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To cite this version:


HAL Id: cea-01478261
https://hal-cea.archives-ouvertes.fr/cea-01478261
Submitted on 11 Mar 2020

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The role of oxygen in magnetron-sputtered Ta$_3$N$_5$ thin films for the photoelectrolysis of water

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1. Introduction

Ta$_3$N$_5$ is an ideal candidate for the efficient water splitting under sunlight illumination thanks to its peculiar electronic band structure with a conduction band minimum below the hydrogen evolution potential [1]. In addition, it absorbs a large portion of the solar spectrum due to its small band gap of 2.1 eV which is close to the optimum band gap for solar water splitting. Recent calculations have shown that a positive effect is expected at least for the onset potential in the photoelectrolysis [5]. Experimental evidence for the changes of key material properties with oxygen incorporation, on the other hand, are rare in the literature. We employed direct current (DC) magnetron sputtering to prepare films of Ta$_3$N$_5$-N with varying oxygen concentration to follow the evolution of material properties relevant to the photoelectrolysis: crystalline structure, band gap and the efficiency-mobility-lifetime product. The chemical stability of the films was evaluated by x-ray photoelectron spectroscopy that was conducted on the same samples before and after photoelectrolysis. These measurements provide a comprehensive picture of the influence of oxygen on magnetron-sputtered Ta$_3$N$_5$ thin films.
2. Thin film preparation

Thin films were deposited in a direct current magnetron discharge using a balanced magnetron with a Ta target of 99.95% purity that was 10 cm in diameter. As a substrate, we chose a conductive Ta foil and an insulating, transparent piece of quartz to comply with different measurement techniques. Each sample was deposited onto both substrates simultaneously.

Before deposition, the substrates were cleaned in isopropyl alcohol and then placed under vacuum for radio-frequency sputtering for 10 min at an effective DC bias of 100 V. The vacuum remained unbroken between cleaning and deposition. At the same time, the target was cleaned with a closed shutter for 20 min in pure Ar at 0.5 Pa, then for further 10 min in the gas mixture in which the sample was deposited after cleaning.

All samples were deposited at a pressure of 0.5 Pa on a substrate maintained at a temperature around 870 K measured by a thermocouple inside the heating ceramics on which the substrates were clamped. The injected N2 gas had a concentration \(c_{N2}\) of 40% and 60% and the oxygen concentration was varied between 0.4% and 2.6%. Argon was added to reach a total flow rate of 50sccm for \(c_{N2} = 40\%\) and a flow rate of 25sccm for \(c_{N2} = 60\%\). The different total flow rates were necessary for technical reasons. It should be kept in mind that the same \(c_{O2}\) was used in the metallic mode with respect to the oxygen, i.e. injected oxygen is immediately gettered by the deposited Ta and by the target.

Throughout this paper, the term concentration will be used to denote the maximum value as a function of the wavelength.

3. Thin film characterization

3.1. Characterization methods

3.1.1. Grazing-incidence x-ray diffraction (GI-XRD)

GI-XRD was performed at an angle of 0.5° with respect to the sample surface using the Kα line of Mo at \(\lambda = 0.070932\) nm. The sample was moved into the incident plane of a beam of 30 µm in diameter by detecting the maximum fluorescent signal of the tantalum L-edge. An x-ray sensitive image plate behind the sample recorded all diffraction angles simultaneously up to a wave vector of \(q = 4\pi/\lambda\sin(0.5\theta)\) which resulted in typical circular diffraction patterns. These were then angularly integrated to yield the diffracagrams. All diffracograms presented here show the raw data without any background subtraction.

3.1.2. Total transmission and reflectance spectroscopy (TTRS)

The total transmission and reflection spectroscopy (TTRS) of samples deposited on quartz were determined using a photospectrometer. The samples were clamped onto the port of an integrating sphere which collected the transmitted or reflected intensity respectively which was then put into relation with the 100% baseline signal to obtain the transmission and reflection value as a function of the wavelength. The monochromator slit width was 2 nm and the wavelengths ranged from 350 to 1000 nm.

The transmission and reflection signal were subsequently fitted to a Tauc-Lorentz model with a single oscillator [7]. In some cases this model was extended by an Urbach tail [8]. These models parameterize the complex relative permittivity \(\varepsilon_\omega = \varepsilon_\infty + i\varepsilon_\omega^\prime\) and use the band gap and the film thickness, among others, as parameters which are thus directly accessible through the model. The absorption coefficient \(\alpha = 4\pi k/\lambda\) used to calculate the efficiency-mobility-lifetime product \((\eta\mu\tau)\), with \(k = 0.5[(\varepsilon_\infty^2 + \varepsilon_\omega^\prime)^{1/2} - \varepsilon_\infty^{1/2}]\), is calculated directly from the relative permittivity. The fitting was automated using an in-house code based on a global optimization algorithm [9].

3.1.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was used to reveal the chemical bonding of the Ta atoms inside the film. The spectra were calibrated in energy by shifting the 4f7/2 peak of a gold sample to a binding energy of 84 eV. Measurements were then done using the samples deposited on a Ta foil which were stuck onto a quartz slide to achieve the same electrical insulation for all samples. The charging of the samples by ejected electrons was compensated by an electron gun. The compensation was verified by assuring that the Au peak did not move for each batch of samples.

3.1.4. Conductivity and efficiency-mobility-lifetime \((\eta\mu\tau)\) product

The electronic transport properties were investigated by depositing two coplanar electrodes of silver on the sample surfaces. For this, the same samples as for the TTRS measurements, namely those deposited on insulating quartz substrates, were used.

Current-Voltage \((I-V)\) measurements were performed in both dark condition and under illumination. The illumination system consisted of a calibrated blue LED light source emitting at 450 nm. The integrated photon flux used for the photocurrent measurements was evaluated to \(10^{15}\) photons \(\cdot cm^{-2} \cdot s^{-1}\). The \(I-V\) curves (not illustrated here) showed an ohmic behavior under dark and illumination for the voltage range between \(-5\) V and \(+5\) V. The determination of the efficiency-mobility-lifetime \((\eta\mu\tau)\) product relied on measuring the photocurrent of \(Ta_{3}N_{5}\) films under above band-gap steady-state illumination. This notably implied to know the film thickness, the optical absorption and surface reflectivity at 450 nm, the applied voltage and the electrode geometry. The details of the calculation of the \((\eta\mu\tau)\) product can be found in [10].

3.1.5. Photoelectrolysis

The photoelectrochemical properties of the samples were studied using a three-electrode photoelectrochemical cell described in detail in [11] except that we used a different electrolyte \(0.1\ M\ K_{2}SO_{4}\) adjusted to \(pH = 11\) similar to [12]. The samples were illuminated by a Xe arc lamp at a power density of 100 mW/cm². Each sample was subjected to voltammetry between \(-0.5\) and \(+0.6\) V vs. Ag/AgCl under chopped white light illumination. After the measurement, the samples were rinsed with distilled water and in this way prepared for a second XPS measurement.

3.2. Characterization results

3.2.1. Grazing-incidence X-ray diffraction (GI-XRD)

The presence of the \(Ta_{3}N_{5}\) phase is evidenced by GI-XRD (Fig. 1). For both nitrogen concentrations tested (40% and 60%), the \(Ta_{3}N_{5}\) phase appears for samples at intermediate \(c_{O2}\) and is observed for a certain range of oxygen concentrations. At the upper limit of oxygen concentrations investigated, i.e. for \(c_{O2} = 1.8\%\) the diffracograms become featureless,
indicating an amorphous phase. At very low oxygen concentrations, we observe a transition to the metallic $\delta$-TaN phase. At $c_{O_2} = 0.4\%$, peaks of the metallic phase appear that are still weak in intensity, but become dominant for the sample at $c_{O_2} = 0.0\%$. Thus, under our experimental conditions, it is necessary to incorporate oxygen into the lattice to stabilize the Ta$_3$N$_5$ phase, the reason for which was discussed in the introduction.

### 3.2.2. Band gap measurements

The band gap for each sample is determined from the simultaneous inversion of the total transmission and reflectance spectra (TTRS). The samples at high oxygen concentration are fitted using a single oscillator Tauc-Lorentz (TL) model [7]. This model can be applied for samples with an oxygen concentration ($c_{O_2}$) higher than 1.0% for both $c_{N_2}$. For sample with oxygen concentrations less than 1.0%, the transmission below the band gap energy, i.e. in the long wavelength range, diminishes, which indicates the presence of in-gap states that cannot be represented by a simple Tauc-Lorentz model any more. Therefore, an Urbach tail (UT) model is added to the single oscillator TL model which results in good fits (Fig. 2). An explanation for these states could be the onset of metallic bond formation as these states appear in the transition region between the pure Ta$_3$N$_5$ and the metallic $\delta$-TaN phase as observed by GI-XRD.

The band gap of all samples follows approximately the same trend line irrespective of the model used for fitting. It widens with $c_{O_2}$ (Fig. 3) which is a direct effect of the increased incorporation of oxygen into the lattice [13][14]. Samples deposited at a low $c_{O_2}$ have a band gap of 1.3 eV, samples at the highest $c_{O_2}$ show a band gap of 2.6 eV.

The samples at high $c_{O_2}$ are already amorphous, though, so that the range of band gaps should be limited to the last sample showing the crystalline Ta$_3$N$_5$ phase, which is the sample at $c_{O_2} = 1.3\%$ ($c_{N_2} = 60\%$) having a band gap of 2.0 eV. These values are low compared to

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experimentally determined band gaps in literature for Ta$_3$N$_5$ films prepared by ammonolysis of Ta$_2$O$_5$, that have band gaps of ~2.0 eV\[15\] and 2.1 eV\[13\]. This could, again, be rationalized by the in-gap states, that successively narrow the band gap. However, already the samples without observable in-gap states at cO$_2$ = 1.1% and 1.3% (cN$_2$ = 60%) have band gaps of 1.9 eV and 2.0 eV which are lower than those measured for films deposited by ammonolysis. Responsible for this could be less oxygen in our samples. But as neither for the films prepared by ammonolysis nor for our films, the absolute oxygen content was determined, this remains a hypothesis. It is known however that even the ammonolysis of Ta$_2$O$_5$ leaves some oxygen in the film \[16\].

3.2.3. Conductivity and efficiency-mobility-lifetime ($\eta\mu\tau$) product

The conductivity of all samples is presented in Fig. 4 (top). A trend line for the samples deposited at cN$_2$ = 40% indicates a linear evolution of the conductivity with cO$_2$. This linear trend extends even up to the sample showing the metallic $\delta$-TaN phase at cO$_2$ = 0.0%, which supports our argument from above that less incorporated oxygen renders a sample increasingly metallic. The plot shows in addition that this transition from a semiconducting phase to a metallic phase is smooth.

The $\eta\mu\tau$ product describes the average distance charge carriers diffuse before recombining. Its evolution as a function of cO$_2$ follows the same trend as the conductivity. It exhibits a very low value for the films deposited at a high oxygen concentration. The amorphous structure found for these films can be held responsible for this as a reduced crystallinity typically promotes recombination. Another type of recombination center may be introduced by the oxygen in the lattice, that is known to form deep-level defects as evidenced by photoluminescence experiments \[17\]. Towards the lowest cO$_2$, the $\eta\mu\tau$ product increases over nine orders of magnitude indicating a much improved charge carrier diffusion length.

A reference value for the mobility-lifetime product was published in \[18\] for films of Ta$_3$N$_5$. They were prepared by sputtering films of Ta-N in an Ar/N$_2$ gas mixture at room temperature followed by annealing in air and in NH$_3$. The authors determined a $\mu\tau$ product around $10^{-12}$ cm$^2$V$^{-1}$s$^{-1}$, which is low compared to our measurements and which we only find for amorphous films at the highest oxygen concentrations. Similar to the difference in band gaps between our magnetron-sputtered films and those prepared by ammonolysis, the difference in the $\mu\tau$ product could be ascribed to an unequal amount of remaining oxygen in the films of both studies. This is in line with our findings, as a reduced oxygen concentration increases the $\eta\mu\tau$. Consequently, as little

Fig. 4. Conductivity (top) and efficiency-mobility-lifetime ($\eta\mu\tau$) product (bottom). A trend line is shown for cO$_2$ = 40% in each of the plots. Grey circles indicate samples with the Ta$_3$N$_5$ phase.

Fig. 5. Evolution of the XPS spectra of the Ta 4f region for samples deposited at cO$_2$ = 40%...
Table 1

<table>
<thead>
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<th>fbefore</th>
<th>flower</th>
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<td>2.1</td>
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<td>60% 1.7%</td>
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<td>0.4</td>
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Fig. 6. Carbon 1s spectra of the samples deposited at cO2 = 40% after photoelectrolysis measured by x-ray photoelectron spectroscopy. Potassium peaks for the two samples at cO2 = 1.8% and cO2 = 2.6% hint towards a surface reaction with the electrolyte. Grey circles indicate samples with the Ta3N5 phase.

Fig. 7. On–off photocurrent curves for two Ta3N5-crystalline samples deposited a cO2 = 40%. Both samples show the Ta2N6 phase.

Fig. 8. Photocurrent of all samples at 0.5 V vs. the silver chloride electrode (Ag/AgCl) for samples deposited at cO2 = 40% (blue) and cO2 = 60% (green) as a function of cO2. Grey circles indicate samples with the Ta3N5 phase. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Photoelectrolysis

Finally, we studied the photoelectrochemical properties of the samples. Fig. 7 shows current density curves as a function of the applied potential for two samples deposited at low oxygen concentration. The samples were measured under chopped light illumination which results in the fragmented curve with an upper plateau corresponding to the current during illumination and the lower plateau to the dark current. The difference between these two curves is the photocurrent. High transients can be observed at the beginning and at the end of each illumination pulse which are typically attributed to the low rate constant for water oxidation [22].

The onset potential, i.e. the minimum potential at which an effect of the light is observed, is small, which is beneficial for efficient solar water splitting. Already around 0 V vs. the normal hydrogen electrode (NHE) a small photocurrent evolves which proves that bias-free photoelectrolysis of water by Ta$_3$N$_5$ is possible.

A summary of the photocurrent densities for all samples measured at a bias of 0.5 V vs. the silver chloride electrode (Ag/AgCl) is given in Fig. 8. We observe two groups of samples that can be distinguished by photoelectrolysis of water by Ta$_3$N$_5$ is possible.

We investigated the variation of material properties of Ta$_3$N$_5$ thin films as a function of oxygen concentration in the injected gas mixture and evaluated its use as a photoanode for solar water splitting.

A clear degradation of properties of the Ta$_3$N$_5$ crystalline phase with incorporation of oxygen is evidenced. The efficiency-mobility-lifetime product decreases over ten orders of magnitude within the small range of oxygen concentrations, the band gap widens and the stability in photoelectrolysis is drastically reduced.

Oxygen, although necessary to trigger the crystallization of the Ta$_3$N$_5$ phase, should be kept to a minimum in magnetron-sputtered films. For the deposition reactor configuration and the magnetron used in this study, an oxygen concentration between 0.4 and 0.9% was found to be the optimum value and we show in this case that Ta$_3$N$_5$ can be used as a photoanode for solar water splitting.

Acknowledgements

The authors are grateful for the funding of this activity by the Centre National de la Recherche Scientifique (CNRS) under the grant agreement ANR-13-IS09-0003-01. We would also like to thank Martine Wery for an insightful discussion on electrochemistry and Jocelyne Leroy and Séverine Le Moal for sharing their knowledge on XPS measurements and fittings.

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