target due to excessive heating. A more efficient target cooling however would permit the use of higher power densities. A 300-s pre-sputtering was performed at 42 W (0.52 W/ cm^2) to condition the target. Non-reactive sputtering $(0\% O_2)$ gives the highest film growth rate of 19.8 ± 0.2 nm/min (shown in Fig. 1), but results in dark grey, conductive films. Reactive sputtering reduces the sputter deposition rate with increasing



Figure 1 Sputter deposition rate as a function of the partial oxygen content at a sputter power of 164 W and a total process pressure of 10 μ bar. The inset shows a photograph of the resulting 40 nm thick films for 0% and 6.6% O₂ content, respectively.

oxygen content and gives transparent, insulating films. Since 6.6% is the lowest possible oxygen content that could be technically realized with the specific deposition set-up and yields the highest deposition rate for the reactive processes ($16.8 \pm 0.1 \text{ nm/min}$), the following discussions concern and compare reactively sputtered films with 6.6% O₂ and non-reactively sputtered ones (0% O₂).

Material properties

The optical properties of 40-nm-thick MTO films on glass are shown in Fig. 2a, where the transmittance (solid lines) and reflectance (dashed lines) spectra are given. While the reactively sputtered films have high transmittance over the whole visible range, the nonreactively sputtered film shows drastically reduced transmittance values, i.e. increased absorption, due to the lack of oxygen that leads to free electron absorption [30]. Interestingly, for the non-reactively sputtered films, the optical properties strongly depend on the sputter power: the lower the applied power, the higher the transmittance of the thin film. To demonstrate this, another 40-nm-thick MTO film is sputtered without oxygen, at a sputter power of 21 W (0.26 W/cm^2). The resulting transmittance (Fig. 2a) is significantly increased as compared to the non-reactively sputtered film deposited at 164 W.

The complex refractive indices (see Fig. 2b) of the 6.6% and the 0% O_2 samples were extracted from the transmittance and reflectance spectra using a transfer matrix method (TMM) calculation [28]. The increased

Figure 2 a Transmittance (solid lines) and reflectance (dashed lines) spectra of 40 nm thick MTO films sputtered on glass with different oxygen partial pressures and different sputtering power,

b corresponding refractive indices (real part n presented as solid lines and imaginary part k presented as dashed lines) calculated from the transmittance and reflectance spectra, Tauc plots of the **c** indirect and **d** direct transitions.



absorption of the non-reactively sputtered films is shown by the higher values of the extinction coefficient k, which is negligible for the reactively sputtered samples in this wavelength range. The real part of the refractive index of the 6.6% O_2 sample lies within the range of literature values of MoO₃ and TiO₂ thin films [31–34].

Figure 2c, d show the Tauc plots [35] for indirect and direct optical transitions, respectively, from where the optical band gap of the films was extracted. The absorption coefficient α was calculated from the transmittance and reflectance spectra of the 40-nm-thick MTO films, using the proportionality: $\alpha \propto \log \frac{(1-R)}{T/T_{glass}}$. The abscissa of the linear fit of the $(\alpha hv)^n$ versus hv plot (hv is the photon energy), in the bandedge window, yields the bandgap energy. For an indirect semiconductor, n assumes the value of 0.5 and for a direct the value of 2.

The oxygen-rich film shows a linear behaviour for both cases of indirect and direct transition. However, for amorphous films (as shown by XRD characterization) one generally considers the band gap to be indirect [36] and DFT studies also assign an indirect bandgap to MoO₃ [37]. Assuming the same for MTO, the reactively sputtered film has an indirect band gap of 3.2 eV, which is in between the literature values for

amorphous MoO_3 and TiO_2 [14, 38–40]. For the 6.6% O_2 film, a direct optical transition is also observed at 3.6 eV, i.e. 0.4 eV above the fundamental absorption edge. As the number of oxygen defects increases, the optical band gap is decreased. In oxygen deficient MoO_x (x < 3), oxygen vacancies act as donor centres, forming a defect band close to the conduction band [38, 41]. This is seen for the non-reactively, 21 Wsputtered MTO film, where an indirect band gap energy of 2.8 eV is extracted. For the 0% O2 film sputtered at 164 W, the absorption coefficient does not show a clear absorption edge, as metallic absorption is enhanced. The lack of oxygen leads to partial occupation of the Mo 4d states, yielding delocalized electrons and can even result in the disappearance of the band gap, as it is reported for MoO₂ [42, 43]. However, direct transitions are observed for both non-reactively sputtered samples, vielding values of 3.5 eV (21 W) and 3.3 eV (164 W). It is assumed that the significant amount of disorder (i.e. the absence of long-range crystal order, the presence of different oxidation states and the mixing of MoO_x and TiO_x) in the sputtered films strongly influences the fundamental absorption behaviour due to defect bands, band tails and a generally more complex density of states.

The oxygen content in the film also impacts the electrical conductivity. An in-line 4-point resistance measurement was performed on 100-nm-thick MTO films on glass. The 0% O₂ film yielded a resistivity of 0.7 Ω cm⁻¹, while the transparent 6.6% O₂ sample was found completely insulating, with resistances in the G Ω -range. For comparison, 100 nm of sputtered MoO_x (deposited at similar conditions, as reported in [14]) shows very similar behaviour, where non-reactively sputtered, absorbing films have a resistivity of approx. 3 Ω cm⁻¹ and the reactively sputtered films vielded a resistivity of 350 Ω cm⁻¹. Any differences in conductivity are mainly due to variations of the oxygen content in the films, which in turn depends on the stoichiometry of the target and the sputter conditions.

The XRD pattern in Fig. 3a confirms the amorphous character of the sputtered MTO layers, as there is no diffraction pattern visible other than the glass substrate background. It may be noted that even thicker layers of 300 nm do not show any diffraction



Figure 3 a XRD characterization of 50-nm-thick MTO layers on glass substrates, **b** EDX mapping of a 300 nm thick 6.6% O_2 MTO film with Mo in purple and Ti in yellow.

peaks. To investigate the composition of the mixed oxide, EDX elemental mapping was performed on a 300-nm-thick 6.6% O_2 film. The result is shown in Fig. 3b, where a homogeneous distribution of Mo and Ti is observed even under high magnification. Therefore, a nanocomposite structure with strong mixing of MoO₃ and TiO₂ is assumed.

DMD electrodes

For the MTO/metal/MTO transparent electrodes, Ag is chosen as the metal layer, having low optical losses in the visible range, as well as high electrical conductivity. However, as reported in a previous work on $MoO_x/Ag/MoO_x$ electrodes [14], the thin Ag layer oxidizes during the reactive sputtering process of the top dielectric layer. Therefore, an additional protective MTO layer (MTO-2), sputtered without oxygen, is introduced (see Fig. 4a). In order to minimize optical losses, this additional layer is very thin (10 nm) and sputtered at low power of 21 W. In this architecture, high transmittance can be combined with fast deposition of DMD electrodes. In the following, TMM simulations have been performed to determine the optimal layer thicknesses of the bottom (MTO-1) and top MTO layer (MTO-3), which lead to the highest possible average transmittance T_{av} in the 400-700 nm wavelength regime. The calculation assumed a fixed Ag thickness of 14 nm and 10 nm for the protective MTO layer (MTO-2). On glass, the simulations yielded maximum T_{av} of 0.80 for an MTO-1 layer of 39 nm and MTO-3 layer of 27 nm (Fig. 4b). On PET, the maximum T_{av} of 0.77 was found for the same thicknesses (Fig. 4c). In any case, the broad dark red region in the images shows that there is a wide thickness window around these values that maximizes the average transmittance.

The experiment shows highest transmittance for the MTO₄₀/Ag₁₄/MTO_{10/30} electrode, where the subscripts denote the respective layer thickness in nm and the top layer is deposited according to the described recipe with 10 nm MTO-0% and 30 nm MTO-6.6% (Fig. 5). For this electrode we obtain $T_{\rm av} = 0.79$ on glass and $T_{\rm av} = 0.73$ on PET. The dashed lines in Fig. 5 demonstrate the strongly reduced reflectance spectra due to the destructive interference of the reflected light in the visible region when the dielectric thicknesses are optimally chosen. The wavelength window for high transmittance can be tuned to the specific application and device



Figure 4 a Schematic view of the DMD electrode design, where y is the thickness of the base and x the thickness of the top MTO layer, heat maps with the average visible transmittance of the

presented layer structure for varying base and top layer thickness on b glass and c PET.



Figure 5 Transmittance (solid lines) and reflectance (dashed lines) spectra of the DMD electrodes with varying dielectric thicknesses on glass (left) and PET (right).



DMD structure and composition

Figure 6 displays the $1 \times 1 \mu m^2$ AFM images of the DMD on glass and PET, as well as the corresponding bare substrate. The roughness of the electrodes is mostly affected by the underlying substrate. The extracted root mean square value (RMS) for the glass substrate (Fig. 6a) is 1.8 ± 0.1 nm and 11.5 ± 4.0 nm for the PET substrate (Fig. 6b). The RMS values of the DMD electrodes are even reduced, yielding RMS = 1.0 ± 0.1 nm for glass/MTO₄₀/Ag₁₄/MTO_{10/30}



Figure 6 AFM images of a bare glass, b bare PET, c $MTO_{40}/Ag_{14}/MTO_{10/30}$ on glass and d $MTO_{40}/Ag_{14}/MTO_{10/30}$ on PET.

(Fig. 6c) and RMS = 4.8 ± 2.0 nm for PET/MTO₄₀/Ag₁₄/MTO_{10/30} (Fig. 6d).

The electronic structure and composition of MTO is determined by XPS and UPS measurements of the MTO₄₀/Ag₁₄/MTO_{10/30} electrodes on both, PET and glass. Figure 7a shows the XPS results, focused on the O 1s, Mo 3d, Ti 2p and Ag 3d core level regions. The experimental data are represented as scattered dots, while the lines report the result of the fitting with Gaussian/Lorentzian mixed functions. The Mo 3*d* spectra consistently display the 5/2-peak for both samples fabricated on PET and glass at the binding energy position of 232.1 eV with a full width half maximum (FWHM) of 1.0 eV. The Ti 2p spectra display the 3/2-peak at the position of 458.3 eV (FWHM = 1.1 eV) for both samples. The position and line shape of the Mo and Ti peaks indicate that mainly Mo⁶⁺ and Ti⁴⁺ oxidation states are found at

the surface [45, 46]. The O 1s spectra have been deconvoluted in two components (grey lines): the main peak located at 530 eV (FWHM = 1.4 eV) is associated with the oxygen bond to Mo⁶⁺ and Ti⁴⁺, and the second peak located at 531.45 eV (FWHM = 1.5 eV) is associated with adventitious oxygen and non-stoichiometric components. Considering the area underneath the peaks, a Ti/(Mo + Ti) ratio of approx. 35% is extracted, irrespective of the substrate or the deposition conditions. Indeed, samples with a non-reactively sputtered top layer (MTO₄₀/Ag₁₄/ MTO^{Ar}₄₀) showed the same oxidation state and atomic ratios on the surface as the reactively sputtered layers. Depth profiling by sequential Ar sputtering was also performed to investigate the evolution of stoichiometry; however, this does not yield reliable values due to preferential sputtering during Ar bombardment, leading to oxygen loss



Figure 7 a XPS spectra of $MTO_{40}/Ag_{14}/MTO_{10/30}$ electrodes on glass (blue) and PET (red), **b** UPS measurement in the secondary electron cut-off (SECO) region and **c** in the valence band (VB) region.





Figure 8 EDX spectrum of MTO_{300} on glass, sputtered with and without oxygen.

[47, 48]. Complementary EDX measurements on 300-nm-thick MTO films on glass are used to gather more information on the film's composition. Although the oxygen-containing glass substrate has still a strong influence on the EDX spectrum (Fig. 8),

the oxygen content is reduced in the non-reactively sputtered sample (resulting in 53 ± 6 at.% oxygen) compared to the reactively sputtered layer (showing 68 ± 7 at.% oxygen). Also the observed Ti content depends on the presence of oxygen during the deposition: 5.7 ± 0.2 at.% Ti and 6.0 ± 0.3 at.% Mo (Ti/(Mo + Ti) = 49%) in the non-reactively sputtered film and 2.7 ± 0.1 at.% Ti and 4.0 ± 0.2 at.% Mo (Ti/(Mo + Ti) = 40%) in the reactively sputtered sample.

UPS measurements are shown in Fig. 7b, c. From the secondary electron cut-off (SECO), displayed in kinetic energy scale, the electrode's work function can be directly extracted, yielding 5.1 eV on glass and 5.0 eV on PET. The valence band maximum is found at 2.8 eV (glass) and 2.9 eV (PET) below the Fermi level (at 0 eV on binding energy scale). This is very similar to what was obtained for MoO₃ films [14], even though TiO₂ generally has a lower work function. Indeed, when mixing two material components with similar density of states, a weighted average of the components' work functions (ϕ_a , ϕ_b) can be expected as the work function, $\phi_{\rm m}$, of the composite material, i.e. $\phi_{\rm m} = x\phi_{\rm a} + (1-x)\phi_{\rm b}$, where *x* is the amount of component a in the composite [49]. A work function of $\sim 4.5 \text{ eV}$ is usually reported for TiO_2 [50], while the values for MoO_3 largely vary between 4.7 and 6.9 eV [2, 51, 52], depending on the material's exposure to water. In fact, a strong reduction of the work function is observed for many metal oxides exposed to ambient atmosphere due to the formation of surface dipoles through hydroxylation and adsorption of water molecules. Because of the high affinity of MoO₃ to hydrolyse, this effect is especially pronounced, while for TiO₂ the change of the work function is negligible [53]. Due to the strong dependence of the MoO3 work function on the surface hydroxylation, it is probable that in the MTO layer, the anticipated reduction of the work function due to the mixing of MoO₃ with TiO₂ is compensated by the smaller affinity of the composite material to react with the ambient humidity, as it is also suggested by the chemical stability experiments presented in the following section. As a net effect, the MTO layer assumes a similar work function to MoO_3 .

Following the results of a previous study on MoO_xbased DMDs [14], where Ag was found on the surface of the DMD under certain conditions, the energy range for Ag 3d is also shown in Fig. 7a. The electrode on glass does not show distinct Ag peaks on the surface, yet a significant amount of Ag is detected on the surface of the electrode on PET. This is attributed to the increased surface roughness of the DMDs on PET, facilitating the diffusion of Ag along grain boundaries to the surface. In fact, the presence of reactive gas (O₂) during the deposition of the top MTO layer strongly accelerates the migration process, as negative oxygen ions draw Ag ions (generated by UV-photoexcitation or energy transfer during the sputter process) to the surface [54]. Indeed, when the top MTO layer is sputtered without oxygen, no Ag was detected on the surface. However, exposure to ambient conditions additionally fosters the Ag diffusion to the surface because the humidity causes further production of Ag ions through electrochemical reactions in water channels within the grain boundaries [55]. Thus, being exposed to ambient conditions for some weeks or months, small Ag grains were also visible for non-reactively sputtered top layers.

Chemical stability

While the electronic structure of MTO resembles that of pure MoO₃, the stability of MTO layers in moisture and liquid water is significantly increased. Long-term exposure to ambient conditions and even direct contact with water does not produce visible changes, opposite to what was observed for MoO_x ($x \approx 3$) [14].

In order to quantify the stability of MTO in water, 40-nm-thick single layers were investigated in a special ICP-MS set-up where DI-water runs over the solid sample surface and is then transported further to the ICP-MS, where the dissolved species are detected. A schematic of the experimental set-up using a flow cell is shown in Fig. 9a. In Fig. 9b, the dissolution rate of Mo from a reactively sputtered MTO layer is displayed as a function of time and compared to the dissolution rate of MoO_x (as previously reported in [14]). While the MoO_{*x*} ($x \approx 3$) layer is completely dissolved within the 10 min of the experiment (when assuming a density of 4.7 g/cm^3 , 40 nm of MoO_x contain approx. 10,000 ng/cm² of Mo), the amount of Mo dissolved from the MTO layer is reduced by a factor of 20 to roughly 500 ng/cm². In a rough estimation, assuming the same density and a Mo/Ti ratio of 60:40, the total amount of dissolved MTO corresponds to approximately 2 nm within the 10 min of measurement. It should be noted at this point that the total amount of dissolved Ti was only 2 ng/cm^2 and is therefore neglected. As shown in the right inset of Fig. 9b, the Mo dissolution rate remains constant for MTO, after a peak-dissolution at the beginning (left inset). This implies that even though the MTO is more stable than MoO_{xy} Mo keeps dissolving from the MTO layer as long as water flows over the sample. And since the Ti dissolution is smaller than expected from the elemental ratio, a certain Ti passivation is expected, which further slows down the Mo dissolution but cannot completely prevent it. In fact, immersion of a 40-nm-thick MTO layer in DI-water for 26 h yields a Mo-depleted and Ti-rich residual layer, according to EDX measurements (Fig. 9c). As responsible mechanism for the observed significant reduction of the MTO dissolution in water, the following is proposed. An oxide's resistance to dissolution is strongly related to its affinity to hydrolyse, i.e. to dissociate H₂O molecules on the surface and form hydroxyl bonds. When the hydrolysis process is viewed from the perspective of acid-base reactions between the metal cations

MTO₄₀ (26 h in H₂O)

Ti (K)

8 9 10

7

Са





(Lewis acids) and the OH⁻ (Lewis base from the dissociation of H₂O on the oxide surface), the surface acidity is reduced with the decrease of the formal charge/oxidation state of the cations [56]. The presence of Ti (in the form of Ti⁺⁴ ions) decreases the average cation formal charge of the material and thus decreases the tendency to hydrolyse. In contrast to MoO_{xy} the MTO is stable enough to withstand processing with water-based solutions. To confirm this, the MTO/Ag/MTO electrodes are tested in combination with a spin-coated layer of PEDOT:PSS, as this is especially relevant for the application in solar cells or OLEDs. Two different dispersions of PEDOT:PSS have been investigated: one based on toluene (Clevious HTL Solar 3, Hereaus) and one water-based formulation (Clevious PH 1000, Hereaus), both spincoated statically at 4000 rpm for 60 s. As a result, the DMD electrodes do not experience any visible zoom-ins at different times, and the legend includes the total amount of dissolved Mo within 10 min, c EDX spectra of 40-nm-thick MTO layer before and after 26 h-immersion in DI water.

energy [keV]

MTO₄₀ (as dep.)

1000

800

600

100

200

0 2.0 2.5 3.0 3.5 4.0 4.5

Mo (L)

30000

25000

20000

15000

10000

5000

0

0 1 2 3 4 5 6

0

Na

Mg

Si

degradation in both cases and maintain their sheet resistance. The SEM cross-sectional images shown in Fig. 10 confirm that the MTO layer stays intact even when water-based PEDOT:PSS (PH 1000) is applied. In comparison, MoO_x -based electrodes were completely dissolved when processed with the PH 1000 water-based solution.

Electrode upscaling

To prove the compatibility of the presented fabrication process with industry-scale production, the DMD electrode was deposited by roll-to-roll (R2R) sputtering on a PET foil with a width of 300 mm. For this, a 300-mm-wide MTO target with the same composition as the one used for the laboratory-scale samples was fabricated (Fig. 11a). The DMD layers were sequentially deposited, with similar power densities as for the laboratory-scale samples. Also, for

100 nm

Figure 10 Cross-sectional SEM images of the DMD electrode with a spin-coated layer of **a** toluene-based (Clevious HTL Solar 3) and **b** water-based (Clevious PH 1000) PEDOT:PSS on top.



Figure 11 a MTO sputtering target for the roll-to-roll fabrication, **b** photograph of the resulting roll coated with $MTO_{40}/Ag_{14}/MTO_{10/30}$, **c** transmittance (solid line) and reflectance (dashed line) spectra of the R2R deposited DMD electrodes.



the top MTO layer, the same approach as before was followed, with first an interfacial layer being deposited non-reactively, while the second one is deposited reactively. Hence, the DMD composition was $MTO_{40}/Ag_{14}/MTO_{10/30}$. The resulting transmittance and reflectance spectra of the roll-to-roll fabricated DMD (Fig. 11b) are shown in Fig. 11c, having an average visible transmittance of 0.76 (400–700 nm) and a sheet resistance of 6.0 ± 0.2 Ω /sq, yielding a figure of merit of $\varphi = 0.011 \Omega^{-1}$. These values are similar to what has been achieved for the laboratory-scale electrodes.

Conclusion

The present study reported on the sputter deposition of mixed molybdenum titanium oxide layers from a specially designed sputter target in DC magnetron mode. With the minimal amount of 6.6% oxygen in the process gas, transparent oxide layers and high deposition rates up to 17 nm/min could be achieved. The optical and electronic properties of the MTO layers, having an indirect optical band gap of 3.2 eV and a work function of ~ 5 eV, were found similar to undoped MoO₃. Contrarily, the stability of MTO in water increased by a factor of 20, as compared to MoO_x ($x \approx 3$). In fact, the Ti passivates the MTO layer and strongly reduces the dissolution of Mo in water. Further, the MTO was used for the design of MTO/ Ag/MTO transparent electrodes on glass and PET substrates, yielding an average transmittance of 0.78 and 0.73, respectively. To avoid the oxidation of Ag during the deposition, a protective MTO layer, sputtered without oxygen, was introduced. Considering the low sheet resistance of ~ 5 Ω /sq, the reported electrodes outperform commercial ITO on PET. Due to the increased chemical stability of MTO, the DMD electrodes showed no damage or degradation after the processing with water-based PEDOT:PSS. Finally, their compatibility with large-scale roll-to-roll manufacturing was demonstrated by depositing MTO/Ag/MTO on a 300-mm-wide PET roll, yielding an average transmittance of 0.76 and sheet resistance of 6 Ω /sq.

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