

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

Sam Macartney¹, Richard Wuhrer² and Leigh R. Sheppard¹

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 TiO₂[2], four decades of research has focused on developing efficient solar to hydrogen water splitting technologies. However, despite large improvements in the capabilities of TiO₂, 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 Ta₃N₅, 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 Ta₃N₅ 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 Ta₃N₅, 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 Ta⁵⁺, to draw stability from the inductive effect of a more electronegative element[5]. As such, the role of oxygen in the synthesis of Ta₃N₅ 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 6110 (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 Ta₃N₅ 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

$p(O_2)$ 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 Ta₃N₅ films.

References:

- [1] Katsushi, F., K. Takeshi, and O. Kazuhiro, Japanese Journal of Applied Physics **44(4L)** (2005), p. L543.
 [2] Fujishima, A. and K. Honda, Nature **238 (5385)** (1972), p. 37.
 [3] Maeda, K. and K. Domen, The Journal of Physical Chemistry Letters **1(18)** (2010), p. 2655.
 [4] Hitoki, G. *et al*, Chemistry Letters **31(7)** (2002), p. 736.
 [5] Rudolph, M. *et al*, The role of oxygen in magnetron-sputtered Ta₃N₅ thin films for the photoelectrolysis of water. Surface and Coatings Technology.

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

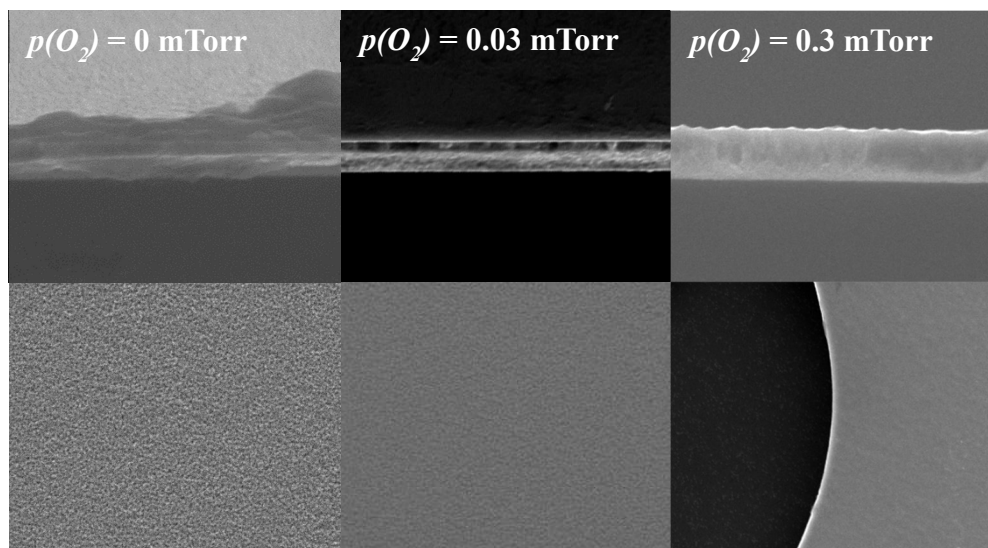


Figure 1. SEM images showing surface features of Ta, O, N based films deposited with varying $p(O_2)$ values. Images were taken at 10,000x, with a working distance of 10cm and accelerating voltage of 10kV.