E-MRS 2011 Spring Meeting Symposium T

Wet ammonia synthesis of semiconducting N:Ta$_2$O$_5$, Ta$_3$N$_5$ and β-TaON films for photoanode applications

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Abstract

Tantalum oxynitride (β-TaON) is a promising photoanode material for photoelectrochemical water splitting. However, the synthesis of phase-pure β-TaON films is a challenging task. This paper describes a novel approach to achieve this by the controlled nitridation of Ta$_2$O$_5$ films under a flow of ammonia gas (ammonolysis), which was obtained by bubbling argon through an aqueous ammonium hydroxide solution followed by a 5Å molecular sieve to remove the water. Depending on the nitridation conditions, either nitrogen-doped Ta$_2$O$_5$ or Ta$_3$N$_5$ was obtained as a thermodynamically stable phase. The evolution of the nitridation process was monitored in-situ using optical transmission spectroscopy, which revealed that the transformation of Ta$_2$O$_5$ to Ta$_3$N$_5$ occurred within minutes, through a series of intermediate oxynitride phases. This suggested the possibility of synthesizing the desired β-TaON phase by quenching the sample at the right time during the nitridation process. By choosing the right ammonolysis conditions (750°C, flow rate 50 ml/min.), we were able to slow down the nitridation process and terminate it before the oxide was fully converted to Ta$_3$N$_5$. A post-nitridation heat treatment at 800°C indeed resulted in the formation of the desired β-TaON phase.

Keywords: Type your keywords here, separated by semicolons ; tantalum oxynitride; photoanodes; water splitting; optical monitoring; tantalum nitride; ammonolysis

1. Introduction

Nitrogen incorporation into transition metal oxides, leading to nitrogen-doped oxide, oxynitride or nitride phases, has recently attracted much interest for the development of new semiconducting materials for photocatalytic water splitting [1,2]. Among the various nitride and oxynitride compounds considered, tantalum nitride (Ta$_3$N$_5$) and tantalum oxynitride (TaON) are particularly attractive due to the high energetic position of Ta 5d orbitals which form the conduction band of these materials. Electrons in this conduction band have a more negative potential than

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the reduction potential of H^+/H_2 (0 V vs RHE), which enables hydrogen evolution without the need for an externally applied bias potential. Bandgap values of 2.1 and 2.4 eV have been reported for Ta_3N_5 and β-TaON, respectively, which results in good visible light absorption in combination with valence bands that are positioned at energies more positive than the H_2O/O_2 oxidation potential (1.23 V vs RHE) [3]. Abe et al. [4] demonstrated that nanoporous β-TaON thin films loaded with IrO_2 nanoparticles can deliver bias-free Incident Photon-to-Current conversion Efficiencies (IPCEs) close to 20% in the visible range.

Tantalum nitrides and oxynitrides are usually obtained by nitridation of tantalum oxide (bandgap ~3.9 eV) under a partial pressure of ammonia (ammonolysis) [5-9]. Despite the significant amount of research on the properties of tantalum nitride and oxynitrides, little is known about the nitridation process itself and reproducible, facile production of the elusive β-TaON phase is currently an unresolved challenge.

In this article we study the nitridation of tantalum oxide thin films in a tube furnace under an ammonia/argon atmosphere while following the optical transmission of the film in-situ. The optical absorption changes in the film can thus be directly correlated to the presence of the Ta_2O_5, β-TaON and Ta_3N_5 phases. By monitoring the evolution of these phases in-situ, we have a convenient tool to obtain new insights into the thermodynamics and kinetics of the nitridation process. This will help us to discover the optimal conditions for the reproducible synthesis of β-TaON.

2. Experimental

To avoid complications due to optical scattering from nanoparticle agglomerates and optical absorption by ligands, the samples chosen for this study were thin dense films of tantalum oxide on fused silica. The samples were fabricated by DC sputtering under an argon plasma atmosphere (3×10^{-3} mbar) at a substrate temperature of 400°C. A 5 nm Ti adhesion layer was deposited first, followed by a 60 nm Ta film. After deposition, the samples were oxidized for 5 hours at 650 °C in air. This resulted in thin films of tantalum oxide on titanium oxide, with a total thickness of 160 nm (Fig. 1(a)). The nitridation was performed in a furnace with a fused silica reactor tube. An Ar/NH_3 mixture was fed into the tube by flowing either argon or argon + oxygen gas through a 28% ammonium hydroxide (NH_4OH) solution [10], followed by a 5 Å molecular sieve to remove water (Fig. 1). Similar experiments with 3 Å and 4 Å molecular sieves resulted in negligible flows of ammonia through the sieves.

In a typical nitridation experiment, the tantalum oxide film was heated to the desired temperature (3 K/min) under a 10 ml/min pure O_2 flow, and then purged for 30 min. under a flow of pure argon. The nitridation process
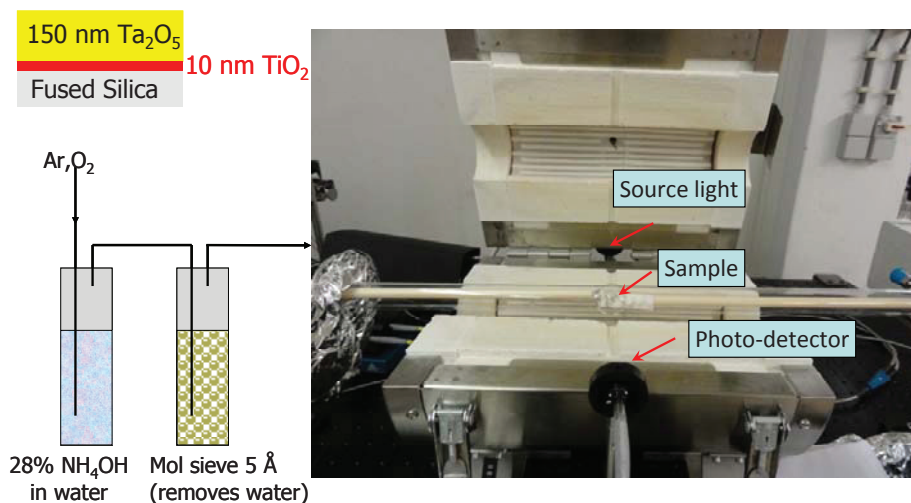

Figure 1: Geometry of the film used in this work (top left) and a photograph of the furnace setup with the optical fiber arrangement.

was started by feeding ammonia into the tube oven and simultaneously recording the optical transmission spectra of the film at regular intervals. A UV-Vis-NIR light source (DH-2000-BAL, Ocean Optics) composed of a halogen

lamp and a deuterium lamp was used for the optical spectroscopy. The light was guided into the oven using a multi-mode optical fiber connected to a collimator, resulting in a near-parallel beam with a diameter of ~4 mm. The collimated light passed through the sample under normal incidence condition and it was collected by a second collimator and transmitted via an optical fiber to a Maya 2000 PRO CCD spectrometer (Ocean Optics). The measured transmission (T) is converted into optical absorbance (A) via $A = -\mathrm{Log}(T)$. No correction for reflection was applied.

Samples suitable for photo-electrochemical characterization were produced by sputtering Ta on platinum electrodes. Pt electrodes were fabricated by sputtering 150 nm Pt on fused silica with a 5 nm Ti adhesion layer. These films were found to delaminate while cooling down from nitridation treatments at 750 and 800°C, due to a mismatch in the thermal expansion coefficients and the resulting thermal stress. Nitridation at a lower temperature (700°C) solved this problem in most cases.

The crystal structure of the samples was determined using a Bruker D8 Advance X-ray diffractometer equipped with LynxEye linear detector in a Bragg-Brentano configuration. Ex-situ UV/Vis transmission measurements were performed on the films at room temperature using the optical spectrometer installed on the nitridation setup, as described above.

Photoelectrochemical experiments were performed under AM 1.5 illumination in a conventional three-electrode cell with a fused silica window, a platinum counter electrode, and an Ag/AgCl reference electrode (saturated KCl, XR300, Radiometer Analytical). AM 1.5 illumination was provided by an EPS 1200S solar simulator (KH Steuernagel Lichttechnik GmbH). A solution of 0.1 M Na_2SO_4 (pH~6) and deionized water (Milli-Q, 18.2 MΩ.cm) was used as the electrolyte. Nitrogen gas was bubbled through the solution to remove any dissolved oxygen. The working area of the electrodes exposed to the electrolyte was 28.3 mm^2 (6 mm diameter) for all samples. Potential control was provided by an EG&G model 283 potentiostat.

3. Results and discussion

3.1. In-situ UV-Vis

Fig. 2 shows the temporal evolution of the optical absorption through Ta_2O_5 film during nitridation at (a) 700°C and (b) 800°C under flow of 100 ml/min Ar in NH_4OH. It shows that as the nitridation proceeds, the absorption edge gradually shifts toward the red part of the spectrum. This shift of the absorption edge stabilizes within minutes, depending on the nitridation conditions. In Fig. 2 (a) it stabilizes at the absorption edge corresponding to nitrogen-doped Ta_2O_5, while it corresponds to Ta_3N_5 in Fig. 2 (b).

Experiments were performed under different flows of Ar and different temperatures for several hours of nitridation so that the absorption edge stabilized. This stabilized optical absorption edge was used for phase identification. All nitridation conditions resulted in either Ta_3N_5 or nitrogen-doped Ta_2O_5 after several hours of nitridation (Fig. 3 (a)). Formation of these crystalline phases was confirmed by XRD measurements performed on the samples whose temporal evolution is depicted in Fig. 2. Fig. 3 (b) shows the diffraction pattern for the sample nitridized at 700°C with 100 ml/min Ar flow for 2 hours. All the diffraction peaks match Ta_2O_5 (PDF 00-025-0922). Although no significant shift in the XRD peak positions is observed after the nitridation treatment, the formation of a thin yellow band around 300–320 nm (Fig. 2(a)) indicates a small red shift of the absorption spectrum, which is attributed to nitrogen doping of the Ta_2O_5 films. Nitridation of Ta_2O_5 at 800°C results in the formation of pure Ta_3N_5 (PDF 01-079-1533), as shown in Fig. 3(c).
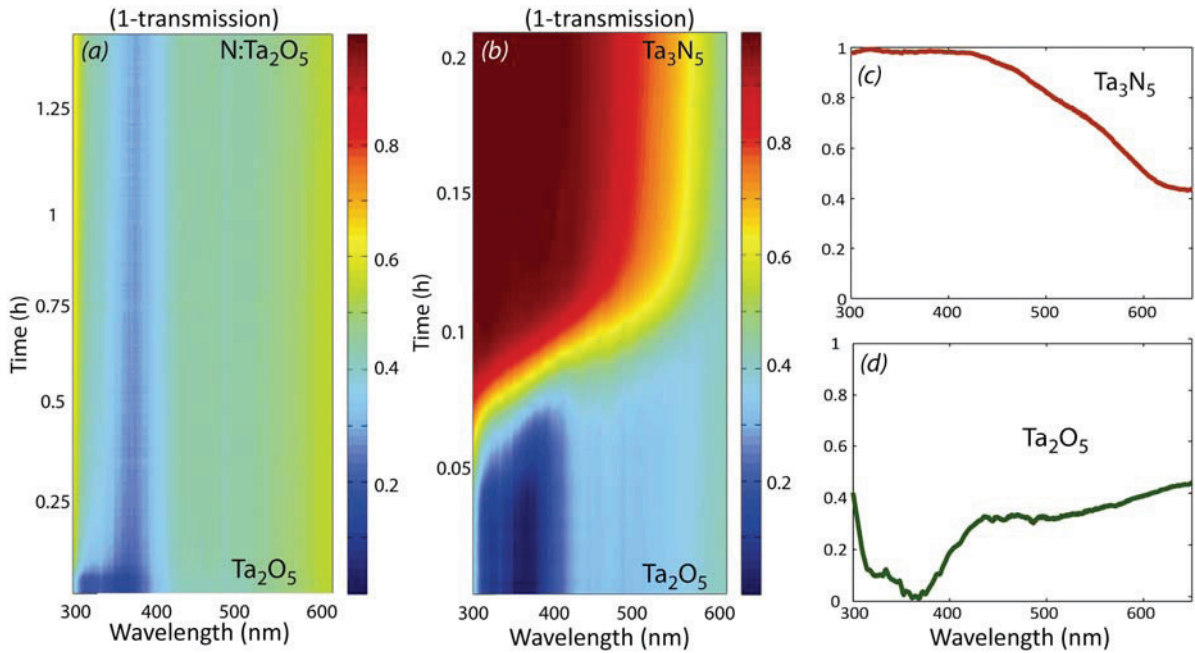
Figure 2: Temporal evolution of the optical absorption edges of Ta_2O_5 thin film upon nitridation under flow of 100 ml/min Ar in NH_4OH at (a) 700°C and (b) 800°C. (c) Line-plot of the Ta_3N_5 and (d) Ta_2O_5 showing the starting and end points in (b).
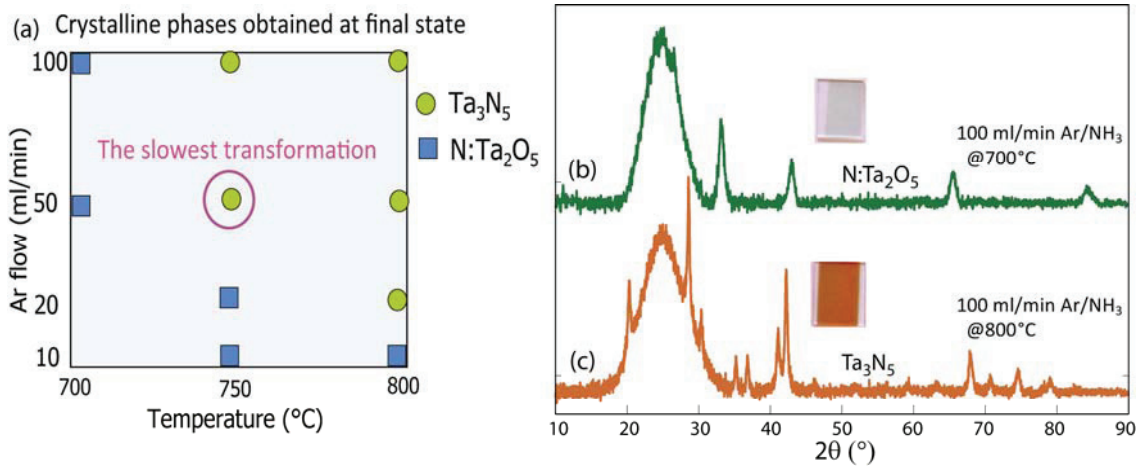

Figure 3: (a) The steady-state crystalline phases obtained after prolonged nitridation. The Ar flow represents the flow of Ar gas bubbled through the 28% NH_4OH solution. (b, c) X-ray diffraction spectra of the samples nitridized to $N:Ta_2O_5$ and Ta_3N_5. All the peaks can be attributed to Ta_2O_5 (PDF 00-025-0922) and Ta_3N_5 (PDF 01-079-1533), respectively.

Closer inspection of the evolution of the optical absorption spectra during nitridation reveals a gradual shift of the absorption edge, as shown in Figs. 4 (a) and (b). This suggests that the transformation of Ta_2O_5 to Ta_3N_5 occurs via a series of intermediate phases, as opposed to a gradual change in the Ta_2O_5-Ta_3N_5 ratio. Based on this observation, it should be possible to obtain the desired tantalum oxynitride phase by quenching the sample and thereby stopping the nitridation process at a certain time.

3.2. Nitridation by flowing Ar/O₂ in NH₄OH

Although quenching the nitridation process may potentially deliver tantalum oxynitride, it is desirable to find nitridation conditions under which TaON phase is thermodynamically stable. It allows prolonged high-temperature treatments that can be used to improve the crystallinity and reduce the number of defects in the material. In our attempts to find thermodynamically stable conditions, small amounts of oxygen have been added to the Ar carrier gas flowing through the NH_4OH solution while nitridizing Ta_2O_5 films. The experiments were performed at 800°C for several hours to ensure that a steady-state was obtained. The results (Fig. 4 (c)) showed a sharp transition from Ta_3N_5 to $N:Ta_2O_5$ when the $Ar:O_2$ ratio is changed from 100:0.8 to 100:1. Clearly, the addition of oxygen does not provide a sufficient degree of control over the process conditions to obtain TaON under thermodynamic equilibrium conditions.
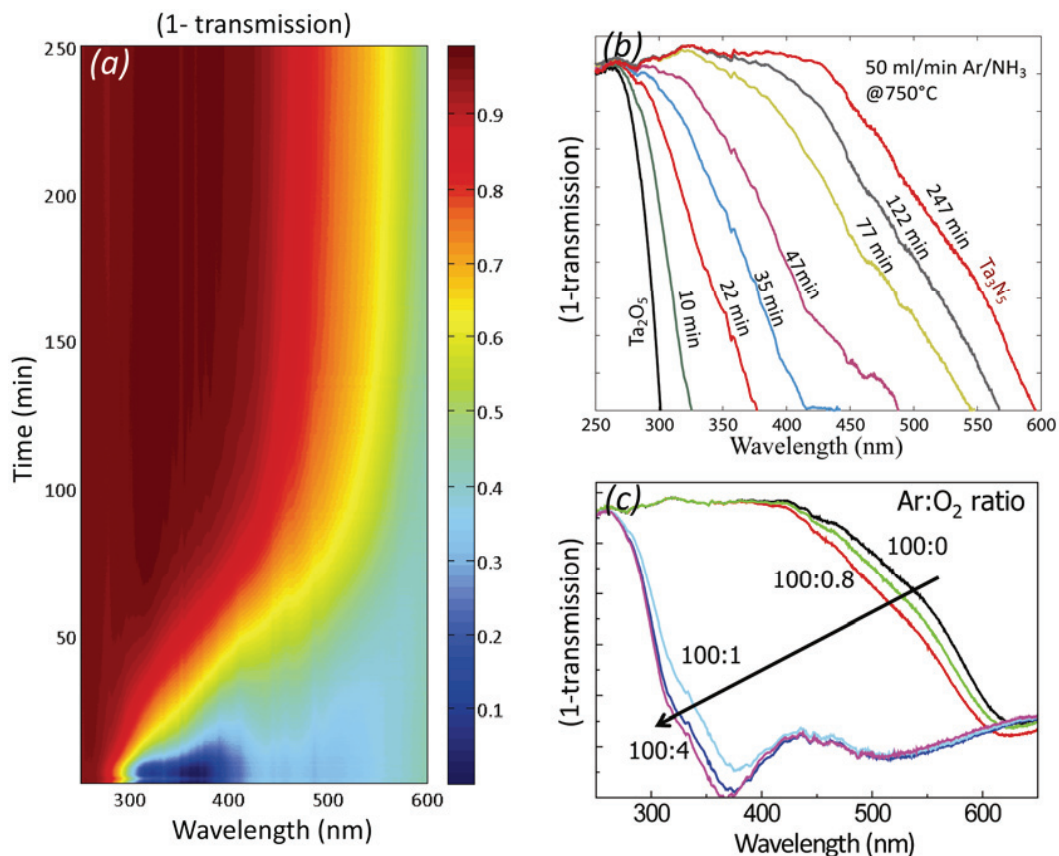

Figure 4: (a) Two-dimensional graph of the evolution of the optical absorption spectrum during nitridation of Ta_2O_5 at 750°C with 100 ml/min Ar flow. (b) Snap-shots of optical absorption spectra during nitridation of the film at 750°C with 50 ml/min Ar flow bubbled through the 28% NH_4OH solution. (c) Optical absorption spectra for thin films of Ta_2O_5 during nitridation at 800°C and flowing different $Ar:O_2$ ratios, ranging from 100:0 to 100:4 ml/min., through the NH_4OH solution.
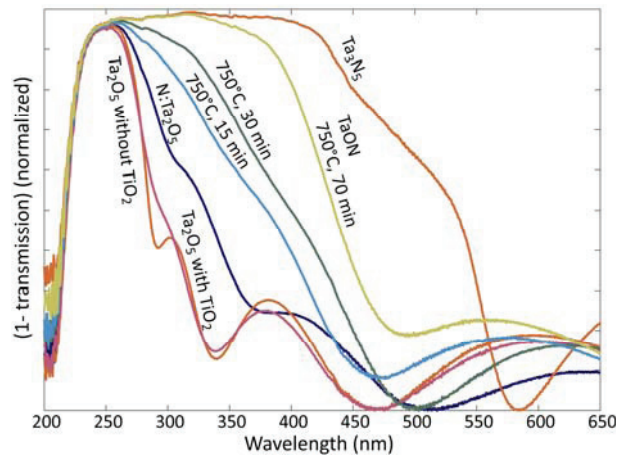
Fig. 5: Ex-situ UV-Vis absorption spectra of the nitridized Ta_2O_5 layer with TiO_2 adhesion layer compared against the absorption spectra of Ta_3N_5, N: Ta_2O_5, Ta_2O_5 with and without TiO_2 adhesion layer.

3.3. Kinetically-controlled nitridation

Three samples were nitridized at 750°C with 50 ml/min Ar at different durations of 15, 30, 70 minutes. Fig. 5 shows the UV-Vis spectra of these samples compared against Ta_2O_5, Ta_3N_5 and N:Ta_2O_5. The contribution of the TiO_2 adhesion layer to the optical absorption was determined by comparing the absorption spectrum of a Ta_2O_5 layer with and without the adhesion layer, and is found to be negligible above 350 nm. N:Ta_2O_5 was obtained by nitridation at 700°C with 100ml/min Ar flow and the Ta_3N_5 layer was obtained by nitridation at 800°C with 100 ml/min Ar flow.

Starting from Ta_2O_5, increasing the nitridation duration results in a red-shift of the absorption edge. Nitridation at 750°C for 15 min shows a larger red-shift in the absorption edge while its XRD pattern shows the same diffraction peaks as N:Ta_2O_5. It indicates the presence of heavier nitrogen doping without formation of a new crystalline phase. Nitridation for 30 min at 750°C shows further red-shift in optical absorption edge and causes the appearance of a new XRD peak at 50° and disappearance of some of the Ta_2O_5 diffraction peaks. This suggests that for some orientations the phase transformation happens faster than for other orientations.

Nitridation for 70 min at 750°C results in a sample with an absorption edge at about 500 nm and crystalline orientations different from Ta_2O_5 (although the sample was not well crystallized). The position of the absorption edge corresponds to that expected for TaON. To confirm the presence of pure TaON with XRD, the sample was further crystallized for a few hours at 800°C under 10 ml/min NH_4OH/Ar. According to Fig. 3 (a), using such a low flow rate does not lead to the formation of Ta_3N_5. The XRD diffraction of the sample (Fig. 6 (e)) shows a number of peaks and all of them match with diffraction lines of β-TaON (PDF 01-70-1193). Thus, β-TaON was successfully synthesized using a kinetically-controlled nitridation process.

3.4. Photo-electrochemical (PEC) characterization

In order to evaluate the photo-electrochemical performance of the nitridized films, several films were deposited on Pt-coated quartz as a conducting substrate. Unfortunately, most nitridation conditions resulted in exfoliation of the Pt film, which renders them unsuitable for PEC characterization. The only condition under which no exfoliation was observed was at 700°C, and we therefore limited our PEC studies to samples nitridized at this temperature. Fig. 7 (a) shows the XRD spectrum of a sample that was nitridized at 700°C for 8 hours under an ammonia partial pressure provided by bubbling 500 ml/min Ar through NH_4OH. The obtained phase is not N:Ta_2O_5 and it does not match with the crystalline phases of the Ta-O-N system present in the ICDD database. It further illustrates the profound influence of ammonia partial pressure on formation of nitride or oxynitride phases, in agreement with Fig. 3 (a). The photocurrent voltammogram shown in Fig. 7(b) reveals that a 450 nm thick film of this phase delivers

photocurrents as large as 0.25 mA/cm^2 at 1.23 V$_{RHE}$, without using any oxygen evolution catalyst.

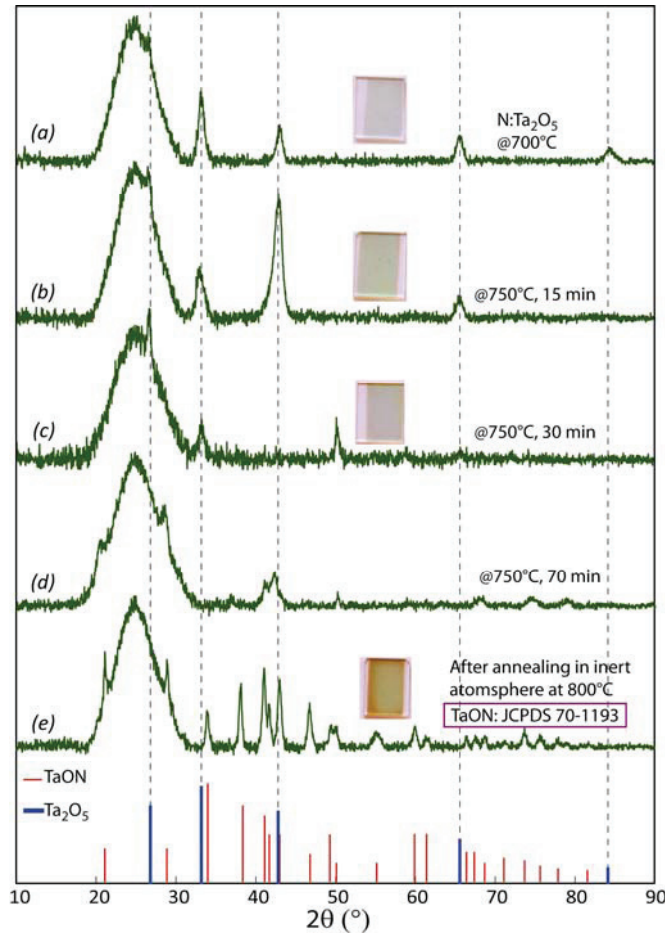Figure 6: XRD patterns of (a) N:Ta$_2$O$_5$ film compared against Ta$_2$O$_5$ films nitridized at 750°C for (b) 15 min and (c) 30 min. XRD pattern of the sample nitridized at 750°C for (d) 70 min. The sample is not well-crystallized but after annealing at 800°C in an inert atmosphere all the peaks correspond to the standard β-TaON diffraction lines. The broad peak is due the background from the fused silica substrate.
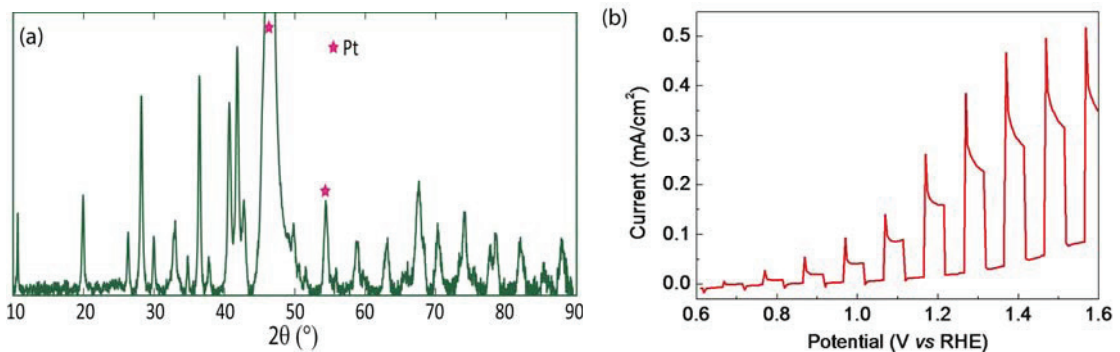

Figure 7: (a) XRD pattern of a Ta$_2$O$_5$ sample on Pt annealed at 700°C for 8h with 500 ml/min Ar flow through NH$_4$OH. The diffraction peaks do not correspond to any known phases of the Ta-O-N system available in the ICDD database. (b) Transient photoresponse under chopped (light on/light off) AM1.5 illumination as a function of the applied potential.

4. Conclusions

In-situ optical absorption edge measurements show that the ammonolysis of Ta_2O_5 thin films is influenced strongly by temperature and ammonia partial pressure. Under the nitridation conditions studied in this work, the obtained thermodynamically stable phases were either $N:Ta_2O_5$ or Ta_3N_5. The addition of small amounts of oxygen does not provide conditions under which the TaON phase is thermodynamically stable. In-situ UV-Vis measurements suggest that the nitridation of Ta_2O_5 to Ta_3N_5 occurs through a series of intermediate oxynitride phases. By choosing the right process conditions, it is possible to slow down the nitridation process and to quench the sample before it is fully converted to the final Ta_3N_5 phase. A subsequent crystallization treatment at 800°C resulted in successful synthesis of β-TaON. This confirms that intermediate oxynitride phases of tantalum can be obtained through a kinetically-controlled nitridation process. PEC characterization of an oxynitride photoanode nitridized at 700°C showed an AM1.5 photocurrent of 0.25 mA/cm^2 at 1.23 V vs. RHE. Higher nitridation temperatures are expected to give lower defect concentrations and higher photocurrents, but may require the presence of a buffer layer to avoid exfoliation.

5. Acknowledgement

6. References

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