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Effect of Oxygen on Sputtered Tantalum Nitride Thin Films for Photoelectrochemical Water Splitting

Sam Macartney[1], Richard Wuhrer[2] and Leigh R. Sheppard[1]

[1.] School of Computing, Engineering and Mathematics, Western Sydney University, Penrith, Australia
[2.] Advanced Materials Characterisation Facility, Office of the Deputy Vice-Chancellor & Vice-President (Research & Development), Western Sydney University, Penrith, Australia

With the rising pressure of climate change pushing research into various areas of renewable energy sources, solar generated hydrogen represents a compelling research avenue. Using solar hydrogen farms, it would be possible to generate enough hydrogen from water and sunlight to support a theoretical hydrogen economy[1]. Since the discovery of photocatalytic water splitting using TiO_2[2], four decades of research has focused on developing efficient solar to hydrogen water splitting technologies. However, despite large improvements in the capabilities of TiO_2, efficient water splitting devices utilising it and other oxides have not eventuated.

In recent years, various nitride materials have been highlighted as possessing great potential for efficient water splitting[3]. Tantalum nitride, specifically Ta_3N_5, is one such nitride, possessing appropriate band edge positions for efficient, bias free overall water splitting and a band gap allowing absorption of visible light[4].

The goal of this project is to deposit thin films of Ta_3N_5 for use in photo-electrochemical cells as novel photo-electrodes. In the current literature, nearly all reports include the use of oxygen in the synthesis of Ta_3N_5, whether thermal nitridation or sputtering routes. The formation of these films is catalyzed by oxygen due to the tendency of high oxidation state transition metals, in this case Ta^{5+}, to draw stability from the inductive effect of a more electronegative element[5]. As such, the role of oxygen in the synthesis of Ta_3N_5 is important and warrants investigation.

A number of films were deposited via RF sputtering with the deposition parameters listed in Table 1, using an AJA Orion 5 magnetron sputtering system (AJA International, Scituate MA). A film of tantalum was deposited prior to oxygen and nitrogen being introduced into the atmosphere. Surface feature imaging and elemental quantification was performed with a JEOL JSM-7001F (JEOL, Tokyo, Japan) Scanning Electron Microscopy (SEM) equipped with a Bruker XFlash 6I10 (Bruker, MA) detector for Electron-Dispersive Spectroscopy (EDS).

Oxygen presence in the sputtering atmosphere had an impact on surface structure, elemental composition and film thickness. X-Ray Diffraction (not displayed) indicated the presence of Ta_3N_5 in the two films with lowest oxygen partial pressures ($p(O_2)$), with a phase transition to TaN taking place at the highest $p(O_2)$. Figure 1 displays surface structures (below) and film cross sections (above). Surface roughness gradually decreased with increasing $p(O_2)$, due to the increasingly amorphous nature of the films. The $p(O_2)$ correlated to the presence of oxygen within the films, however even with a $p(O_2)$ of 0 mTorr, a not insignificant amount of oxygen was still detected in the films; the source of this is still to be determined. Despite the $p(O_2)$ matching the nitrogen partial pressure ($p(N_2)$) at 0.3 mTorr, a larger amount of nitrogen was still observed in the films, suggesting a decrease in oxygen gettering at higher

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p(O_2) values. The observation of TaN at *p*(O_2) = 0.3 mTorr further indicates this. This data provides a basic view of the relationship between oxygen, nitrogen and tantalum in our systems atmosphere while utilising RF magnetron sputtering. It is apparent that oxygen must be controlled to within a few % of the total sputtering atmosphere in order to deposit Ta_3N_5 films.

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Table 1. Processing parameters for Ta, O, N based films deposited with varying *p*(O_2), and the resulting film thickness and composition. EDS was performed with an accelerating voltage of 5kV.

***p*(Ar):*p*(N_2):*p*(O_2)** (mTorr)	**Deposition Pressure (mTorr)**	**Film Thickness (nm)**	**Dep. Rate (nm/min)**	**Bias (*V*)**	**T_{sub} (°C)**	**[N] (at. %)**	**[Ta] (at. %)**	**[O] (at. %)**
2.4:0.3:**0.3**	3	463	1.54	280	700	41	29	30
2.67:0.3:**0.03**	3	403	1.34	280	700	55	31	14
2.7:0.3:**0**	3	611	2.03	280	700	53	35	12

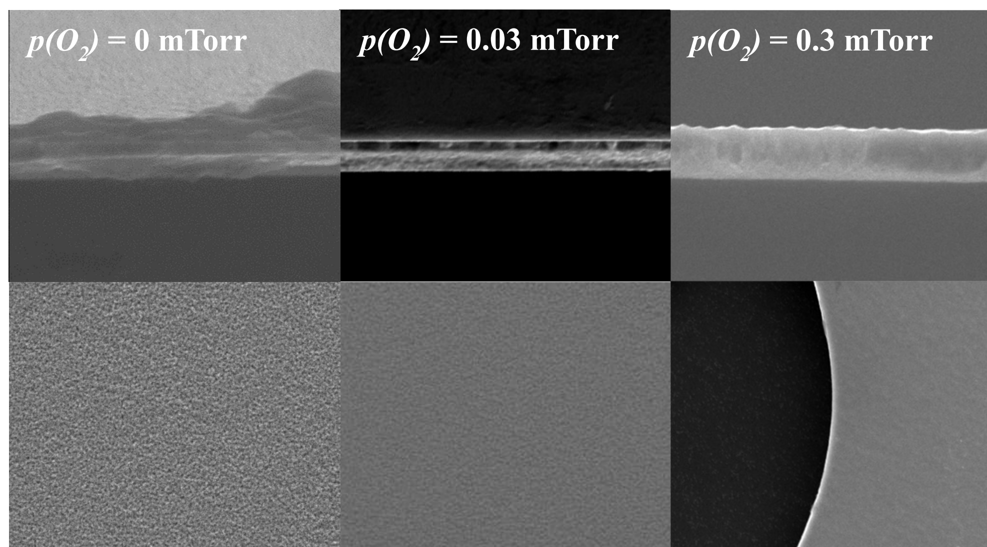

Figure 1. SEM images showing surface features of Ta, O, N based films deposited with varying *p*(O_2) values. Images were taken at 10,000x, with a working distance of 10cm and accelerating voltage of 10kV.

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